TÜRKİYE BİLİMSEL VE TEKNİK ARAŞTIRMA KURUMU

THE SCIENTIFIC AND TECHNICAL RESEARCH COUNCIL OF TURKEY

OLİGO-2-[(2-HİDROKSİ-6-METOKSİ-BENZİLİDEN)AMİNOPRİDİN-3-İL-İMİNOMETİL-3-METOKSİFENOL] VE OLİGO-4-[(2-HİDROKSİ-6-METOKSİFENİLMETİLEN) AMİNOFENİLİMİNOMETİL-3-METOKSİFENOL]'ÜN SENTEZİ, KARAKTERİZASYONU, TERMAL, ANTİ-MİKROBİYAL, İLETKENLİK ÖZELLİKLERİ VE GIDALARA UYGULANMASI

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ÖZET

Bu çalışmada, *o*-vanilin ile 2,3-diaminopridin ve *p*-fenilendiaminin kondenzasyon reaksiyonundan Schiff bazları elde edildi. Sentezlenen monomerler NaOCl, H_2O_2 ve hava oksijeni ile bazik ortamda polimerlerine dönüştürüldü. Prosesin temel değerleri ve optimum reaksiyon koşulları belirlendi. Sentezlenmiş ürünlerin yapıları element analizi, FT-IR, ^{1}H-NMR, ^{13}C-NMR ve UV-vis spektrumlarındaki verilerinden faydalanarak belirlendi. ^{1}H-^{13}C-NMR verilerine göre; polimerizasyon, monomerlerin -OH gruplarına göre, *para* ve oksifenilen konumlarından gerçekleşmektedir. Büyüklükçe ayırma kromatografisine (SEC) göre, PHMPMDAP'in sayıca ortalama molekül ağırlığı (M_n), ağırlıkça ortalama molekül ağırlığı (M_w) ve heterojenlik indeksi değerleri hava oksijeni, NaOCl ve H_2O_2 yükseltgenlerine göre sırası ile 6200, 4100 ve 5400 g mol^{-1}, 6900, 16200 ve 7700 g mol^{-1} ve 1,113, 3,951, 1,426 olarak hesaplandı. SEC analizlerine göre, OPBNMBMP'in sayıca ortalama molekül ağırlığı (M_n), ağırlıkça ortalama molekül ağırlığı (M_w) ve heterojenlik indeksi değerleri NaOCl ve hava oksijeni oksidantlarıyla elde edilen ürünler açısından sırası ile 1300 g mol^{-1}, 1500 g mol^{-1}: 1900, 1500 g mol^{-1} ve 1.267 ve 1,154 olarak hesaplandı. Ayrıca, DTA ve TG analizleri sentezlenen polimer ve oligomerin monomerlerine göre termal bozunmaya karşı daha dayanıklı olduğunu gösterdi. Polimerlerin dört nokta prob tekniği ile iletkenlik özellikleri incelendi. Monomer, polimer ve polimer-metal komplekslerinin bazı seçilmiş bakterilere karşı anti-mikrobial aktiviteleri belirlendi.

Ayrıca sentezlenen PHMPMDAP bileşiği gıdalarda nikel iyonunun spektrofotometrik olarak tayini için yeni bir ligand olarak denendi ve elde edilen çalışma sonuçları değerlendirildi.

Anahtar Sözcükler: Oksidatif polikondenzasyon, Schiff bazı oligomer, anti-mikrobial aktivite, yarı iletkenlik, termal kararlılık

ABSTRACT

In this study, Schiff bases were obtained from the condensation reaction of 2,3-diaminopyridine and *p*-phenylendiamine with *o*-vanillin. Then, oxidative polycondensation reaction conditions of monomers with air oxygen, H_2O_2 and NaOCl were examined in alkaline aqueous media and Optimum reaction conditions and the main parameters of the process were determined. Some metal complexes of polymers were synthesized. The structures of the all products were determined by element analysis, FT-IR, ^{1}H-NMR, ^{13}C-NMR and UV-vis spectra. The ^{1}H-^{13}C-NMR data showed that the polymerization proceeded with C-C and C-O-C coupling system of *para* positions and oxyphenylene according to –OH group of monomers. According to the size exclusion chromatography (SEC) analyses of PHMPMDAP, the number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) values were found to be 6200, 4100 and 5400 g mol^{-1}; 6900, 16200 and 7700 g mol^{-1}; 1,113; 3.951 and 1.426 by using air O_2, NaOCl and H_2O_2 oxidants, respectively. According to SEC measurements of OPBNMBMP the number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) values were found to be 1500, 1300 gmol^{-1} ; 1900, 1500 and 1.267, 1.157 by using air O_2 and NaOCl oxidants, respectively. Also, DTA and TG analyses were shown to be stable of polymer and oligomer than that of monomers against thermal decomposition. Semiconductivity properties of oligophenols were examined by four-point prob technique. Also, antimicrobial activities of the compounds were tested against some microorganisms. PHMPMDAP compound were used as a ligand for determination of nickel ions in food stuff by a spectrophotometric method.

Keywords: Oxidative polycondensation, Schiff Base oligomer, antimicrobial activity, semi-conductivity, thermal stability.

SİMGELER VE KISALTMALAR

Simge	Açıklama
HMPMDAP	[2,3-*bis*[(2-hidroksi-3-metoksifenil)metilen]diamino piridin
PBNMBMP	2,2'-{1,4-fenilenbis [nitrilo metiliden]}bis(6-metoksifenol)]
PHMPMDAP	Poli-[2,3-*bis*[(2-hidroksi-3-metoksifenol)metilen]diamino piridin]
OPHMPMDAP	Oligo-[2,3-*bis*[(2-hidroksi-3-methoksifenil)metilen]diamino piridin]
DMF	Dimetilformamid
THF	Tetrahidrofuran
DMSO	Dimetilsülfoksit
H_2O_2	Hidrojen Peroksit
NaOCl	Sodyum Hipoklorit
FT-IR	Foruer Transform İnfrared Spektroskopisi
UV-vis	Ultraviole Görünür Bölge Spektroskopisi
TG	Termogravimetrik Analiz
DTA	Diferansiyel Termal Analiz
NMR	Nükleer Manyetik Rezonans
SEC	Büyüklükçe Ayırma Kromatografisi
M_n	Sayıca Ortalama Molekül Ağırlığı
M_w	Ağırlıkça Ortalama Molekül Ağırlığı
PDI	Poli Disperstlik İndeksi
HOMO	En yüksek enerjili dolu moleküler orbital
LUMO	En düşük enerjili boş moleküler orbital

TABLOLAR DİZİNİ

ŞEKİLLER DİZİNİ

İÇİNDEKİLER

SAYFA NO

1.GİRİŞ

Polimerler; hafif, ucuz, mekanik özellikleri çoğu kez yeterli, kolay şekillendirilebilen, değişik amaçlarda kullanıma uygun, dekoratif, kimyasal açıdan inert ve korozyona uğramayan maddelerdir. Bu üstün özelliklerinden dolayı yalnız kimyacıların değil; makine, kimya, tekstil, endüstri ve fizik mühendisliği gibi alanlarında çalışanların da ilgisini çeken materyallerdir. Tıp, biyokimya, biyofizik ve moleküler biyoloji açısından da polimerlerin önemi büyüktür. Bu değerlendirmeler ışığında polimer kimyası, kimya yanında yukarıda sözü edilen çoğu bilim alanını kapsayan ayrı bir bilim disiplini olarak gözükmektedir (Saçak 2002).

Reaktif (reaksiyona giren) polimer ve oligomerlerin sentezi ve kullanımı, polimer kimyasının gelişmesinin en önemli nedenlerinden biridir. Bu tür polimerlerden biri olan poli ve oligofenoller ve onların Schiff bazı sübstitüentli ürünleri birçok sanayi ve teknik alanlarda geniş çaplı kullanılmaktadır. Polifenoller başlıca uzay ve uçak sanayinde, makine yapımı ve roket tekniklerinde, elektroteknik, radyoteknik ve elektroniğin gelişmesi alanlarında kullanıldığı gibi, bağlayıcı, tutkal, boya, cam, grafit ve polimer plastiklere karşı da kullanılmaları mümkündür. Poli ve oligofenollerin ve bunların Schiff bazı sübstitüentli ürünlerinin, plazmaya, gama ışınlarına, radyasyona ve daha yüksek sıcaklığa dayanıklılık, antistatik vb. gibi özellikleri onları endüstride kullanışlı hale getirmiştir. Bu yönde 1960'lı yıllardan itibaren yürütülen düzenli ve temel araştırmalar konjuge bağlı oligo ve polifenoller ile onların çeşitli türevlerinin sentezlenmesine, sentez yöntemlerinin ve teknolojisinin hazırlanması ve geniş alanda uygulanmasına neden olmuştur (Berlin ve Rahimov 1962).

Poli ve oligofenollerin azometin (-HC=N-) grupları içeren üyelerinin katalizör, kompleks oluşturucu ve antimikrobiyal gibi önemli niteliklere sahip oldukları günümüzde bilinmektedir. Schiff bazı sübstitüentli oligofenoller ve onların türevleri; etkin katalizörler, yarı-iletkenler, sıcaklığa dayanıklı bileşikler ve yeni metal-polimer komplekslerinin eldesi gibi, birçok bilimsel ve teknik problemlerin çözümünde uygun maddeler olarak kullanılmaktadır.

Bunlar dikkate alındığında bu çalışmanın amaçlarını aşağıdaki gibi sıralayabiliriz.

1. Yapısında azometin grupları bulunduran bazı oligofenollerin hava oksijeni, sodyum hipoklorit ve hidrojen peroksit varlığında oksidatif polikondenzasyon reaksiyonu ile sentez şartlarının belirlenmesi,

2. Sentezlenen bu polimerlerin çözünürlük, termal kararlılık, iletkenlik, optik ve elektrkimyasal özelliklerinin incelenmesi.

1.1. OKSİDATİF POLİKONDENZASYON REAKSİYONU VE SCHİFF BAZI SÜBSTİTÜENTLİ OLİGOFENOLLER

1.1.1. Schiff Bazı Polimerleri

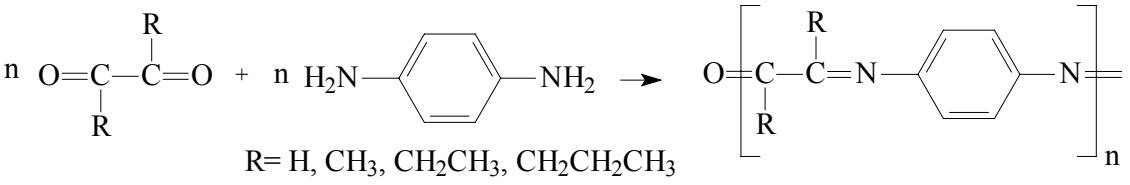
Azometin gruplarının (-HC=N-) kimyasal aktifliğinin yüksek olmasından dolayı, ana ve yan zincirde bu grupları içeren polimerler kimyacıların ilgisini çekmektedir. Bu çeşit polimerler, metallerle kompleks oluşturmalarından dolayı polimer şelatların elde edilmesinde önemlidir (Marvel, 1958; Patel, 1986; Kaya, 2002).

Kassem ve çalışma grubunun yaptıkları çalışmada, kükürt taşıyan Schiff bazı polimerlerinin termal kararlılıklarının Schiff bazının yapısına bağlı olduğunu belirtmişler. Aromatikliğin, konjugasyonun ve güçlü polar grupların artışıyla termal kararlılığın da doğru orantılı olarak arttığı sonucuna varmışlardır (Kassem, 1992).

Sain Schiff bazı Cu(II) kompleksi varlığında 2-naftolün binaftole dönüşümü için oksidatif coupling yöntemi geliştirmiştir (Sain , 2004).

Ayrıca Sain ve çalışma grubu bir başka çalışmada ikincil alkollerin ketonlara yükseltgenmesi için kobalt (II) Schiff bazı katalizörlü aerobik oksidasyon yöntemi geliştirmişlerdir (Sain, 2004).

Xiaochang Li ve çalışma grubu dialdehit ve diamin grupları içeren poli Schiff bazları sentezlemişlerdir ve sentezlenen Schiff bazlarının elektriksel iletkenliklerini hesaplamışlardır.



Schiff bazı polimerlerinin iletkenliğin ölçülmesi işlemi iyot ile doping yöntemi ile gerçekleştirilmiştir. Doping işlemi uygulandıktan sonra polimerlerin iletkenliğinin 10^7-10^9 kat arasında arttığı görülmüştür (Xiaochang Li, 1993).

Li ve çalışma grubu tarafından yapılan çalışmada, $FeSO_4$ ile oluşan Schiff bazı polimer komplekslerinin ferromanyetik özellikleri araştırılmış ve oda sıcaklığında yüksek ferromanyetiklik gösterdiği bulunmuştur (Li,1994).

Yudkin ve çalışma grubunun yapmış olduğu bir çalışmada 2,6-dimetilfenol'ün oksidatif polikondenzasyonu üzerinde çözücünün etkisi araştırılmıştır (Yudkin, 1975).

Aly ve çalışma grubu 2,5-bis(*m*-aminabenziliden)siklo pentanon, 2,6-bis(*m*-aminobenziliden) siklo hekzanon, 2,6-bis(*p*-aminobenziliden) siklo hekzanon, ve 2,6-bis(*m*-aminostiril)pridin diamin bileşiklerinin teraftaldehit ile polikondenzasyon sonucu yeni ve konjuge sisteme sahip poliazometinler sentezlemişler ve bu konjuge poliazometinlerin iletkenlik özelliklerini incelemişlerdir (Aly, 2000).

Catanescu ve çalışma grubu, aktif hidroksi grubu taşıyan yeni alifatik-aromatik poli Schiff bazı sentezlemişler bu poli schiff bazlarının termal özelliklerini incelemişlerdir (Catanescu, 2001). Bir diğer çalışma Diaz ve çalışma grubu tarafından gerçekleştirilmiştir. Selenofen'den türetilen poli iminlerin sentezi, karakterizasyonu ve elektriksel özellikleri incelenmiştir (Diaz, 1999).

Dutta ve çalışma grubu ise yeni poliazometin eterleri doğrusal olmayan optiksel uygulamalar için sentezlemişler ve yapıyı aydınlatmışlardır (Dutta, 2003).

Misra ve çalışma grubu tarafından N, N'-bis(*p*-klorbenzilidin)-2,6-diaminopiridin'in sodyum sülfit ile nükleofilik yer değiştirme polimerizasyonu ile yeni hetero siklik poli (Schiff bazı sülfit) polimerleri sentezlenmiştir (Misra, 1998).

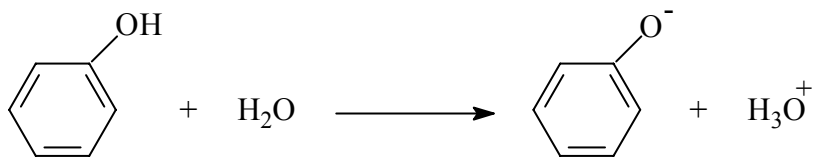
Sun ve çalışma grubu tarafından bistiyazol halka içeren poli Schiff bazlarının özellikleri incelenmiştir (Sun, 1997).

Suh ve arkadaşları tarafından ise yüksek foto iletkenliğe ve doğrusal olmayan optiksel özelliğe sahip poliazometinler sentezlenmiştir. Ayrıca yapıları da uygun spektroskopik metotlar kullanılarak aydınlatılmıştır (Suh, 2000).

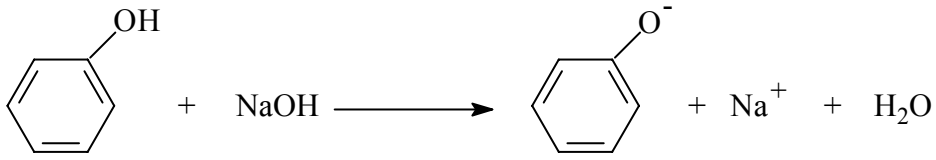
1.1.2. Fenollerin Oksidatif Polimerizasyonu

Fenoller ve aromatik amin bileşiklerinin yapılarında fonksiyonel grup olduğundan, yükseltgenlere karşı aromatik hidrokarbonlardan daha kolay oksidatif polimerizasyon reaksiyonu verirler. Bilindiği gibi; O-H bağı, aromatik C-H bağından daha az enerjili ve polaritesi daha fazladır. Bu nedenle fenollerdeki O-H bağının, yükseltgenlerin etkisiyle homolitik parçalanması daha kolay olmaktadır.

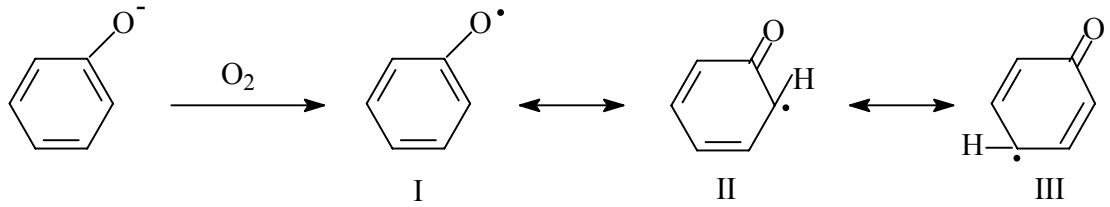
Fenoller, örneğin su gibi, polar çözücü ortamında çözücü moleküllerinin etkisiyle iyonlaşır.



Bazik ortamda iyonlaşma daha fazla olmakta ve fenolat anyonları oluşmaktadır.

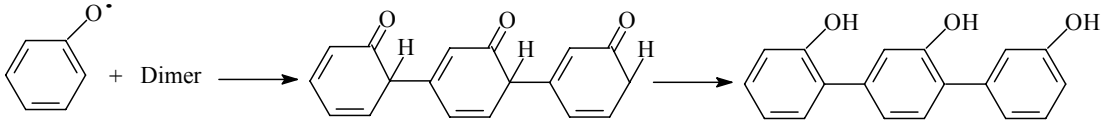


Fenolat anyonları, oksidatif polikondensasyon reaksiyonlarında yükseltgenlerin varlığında kolay ve hızlı bir biçimde fenoksi-radikallere dönüşmektedir.

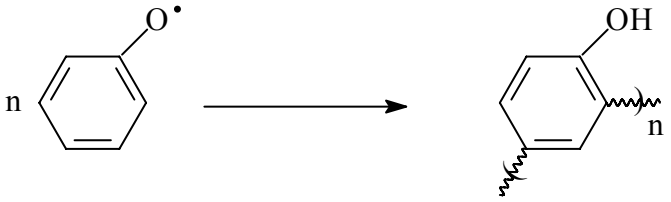


Fenoksi radikaller çok aktif ve kararsız yapıda moleküller olduklarından büyük bir hızla birbirleriyle birleşerek difenol yapısını oluştururlar.

İkinci basamakta difenolatlar ortamdaki yükseltgenlerin etkisiyle, yine fenol-fenoksi radikallere dönüşmekte ve bu yeni radikaller de birbirleriyle birleşerek trimer ve tetramer oluşturmaktadırlar.



Sonraki basamaklarda ise di-, tri-, tetra- ve polimerler meydana gelmektedir.



Günümüzde fenol, krezol, α- ve β-naftoller, hidrokinon ve rezorsinol gibi bazı fenol türevleri kullanılarak oksidatif polimerizasyon yöntemiyle çeşitli polifenoller sentezlenmiştir. Yapılan bu çalışmalarda; aromatik alkollerdeki -OH grubu sayısı ve aromatik halka sayısının

artmasıyla oksidatif polikondensasyona girme yatkınlığının yükseldiği rapor edilmiştir. Bu aktiflik sırası aşağıda bazı moleküller üzerinde gösterilmiştir.

Fenol < *p*-krezol < oksininolin < α-naftol < β-naftol < katekol < rezorsinol < hidrokinon

Bu moleküllerden dioksi bileşikleri, çok yüksek aktiviteye sahip olduklarından oda sıcaklığında bile H_2O_2 ve NaOCl ile yüksek hızla ve ısı vererek oksidatif polikondensasyona girerler. Diğer fenol türevlerinin polikondensasyonu için ısıya gereksinim vardır. Fenollerin yüksek reaktivitesi sebebiyle polimerleşmelerinde, aromatik hidrokarbonlardaki gibi katalizöre ihtiyaç yoktur.

Fenollerin oksidatif polikondensasyonunda yükseltgen olarak başlıca H_2O_2, NaOCl ve oksijen kullanılır.Bu yükseltgenlerin pratikte bir çok kullanım avantajları vardır: Yaygın, ucuz ve teknolojik yönden elverişli olması bunlardan bazılarıdır.

NaOCl, bu yükseltgenler arasında oksidatif polikondensasyon reaksiyonları için en aktifi olup aktivitesi düşük olan fenollerin oksidatif polikondensasyonunda kullanılır. NaOCl kullanımında yan ürün olarak NaCl oluşur. Bu tuzu saflaştırılıp başka amaçlar için kullanmak mümkündür.

Hidrojen peroksitin yükseltgen olarak avantajı, reaksiyonda suya çevrilmesi ve yan ürün oluşturmamasıdır. Diğer taraftan da H_2O_2, bazı katalizörlerin çok küçük (%1-2) miktarları varlığında çok düşük sıcaklıklarda (20-50°C) bile fenolleri oksidatif polikondensasyona uğratmaktabilmektedir. H_2O_2 diğer yükseltgenlere göre pahalıdır.

Hava oksijeni ise oksidatif polikondensasyon reaksiyonunun en uygun yükseltgeyici reaktifidir. Çünkü çok ucuz ve tükenmez bir kaynağa sahiptir. Ayrıca reaksiyon süresince suya çevrilerek hiçbir yan ürün oluşturmaması oksijenin en büyük avantajlarından birisidir.

Hava oksijeni, ılımlı bir yükseltgen olduğundan her türlü fenolün polimerizasyonunda kullanılamaz.

Aromatik hidrokarbonların oksidatif polikondensasyonunda aromatik ve alifatik çözücüler kullanılır. $AlCl_3$ katalizörü, nitrobenzen bileşikleri dışında polar çözücülerle etkilendiğinden bu reaksiyonlar apolar organik sıvılarda yürütülür.

Fenollerin oksidatif polimerizasyonu katalizörsüz yürüdüğünden, reaksiyon polar çözücülerde (su, dioksan, THF, asetik asit, alkol v.b.) gerçekleştirilir. Bu bakımdan, polimerlerden kolay ayrılan, ucuz ve tehlikesiz en önemli çözücü sudur.

1.1.3. Polifenollerin Özellikleri

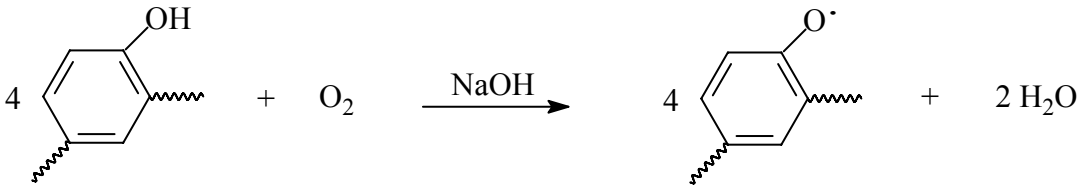
Polifenoller; genelde kahve bazen ise siyah renkli, katı toz halinde maddelerdir. Polifenoller, makromoleküllerini oluşturan birimlerin yapısal özellikleri ve mol kütlesine

bağlı olarak 80-220°C'de eriyen, polar çözücülerde (bazik su, etanol, dioksan, THF, DMF v.b.) çözünen maddelerdir ve onların mol kütleleri 450-40.000 arasında değişebilmektedir.

Polifenoller, konjuge bağ düzenine sahip olduklarından σ-bağlı polimerlerden ve reçinelerden farklı özelliklere sahiptirler. Bu özellikleri; elektriksel yarı-iletkenlik, paramagnetizma, yüksek sıcaklığa, plazma ve radyasyona dayanıklılık, ısıya kararlı kılıcılık, inhibitör, elektron değiştiricilik v.b. şeklinde sıralayabiliriz.

Ayrıca polifenoller, poliarilenlerden ve fenol-formaldehit reçinelerinden farklı olarak çeşitli reaksiyonlara karşı yüksek derecede aktiflik gösterirler. Bu reaksiyonları şu şekilde sıralayabiliriz.

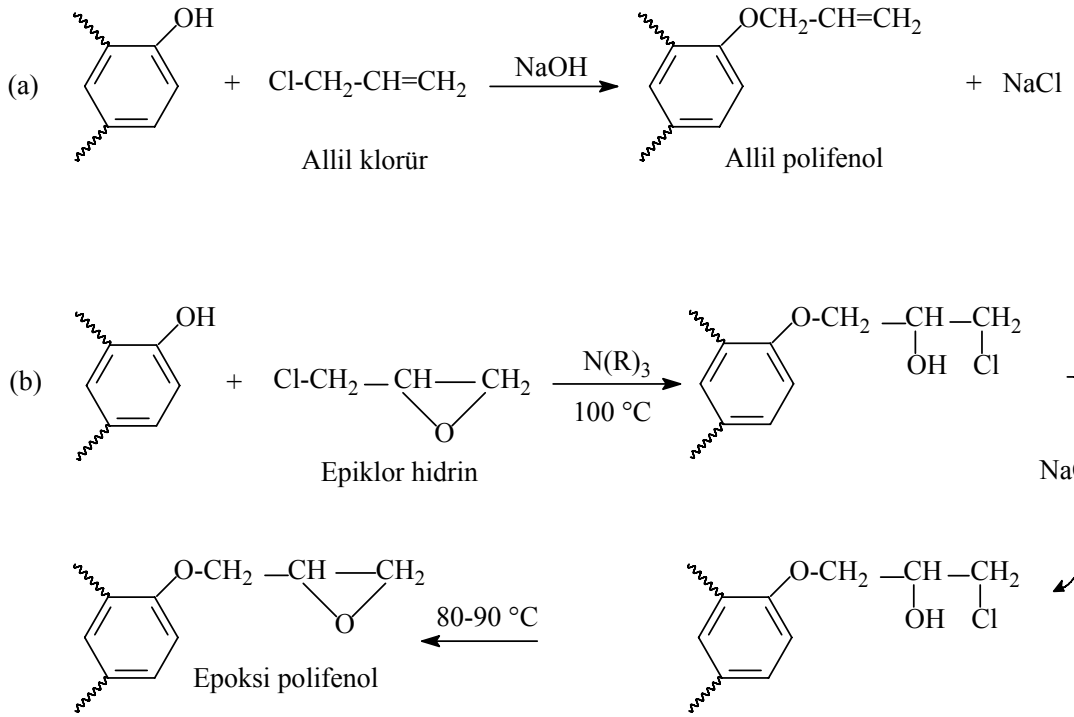
1. Bazik ortamda polifenoller hava ile yükseltgenerek makrofenoksi radikaller meydana getirirler (Mamedov, 1984, 1987).



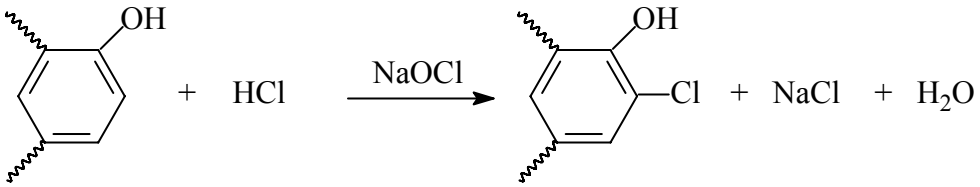
Bu radikallerin çiftleşmemiş elektronları, polimerin konjuge bağ düzeni ile etkileşerek yüksek kararlılık kazanırlar. Sonuçta oluşan polifenoksi radikaller katı halde aylarca sabit kalabilmektedir. Bunların elektriksel iletkenlikleri polifenollere oranla 10^5 kat daha fazladır (Ragimov, 1997).

2. Polifenollerin –OH grupları, fenollerden daha aktiftir. Bu sebeple allil klorür ve epoksi türevleri ile bazik ortamda kolayca tepkime verebilirler (Ragimov, 1985, 1986).

Allil polifenolller ve epoksi polifenoller, termoset polimerler olup yüksek ısıl ve mekanik özelliklere sahip plastik malzemeler oluştururlar.

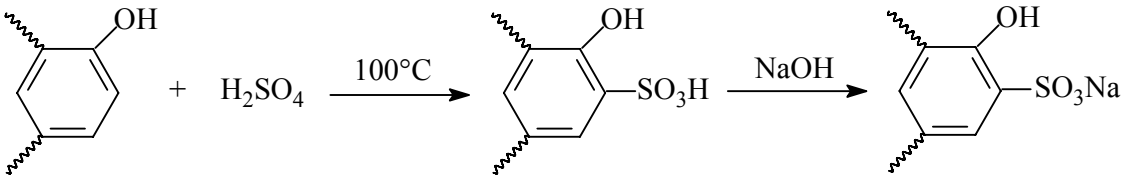


3. Polifenoller, halojenlenme reaksiyonu verebilirler (Ragimov, 1975).



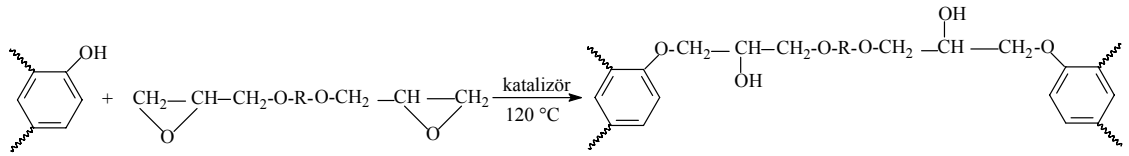
Polifenollerin halojenlenmesi sonucunda; çok değerli aleve karşı dayanıklı maddeler elde edilebilir.

4. Polifenollerin önemli reaksiyonlarından biri de sülfolanma reaksiyonudur (Ragimov, 1985).



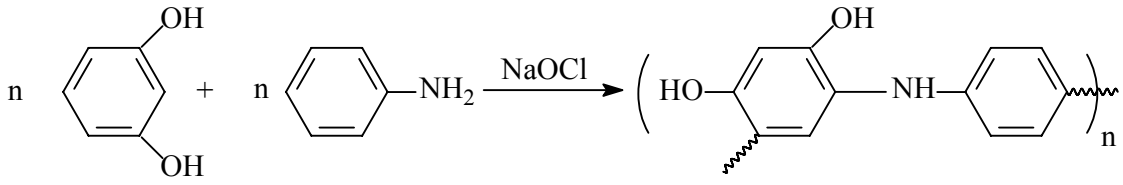
Bu reaksiyon süresince aktif deterjanlar elde edilir.

5. Polifenoller, katalizör varlığında epoksi reçinelere katılarak ağ yapılı polimerler oluştururlar (Mamedov, 1976).



Bu polimerler, yüksek ısıl ve mekaniksel özelliklere sahiptir.

6. Polifenollerin anilinle kopolimerleri elde edilmiştir. Bu amaçla fenoller anilinle beraber oksidatif polimerizasyona uğratılmıştır (Ragimov, 1994).



Yapılan analizler sonucunda, anilinin polimer zincirine fenolden farklı olarak -NHC_6H_5- bağı ile bağlandığı tespit edilmiştir.

7. Yapısında –OH'den farklı olarak –CHO veya $–NH_2$ gibi aktif fonksiyonel grup bulunduran polifenoller sırasıyla aminlerle ve aldehitlerle Schiff bazı verecek şekilde kondensasyona girebilir (Kaya ve ark. 2001, Mart, 2004).

Son yıllarda, konjuge bağ ve aktif hidroksil grupları(-OH) içeren Schiff bazı polimerleri üzerine yapılan araştırmaların sayısı oldukça fazladır. Bu tip polimerler, paramagnetizm, yarı-iletkenlik, elektrokimyasal hücreler ve yüksek enerji etkilerinde kararlılık gibi kullanışlı özelliklere sahiptir (Mamedov ve ark.1997, Suh ve Shim, 2000). Bu özelliklerinden dolayı yüksek sıcaklıkta yüksek kararlılığa sahip kompozitlerin hazırlanmasında, termostabilizörlerde, grafit materyallerde, epoksi oligomer ve blok kopolimerlerde, fotorezistlerde, antistatik ve aleve dayanıklı malzemelerin hazırlanmasında kullanılmıştır (Baughman ve ark. 1982, Ragimov ve ark.1997, El-Shekeil ve ark.1997, Diaz ve ark.1999, Aly ve Khalaf, 2000, Grigoras ve Catanescu, 2004).

Oligofenollerin Schiff bazı sübstitüentli üyelerinin sentezi ve karakterizasyonu Kaya ve çalışma grubu tarafından incelenmektedir.

Kaya ve çalışma grubu, NaOCl, H_2O_2 ve hava oksijeni gibi oksidantlar kullanarak, bazik ortamda 2-*p*-tollilazometinfenolün oligomerini sentezlemişlerdir. Bu çalışmada en yüksek verim, 80 °C' de bazik ortamda oksitleyici olarak NaOCl kullanılması ile elde edilmiştir. Bu şartlarda elde edilen oligomer iki fraksiyonlu olup, sayıca (M_n) ve ağırlıkça ortalama molekül ağırlığı (M_w) değerleri sırasıyla; 625 g mol^{-1} ve 1850 g mol^{-1} olarak belirlenmiştir. Ayrıca elde edilen oligomerin bazı metal kompleksleri sentezlenerek, termal kararlılık ve antimikrobiyal aktivite gibi özellikleri incelenmiştir (Kaya, 2002).

Kaya ve çalışma grubu tarafından yapılan diğer bir çalışmada, salisilaldehitin NaOCl ve hava oksijeni gibi oksidantların varlığında bazik ortamda oligomeri sentezlenmiş ve sentez şartları araştırılmıştır. Ayrıca oligosalisilaldehitin anilin, *o*-toluidin ve nitro anilin ile Schiff bazı oligomerleri sentezlenip termal kararlılıkları incelenmiştir. Bu çalışmanın sonucunda; en iyi oksidantın NaOCl olduğu belirlenmiş ve %70 civarında oligomer oluşumu gözlenmiştir (Kaya, 2001).

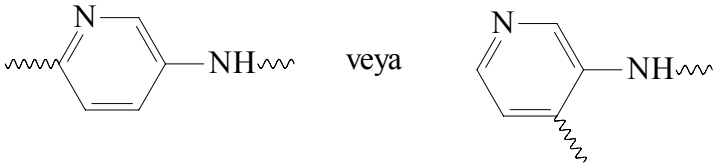
Kaya ve çalışma grubu, oligo-*o*-fenilazometinfenolü sentezleyip, bazı metal komplekslerini yaparak, termal ve antimikrobiyal özelliklerini incelemişlerdir. En yüksek antimikrobiyal aktiviteyi ise oligomer metal komplekslerinin gösterdiği görülmüştür.

Kaya ve çalışma grubu oligosalisilaldehit ve oligoanilinin Schiff bazı graft oligomerini sentezleyip, yapı ve özelliklerini incelemişlerdir (Kaya, 2002).

Yapılan bir başka çalışmada Oligosalisilaldehit'in dietilenglikol bis(2-aminofenil eter) ve trietilenglikol bis(4-aminofenil eter) ile reaksiyonu sonucu elde edilen yeni tür Schiff bazlarının sentezi yapılmış, sayıca (M_n) ve ağırlıkça (M_w) ortalama molekül ağırlıkları sırasıyla; dietilenglikol bis(2-aminofenil eter) için 1690 g mol^{-1} ve 5150 g mol^{-1}, trietilenglikol bis(4-aminofenil eter) için 1100 g mol^{-1} ve 5400 g mol^{-1} olarak bulunmuştur (Kaya, 2002).

2-Hidroksi-1-naftaldehitin NaOCl, H_2O_2 ve hava oksijeni varlığında oksidatif polikondezasyon reaksiyonu yardımıyla oligo-2-hidroksi-1-naftaldehit sentezlenip optimum reaksiyon şartları belirlenmiştir. Ayrıca oluşan ürünün termal özelliklerinin incelenmesi sonucu 1000 °C'de yaklaşık %40 oranında kalıntı bıraktığı ve termal kararlılığının oldukça yüksek olduğu gözlenmiştir (Kaya, 2003).

Oligo-3-aminopiridinin sentezi ve reaksiyon şartları asidik ve nötr ortamda çalışılmış ve %80 civarında vedrim elde edilmiştir. ^{1}H-NMR ölçümleri sonucu yapıların aşağıdaki gibi olduğu saptanmıştır (Kaya, 2003).



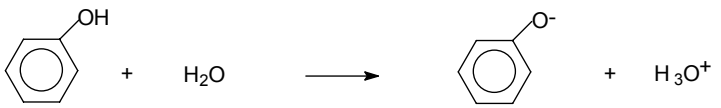
Yapılan çalışmalar sonucunda oligofenoller, yapılarında konjuge π bağları içerdiklerinden dolayı yarı-iletken özellik gösterdikleri gözlenmiştir. Yapılarında –OH, -C=N- gibi grupların bulunması metaller ile ağ yapılı makro moleküller oluşmasına sebep olmaktadır. Ayrıca, oligofenollerin ve oligofenol-metal komplekslerinin, antimikrobiyal aktivite, termal kararlılık, radyasyon ve yüksek enerjiye dayanıklılık, kimyasal reaktiflik, paramagnetizma, boyar madde (tekstil sanayi) olarak kullanım gibi yararlı özelliklerinin olduğu yapılan çalışmalar sonucunda bulunmuştur.

Bu polimerlere başka fonksiyonel grupların da katılmasıyla, yeni kullanışlı bir çok özellikler kazandırılabilmektedir. Schiff bazı polimerleri çeşitli bakteri, maya ve mantarlara karşı anti-mikrobiyal aktivite göstermiştir (Kaya ve ark., 2002a,b). Çeşitli fonksiyonel gruplara sahip polifenoller, endüstriyel atık suların içerdiği zehirli ağır metallerin temizlenmesi işleminde kullanılabilir. Bu nedenle polimer-metal komplekslerinin sentezi, analitik ve çevre kimyası açısından önemlidir. Bu avantajlar göz önüne alınarak polimer yapılı ligandlar hazırlanmış ve geçiş metallerinin bir çoğu ile kompleks formları denenmiştir. Böylece büyük oranda uygulama alanına sahip olmuştur (Kaya ve Gül, 2004).

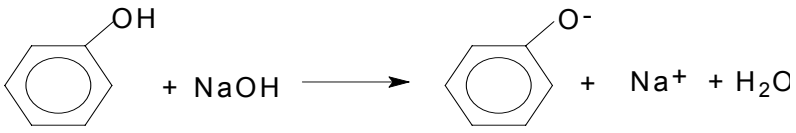
1.1.4. Oksidatif Polikondenzasyon Reaksiyonunun Temel Özellikleri

Fenoller ve aromatik aminler aktif fonksiyonlu grup içerdiklerinden, aromatik hidrokinonlardan daha kolay, oksidatif polikondenzasyon reaksiyonuna katılırlar. Fenoldeki –OH bağı aromatik –CH bağından daha az enerjili ve daha çok polardır. Bu sebepten, -OH grubu, oksitlenme reaksiyonlarında daha kolay homolitik parçalanmaya uğrar.

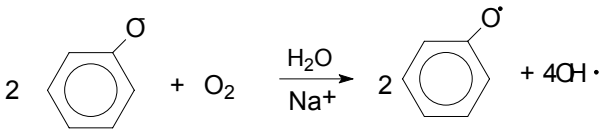
Fenoller polar çözücülerde, örneğin suda, çözünürken, çözücü moleküllerin etkisiyle iyonlaşırlar.



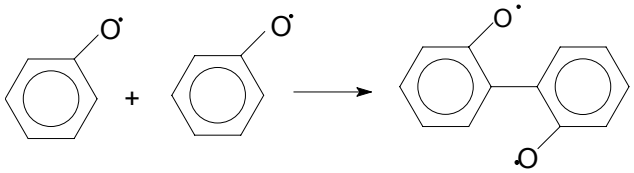
Fenollerin iyonlaşması, bazik ortamda daha kuvvetli olur ve fenolat iyonu oluşur.



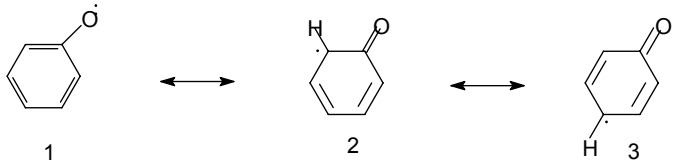
Fenolat iyonları, oksidatif polikondenzasyon reaksiyonlarında oksitlendiricilerin etkisiyle fenoksi radikallere dönüşür.



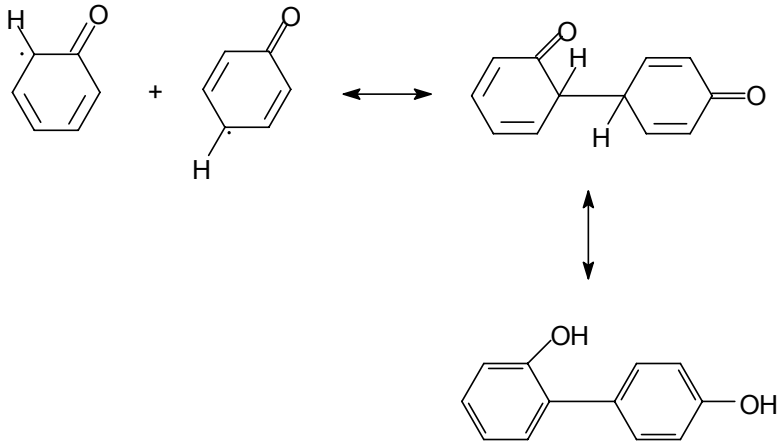
Fenoksi radikaller, birbirleri ile katılarak difenoksi radikalleri oluştururlar.



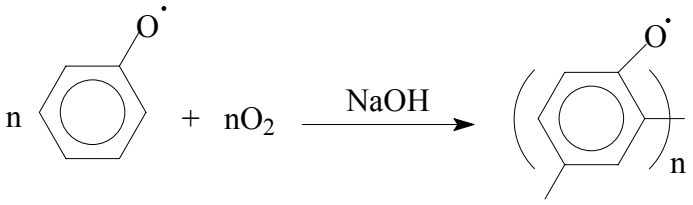
Fenoksi radikaller, Smith ve Oterson'un hesaplamalarına göre 3 mezomer şeklinde olur.



Bu mezomerlerden 2 ve 3 daha kararlı olduğundan, onlar birbiriyle katılarak dimer (difenol) verirler.



Üçüncü aşamada difenoller oksitlenerek, fenolilfenoksi radikallere dönüşürler. Bu dimerik radikal, sonraki basamaklarda birbirleriyle ve fenoksi radikalleriyle katılarak tri ve tetramere çevrilirler. Son olarak oksidatif polikondenzasyon prosesinin sonucu olarak oligofenoller oluşur.



Fenoller oksidatif polikondenzasyon reaksiyonlarında aşağıdaki sıraya göre aktiflik gösterirler:

Fenol<*p*-kresol<oksikinolin<α-naftol<β-naftol<katekol<rezorsinol <hidrokinon

Bu reaksiyonların aşağıdaki özelliklerine göre, katılma polimerizasyonuna ve kondenzasyon polimerizasyonuna benzer ve farklı yönleri vardır.

- Bu reaksiyonlar başlıca aromatik bileşiklerle gerçekleştirilir.
- Oksidatif polikondenzasyon reaksiyonlarında, oksitlendiricilerin varlığı önemlidir.
- Bu reaksiyon basamaklı polimerizasyon olup, polimerlerle birlikte küçük moleküllü maddeler de (H_2O, HCl) oluşturur.
- Oksidatif polikondenzasyon reaksiyonlarında, elektron veren sübstitüentler, reaksiyonun verimini ve monomerlerin aktifliğini arttırır.
- Bu reaksiyonlar tersinmezdir ve oluşan polimer zinciri, diğer polimerler ve küçük moleküllü bileşiklerle etkileşmezler.
- Oksidatif polikondenzasyon reaksiyonu süresince ortamda her zaman monomer olur.

Görüldüğü gibi oksidatif polikondenzasyon reaksiyonları, bazı özelliklerine göre katılma polimerizasyonuna, diğer özelliklerine göre ise polikondenzasyon reaksiyonlarına benzerler. Bu sebepten bu prosese literatürde gerek oksidatif polikondenzasyon gerekse de oksidatif polimerizasyon denir.

Fenolün yapısındaki halkaların ve hidroksil gruplarının sayısı arttıkça aktifliği de artar. Örneğin monofenollerin oksitlenmesi için ısıtmak (80-90 °C) gereklidir. Difenoller oda sıcaklığında ve büyük bir hızla ısının ayrılmasıyla oksitlenme reaksiyonu verirler. Fenoller yüksek aktivitelerinden dolayı, aromatik bileşiklerden farklı olarak oksidatif polikondenzasyon reaksiyonunu katalizörsüz verirler.

Oksidatif polikondenzasyon reaksiyonlarında en çok kullanılan oksitlendiriciler, organik peroksitler, sodyum hipoklorit, hidrojen peroksit ve hava oksijenidir. Organik peroksitler varlığında oluşan oligofenoller, düşük verimli karmaşık bir yapıya sahiptir.

Sodyum hipoklorit (NaOCl) oligofenollerin sentezinde çok yararlı bir oksitlendiricidir. Çünkü onun varlığında yüksek verimle saf oligofenoller oluşur. Bu reaksiyonlar, 70-90°C' de gerçekleşir. Ancak sodyum hipoklorit reaksiyonunda NaCl yan ürünü oluşmaktadır.

Hidrojen peroksit varlığında en temiz ve saf yapılı oligomerler oluşur. Reaksiyonda hiçbir yan ürün meydana gelmez. Bu reaksiyonun en büyük avantajlarından biri de %0.5 Fe(II) varlığında reaksiyonun 35-40°C'de yürüyebilmesidir.

Kullanılan oksitlendiricilerden en önemlisi hava oksijenidir. Hava ucuz ve tehlikesizdir. Havanın varlığında meydana gelen reaksiyonda atık meydana gelmez.

Fenollerin oksidatif polikondenzasyonunda çözücü olarak; apolar çözücüler ve dioksan, THF ve su kullanılır. En çok kullanılan çözücü sudur. Aromatik hidrokarbonların oksidatif polikondenzasyonunda ise temel olarak, aromatik ve alifatik hidrokarbonlar ve onların halojen türevleri kullanılır.

1.1.5. Oligofenollerin Elektriksel Özellikleri

1977 yılında dopinglenmiş asetilenin metalik iletkenliğinin açıklanmasından sonra, iletken polimerler hakkındaki araştırmalar farklı yönlerde hızlı bir şekilde artmıştır. Son zamanlarda, yüksek saflıkta polimerlerin elde edilebilmesi ile birlikte, yarı-iletken aletler üzerinde de bir çok çalışma başlatılmıştır. Bu aletler, normal transistörleri, alan-etkili transistörleri (FET), fotodiyotları ve ışık yayma diyotlarını kapsarlar.

Oligofenollerin ve Schiff bazı substituentli polimerlerin iletkenliklerinin incelendiği dökümanlar literatürde mevcuttur. Ragimov ve arkadaşları tarafından yapılan iki çalışmada naftoksi tipi poliradikallerin elektriksel özellikleri ESR (Elektron Spin Rezonans) spektroskopisi ile incelenmiştir. Çeşitli sıcaklıklarda (60-120ºC), vakum altında yapılan incelemede artan sıcaklıkta ESR sinyalinin artmasıyla radikal miktarında bir artış beklenmiş ve elektriksel iletkenliğin arttığı gözlenmiştir (Ragimov, 1984, 1988).

Ragimov ve arkadaşları tarafından yapılan bir başka çalışmada polikonjuge oligoaminofenollerin (*o*-, *m*-, *p*-) sentez şartları ve iletkenlikleri incelenmiştir. *m*-Oligoaminofenolün (*m*-OAP), polietilen (PE), polistiren (PS) ve polipropilen (PP) ile %5 oranında karıştırılmasından önce ve sonraki direnç değerleri ölçülmüş ve bulunan değerler aşağıdaki Tablo 1.1.5.1.de verilmiştir.

Tablo 1.1.5.1. *m*-OAP'ün PE, PS, PP ile karıştırılması sonucu elde edilen direnç değerleri

Kompozisyon	P_s (ohm)	
	Karıştırma işleminden önce	Karıştırma işleminden sonra
PE + *m*- OAP	6.13×10^{13}	5.4×10^{8}
PS + *m*- OAP	6.9×10^{13}	1.2×10^{9}
Pp + *m*- OAP	5.3×10^{13}	3.7×10^{8}

Tablo 1.1.5.1.'den de görüldüğü gibi *m*-OAP'ün antistatik aktivite gösterdiği gözlenmektedir. *m*-OAP'ün termoplastiklerle muamelesi sonucunda (PS, PP, PE) makroaminofenoksil radikal miktarında meydana gelen artış, bu materyalin yüzeyindeki paramanyetik merkezin konsantrasyonunu artırmış buna bağlı olarak elektriksel iletkenlik artmıştır. Bu verilere dayanarak oligoaminofenollerin endüstriyel polimerler için antistatik katkı maddesi olarak kullanılabileceği bulunmuştur. Oligoaminofenoller için sabit akımda (akımla potansiyel doğrusal olarak değişir) elektriksel iletkenliğin sıcaklıkla üstel bir değişiminin söz konusu olduğu belirlenmiştir. Çeşitli elektrik alanlarında, elektriksel iletkenliğin frekansla değişimi $\sigma \sim f$ ifadesiyle verilmiştir. Burada n=1.0-0.8 arasında değişmektedir. Bunun sonucunda, oligoaminofenollerin yarı-iletken oldukları belirlenmiştir (Ragimov, 1996).

Mamedov ve arkadaşları tarafından yapılan başka bir çalışmada Oligo-rezorsinol'ün sentez şartları ve sıcaklığa bağlı iletkenliklerde değişim ESR spektroskopisi kullanılarak incelenmiştir. Sıcaklık arttırıldığında radikal miktarlarındaki artışa bağlı olarak iletkenlikteki değişim irdelenmiştir (Mamedov, 1997).

2. DENEYSEL ÇALIŞMALAR

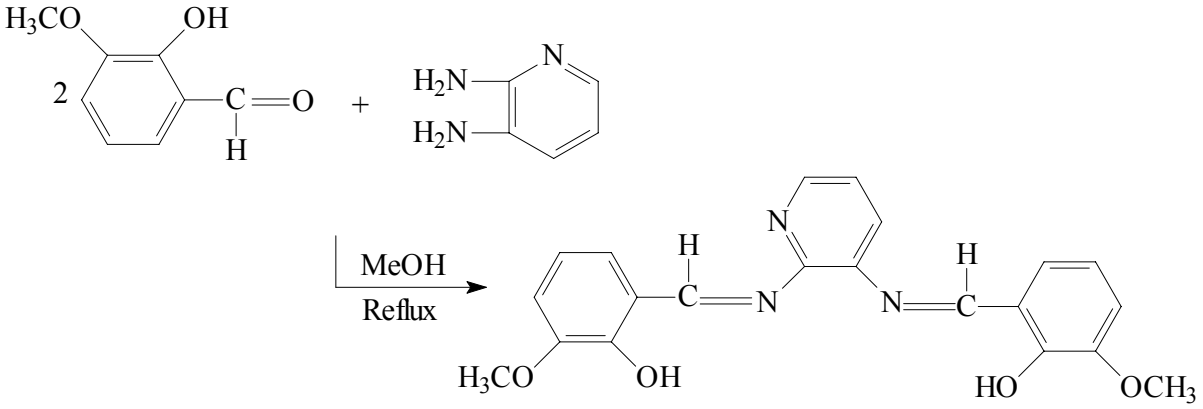
2.1. Schiff Bazı Sübstitüentli Poli/Oligofenollerin Sentezi

Fonkiyonel hidroksi grupları içeren Schiff Bazı monomerleri [2,3-*bis*[(2-hidroksi-3-metoksifenil)metilen]diamino piridin **(1)** (HMPMDAP) ve 2,2'-{1,4-fenilenbis [nitrilo metililiden]}bis(6-metoksi)fenol **(2)** (PBNMBMP) sırasıyla vanilinin; 2,3-diaminopiridin ve *p*-fenilendiamin bileşikleri ile kondenzasyonu sonucu elde edildi. Saflaştırılan ürünler belirli miktarda potasyum hidroksit çözeltisi ile çözülerek hava oksijeni ve sodyumhipoklorit yükseltgenleri ile polimer ve oligomerlerine dönüştürüldü. Reaksiyon tamamlandıktan sonra karışım oda sıcaklığında başlangıçta kullanılan baza eşdeğer miktarda asitle nötralleştirilerek sonlandırıldı (%37 HCl). Reaksiyonda oluşan tuz saf suyla yıkanıp uzaklaştırıldıktan sonra ham ürün 105 °C'de etüvde kurutuldu ve % verim oranları hesaplandı. Her bir polimer için sıcaklığın, zamanın ve yükseltgen derişimlerinin etkisi incelenmesi suretiyle optimum reaksiyon şartları belirlendi. Sentezlenen oligomerlerin metal kompleksleri hazırlandı.

Elde edilen monomer ve polimer/oligomerlerin yapıları UV-vis, FT-IR ve ^{1}H-NMR analizleri yapılarak aydınlatılırken, termal davranışları ile molekül kütleleri dağılımı ise DTA-TG ve büyüklükçe ayırma kromotografisi (SEC) verilerinden faydalanarak, daha ileri karekterizasyon ise monomer, polimer/oligomer ve polimer-metal komplekslerinin bant boşluklarının ve iletkenlik değerlerinin hesaplanmasıyla belirlendi. Sentezlenen monomer ve polimerler ve polimer-metal komplekslerinin antimikrobiyal testleri 5 bakteriye karşı test edildi. Ayrıca gıdalarda nikel tayini için uygulanan metodlara göre sentezlenen PHMPMDAP bileşiği yeni bir ligand olarak denendi ve etkinliği diğer reaktiflerle karşılaştırıldı.

2.1.1. Monomer (1) Sentezi: [2,3-*bis*[(2-hidroksi-3-metoksifenil)metilen]diamino piridin'in (*HMPMDAP*) Sentezi]

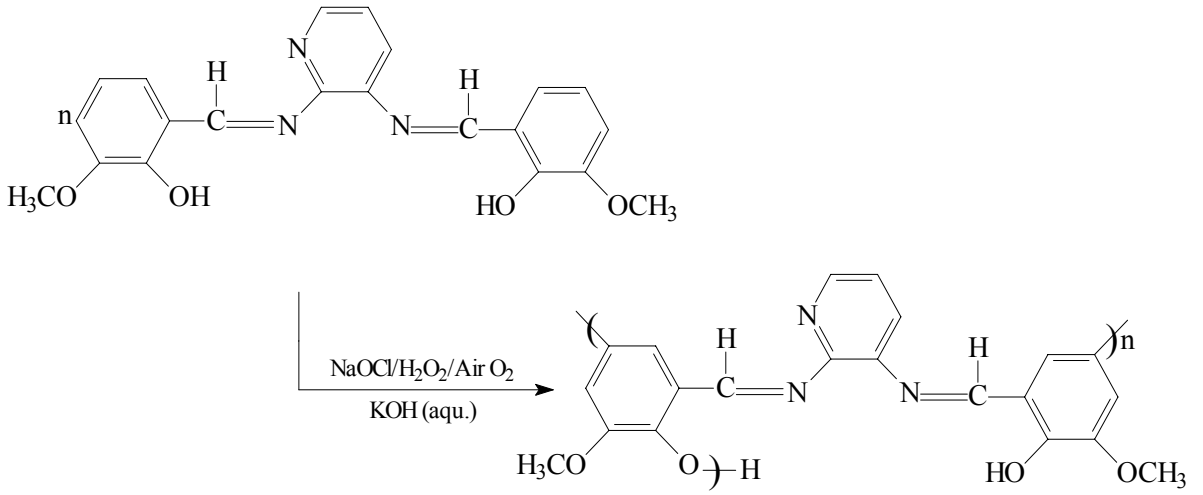
o-Vanillin (1.36 g, 0.01 mol) ve *2,3-di*-aminopyridine (0.545 g, 0.005 mol) oranlarında alınıp 50 mL'lik balonda 15 mL metil alkolde çözüldükten sonra 3 saat geri soğutucu altında manyetik karıştırıcılı ısıtıcı ile ısıtılarak aşağıda reaksiyonda gösterildiği gibi sentezlendi. Reaksiyon sonunda oluşan ürün etil alkolde tekrar kristallendirilerek saflaştırıldı .



2.1.2.Polimer (1) Sentezi

2.1.2.1. 2,3-*bis*[(2-hidroksi-3-metoksifenil)metilen]diaminopiridin'in (PHMPMDAP) NaOCl ile Oksidatif Polikondenzasyonu

HMPMDAP (0,213 g, 0,01 mol), stokiyometrik oranlarda belirlenen KOH çözeltisi ile karıştırılarak saf su içerisinde çözüldü. Reaksiyon karışımı geri soğutucu altında manyetik karıştırıcılı ısıtıcı ile belirlenen sıcaklığa kadar ısıtılıp reaksiyon süresi boyunca reaksiyon ortamına damla halinde NaOCl ilave edildi. Reaksiyon sonunda ortamın nötralleşmesi için eşdeğer miktarda HCl (%37) eklendi ve çöken kısım süzülerek ayrıldı. Katı kısım sıcak saf su ile yıkanarak mineral tuzlardan arındırıldı. Reaksiyona girmeyen monomer etanol ile yıkanarak üründen uzaklaştırıldı ve daha sonra örnek etüvde 105 °C'de kurutuldu.



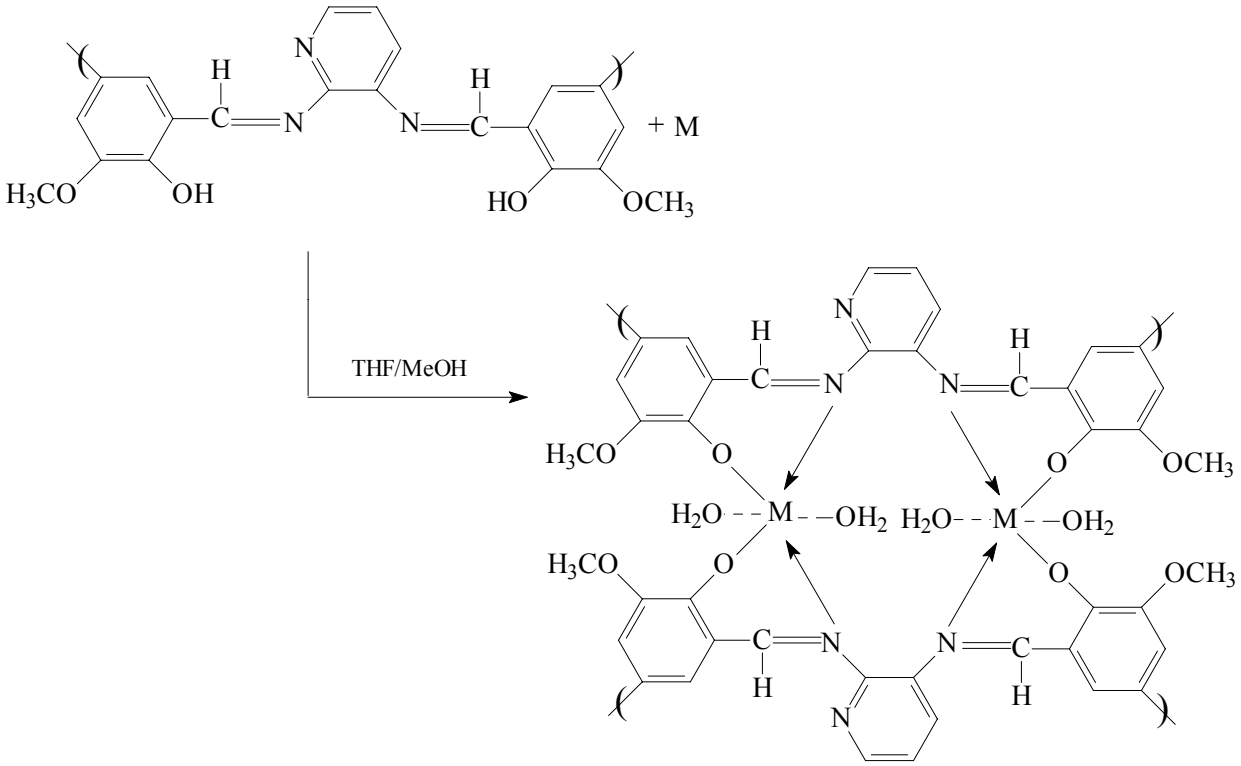
2.1.2.2 HMPMDAP Hava Oksijeni ile Oksidatif Polikondenzasyonu

HMPMDAP (0,213 g, 0,01 mol) stokiyometrik oranlardaki KOH'in sulu çözeltisi içerisinde çözülerek, manyetik karıştırıcılı ısıtıcı üzerinde ve geri soğutucu altında üç boyunlu 100 ml'lik bir balon içerisine yerleştirildi. Deney balonunun bir boyununa termometre takıldıktan sonra reaksiyon ortamına hava göndermek için diğer boyuna bir cam boru takıldı.

Havanın reaksiyon ortamındaki akış süresi 8,5 L/s hıza ayarlandı. Reaksiyon ortamındaki suyu kaybetmemek ve NaOH'un havadaki CO_2'i nötralize etmesi için hava oksijeni reaksiyon balonuna gönderilmeden önce 200 ml % 20'lik NaOH çözeltisinden geçirildi. Reaksiyon tamamlandıktan sonra karışım oda sıcaklığında başlangıçta kullanılan baza eşdeğer miktarda asitle nötralleştirildi (% 37 HCl). Reaksiyonda oluşan tuz saf suyla yıkanıp uzaklaştırıldıktan sonra ham ürün 105°C'de etüvde kurutuldu.

2.1.3. PHMPMDAP Metal Komplekslerinin Sentezi

Polimerin THF daki çözeltisini Co $(AcO)_2$ $4H_2O$, Cu $(AcO)_2$ $4H_2O$, $FeSO_4$ $7H_2O$, $Zn(AcO)_2$ $4H_2O$, $Pb(AcO)_2$ $3H_2O$ tuzlarının uygun çözücülerdeki çözeltileri ile 70 C'de 3 saat karıştırmak suretiyle polimer metal kompleksleri sentezlendi. Reaksiyon ortamında oluşan kalıntı süzülerek ayrılarak soğuk su ile yıkandı ve daha sonra soğuk MeOH/THF (1:1) karışımından süzülerek vakum fırınında kurutuldu.

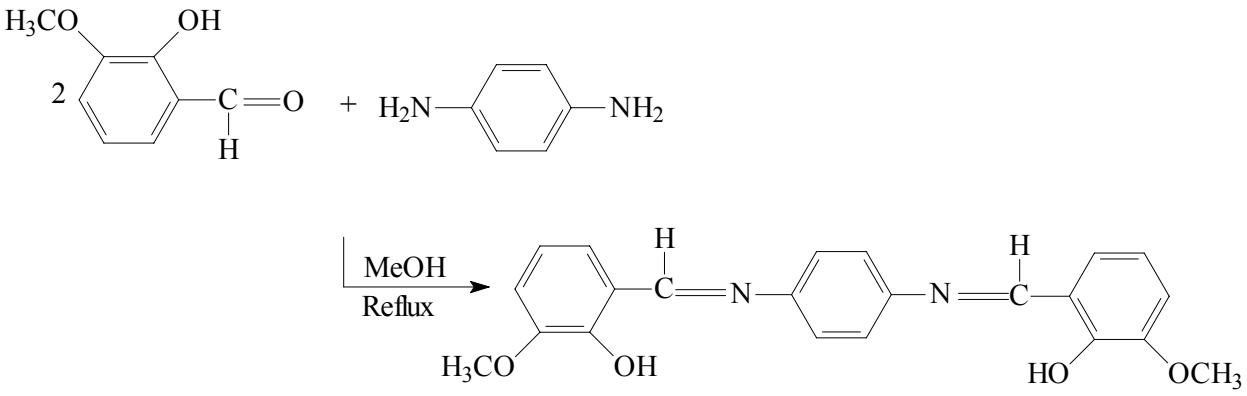


2.2. Monomer (2) Sentezi:

2.2.1. 2,2'-{1,4-phenylenebis [nitrilo methylylidene]}bis(6-methoxyphenol) (PBNMBMP) Sentezi

o-Vanilin (10.88 g, 0.08 mol) ve *2,3-d*iaminopiridin (4.32 g, 0.04 mol) oranlarında alınıp 75 mL metil alkolde çözüldükten sonra 3 saat geri soğutucu altında manyetik

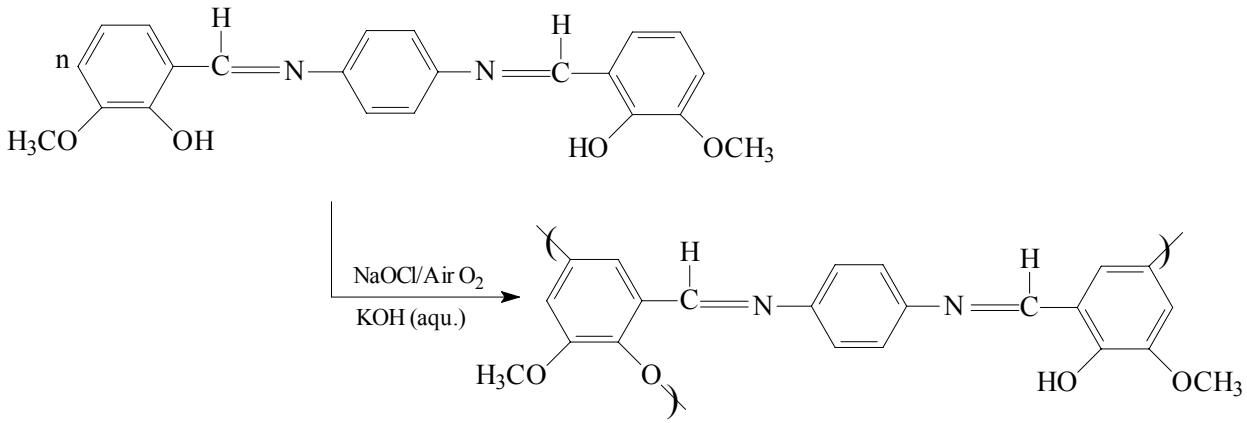
karıştırıcılı ısıtıcı bulunan bir sistemde ısıtılarak bir önceki monomer sentezinde olduğu gibi sentezlendi. Reaksiyon sonunda oluşan ürün etil alkolde tekrar kristallendirilerek saflaştırıldı.



2.2.2. Oligomer (2) Sentezi:

2.2.2.1. 2,2'-{1,4-phenylenebis [nitrilo methylylidene]}bis(6-methoxyphenol)'ün (PBNMBMP) NaOCl ve Hava Oksijeni ile Oksidatif Polikondenzasyonu

PBNMBMP'in polimerizasyonu bir önceki monomerin polimerize edilmesinde olduğu gibi aşağıdaki akım şemasına göre sentezlenmiştir.



2.2.3. OPBNMBMP'in Bakır Komplekslerinin Sentezi

Oligomerin THF daki çözeltisine Cu $(AcO)_2$ $4H_2O$'ın metil alkoldeki çözeltisi ile 70 C'de 3 saat karıştırmak suretiyle bakır kompleksi sentezlenmiştir. Reaksiyon ortamında oluşan ham ürün süzülerek soğuk su ile yıkandı ve daha sonra soğuk MeOH/THF (1:1) karışımından süzülerek vakum etüvünde kurutuldu.

2.2.4. OPBNMBMP ile Gıdalarda Nikel İyonunun Spektrofotometrik Olarak Tayini

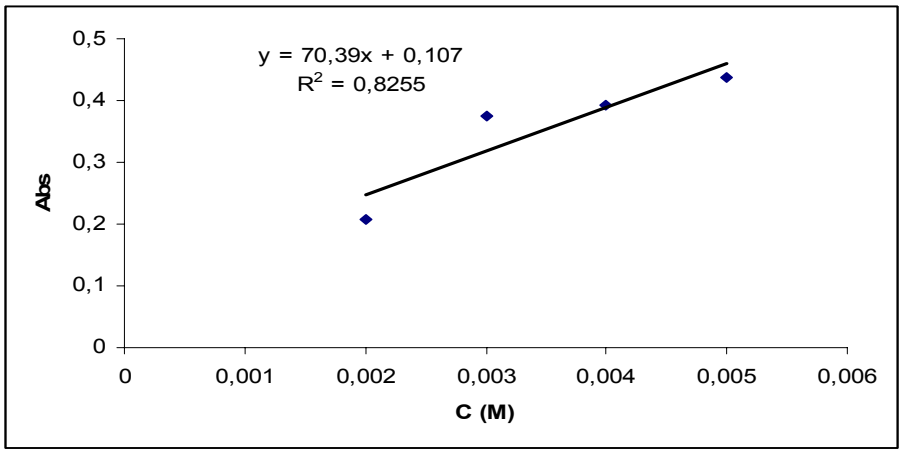
2.2.4.1. Reaktifler

Kullanılan reaktifler analitik saflıktadır ve tüm çözeltiler iki kere destile edilen saf su ile hazırlandı.

%1(w/v)'lik kromojenik reaktif çözeltisi uygun miktarlardaki PHBMPBAB'nin THF'deki çözeltisi ile hazırlandı. Çalışma solusyonları hazır olarak temin edilen [Ultra Scientific Analytical solution (1000 µg/ml) Matriks= (%2'lik HNO_3)] çözeltisinden uygun miktarlar alınarak hazırlandı. 0,001M Boraks çözeltisi 0.38 g $Na_2B_4O_7$. $10H_2O$'nın 100ml'ye tamamlanması ile elde edildi.

2.2.4.2. Nikel Tayini

Standart stoklardan hazırlanan bir seri nikel solüsyonundan birer mililitre 25 ml'lik balon joje içerisine alındı. 0.2ml boraks tamponu ve %1(w/v)'lik kromojenik reaktif çözeltisinden 1 ml'si balon jojeye ilavesinden sonra işaretli çizgisine kadar saf su ile doldurduldu. Ağzı kapatıldıltan sonra balon joje bir vortkste beş dakika kadar karıştırıldı. Reaktif solusyonun ilavesi ile beklenen renk değişimi gözlendi. Yaklaşık 465 nm'de ölçümler alındı. Ultraviyole spektrumunda polimerde gözlenmeyen 465nm dalga boyundaki pik metal kompleksleri için d-d geçişlerine aittir. Optimum deney şartlarını aşağıda anlatıldığı şekilde belirlenmesinden sonra $2x10^{-3}$ M , $3x10^{-3}$ M , $4x10^{-3}$ M, $5x10^{-3}$ M konsantrasyonlarında hazırlanan nikel solüsyonlarının birer mililitresi ile 1ml 0,01%'lik reaktif solüsyonun karıştırıldı. 0.2ml boraks tamponu bu karışıma ilave edilmesini takiben votekste 5 dakika karıştırıldı ve 465nm de ölçümler alınarak aşağıdaki şekilde olduğu gibi konsantrasyon değerlerine karşı elde edilen absorbans değerleri grafiğe geçirildi. Lineer regrasyon eşitliği y= 70.39 x + 0.107 (r=0,8225) olarak elde edildi.Bu eşitlikte x nikelin molaritesini, y değeri ise absorbansını vermektedir.



Şekil 2.2.4.2.1. Nikel tayini için elde edilen kalibrasyon grafiği

Konsantrasyon(M)	Absorbans (λmax)
$2x10^{-3}$	0,20848
$3x10^{-3}$	0,37449
$4x10^{-3}$	0,39364
$5x10^{-3}$	0,43673

2.2.4.3. P^H'nın Etkisi

Yapılan bu çalışmada P^H'nın etkisi can alıcı derecede önemlidir. Reaktif solüsyonu ve nikel solüsyonlarının uygun miktarlarının karıştırılmasından sonra ölçümden önce oluşması gereken renk dönüşümü P^H değerinin belirlenmesiyle mümkün olmaktadır. PHBMPBAB-Ni kompleksi için maksimum absorbans ölçümleri P^H 6.5- 7,5 arasında alındı. P^H 7 bu deneyler için optimum P^H değeri olarak seçildi. Bu ise yaklaşık 0,2 ml boraks tampon çözeltisinin ilavesi ile sağlanabilir.Bu yüzden deneylerde 0,2 ml boraks çözeltisi kullanıldı.

2.2.4.4. PHBMPBAB'nın Derişiminin Etkisi

PHBMPBAB-Ni kompleksinin absorbansında PHBMPBAB'nin konsantrasyonunun etkisi de incelendi. Bu amaçla 1.0×10^{-3}M nikel içeren 1 ml solüsyon yaklaşık 1 ml %0,001'lik PHBMPBAB in tamamı ile reaksiyona girdiği belirlendi.Bu amaçla 1 ml %0,001'lik PHBMPBAB çözeltisi deneylerde kullanıldı.

2.2.4.5. Metodun doğruluğu

Bu metodun doğruluğunu test etmek amacıyla içerisindeki nikel miktarı atomik absorbsiyon spektrometresi ile önceden tayin edilen numuneler kullanıldı. Elde edilen sonuçlar Tablo 2.2.4.5.1'de verildi

Tablo 2.2.4.5.1. Atomik absorpsiyon sonuçları

AAS ile bulunan değer (_g g^{-1})	Önerilen metod ile bulunan değer (_g g^{-1})
0,33[a]	24
0.52[b]	41

a= Un mumunesi
b= Çay numunesi

2.2.4.6. Gıda Ürünlerinde Nikelin Tayini

Gıda ürünlerinde nikel tayini için standart bir analitik prosedür uygulandı. Bu amaçla analiz edilecek numune 70 °C'de bir gün kurutuldu. Sonra desikatörde soğutuldu. Kurutulmuş numune homojenize edilerek 10 g alındı. Enfrarüj lambasında yakma işleminden sonra (bu işlem etil alkol ile de yapılabilir) 500°C de külleştirildi. Eğer un ürünleri ise sıcaklık 900°C'dir. Külleştirme işlemi sonunda kroze içindeki kül rengi gri-beyaz arasında olmalıdır. Yakma işlemi sonucu bu renk elde edilmemişse külleştirme işlemi tam yapılmamış olup sonuçların doğruluğunu etkileyecektir. Bu amaçla bir iki damla destile su krozeye ilavesinden sonra beyaz-gri renk elde edilene kadar bu işleme devam edilir. Krozede külleştirilen numune 20 ml derişik nitrik asitle kaynatılarak kuruluğa kadar buharlaştırıldı. Soğutulduktan sonra tuzları çözmek için 10ml soğuk su ilave edildi. 25 ml'lik standart balon jojeye konuldu. 1ml %9 luk tiyoüre solüsyonu ve 2ml %2 lik sodyum florür ilavesinden sonra balon joje çizgisine kadar doldurudu. Kör için de aynı işlemler yapıldı. Bulunan sonuçlar atomik absorbsiyon sonucu ile karşılaştırıldı.

2.2.4.7. PHBMPBAB'nın kullanılan diğer reaktiflerle karşılaştırılması

Nikel iyonlarının spektrometrik tayini için bir çok reaktif mevcuttur. Ancak bu kullanılan reaktiflerin çoğu bazen duyarlılık, seçimlilik sorunları, yabancı iyon etkisi, bazen de uygulama prosedürlerinin oldukça karışık olması gibi sorunları beraberinde getirmiştir. Çok dişli ligandlar olan Schiff bazı oligomerleri geçiş metal iyonları ile oda sıcaklığında bile çok kararlı kompleksler vermektedir. Geçiş metallerinin belirlenmesi için polimerik veya oligomerik bileşiklerin kullanılması ile ilgili olarak herhangi bir literatüre rastlanmamıştır. Bu yüzden monomer bileşiklerin polimerleri hazırlanarak bu çalışmalarda etkin ligand olarak kullanılıp kullanılmayacağı incelenmek istendi. Gıdalarda, UV spektroskopisi kullanılarak ağır metal iyonu tayini için bazı reaktif ve bu reaktifler için UV parametreleri Tablo 2.2.4.7.1.'de verildi.

Tablo.2.2.4.7.1. Nikel'in spektrofotometrik tayini için kullanılan reaktifler

Metal İyonu	Reaktif	Dalga Boyu ƛ (nm)	Absorbans Değeri (ε)	PH Aralığı
Nikel (II)	Dimethyl glyoxime	445	1.5×10^{-4}	1.16
Nikel (II)	5,17-Bis(quinolyl-8-azo)-25,26,27,28-tetrahydroxy calix[4]arene	580	1.28×10^{-5}	10.7
Nikel (II)	5-(6-Methoxy-2-benzothiazoleazo)-8-aminoquinoline	623	1.28×10^{-5}	9.5–10.5
Nikel (II)	Benzothiaxolyldiazaoaminoazobenzene	550	1.96×10^{-5}	9–9.8
Nikel (II)	2-[2-(5-Methylbenzothiazolyl)azo]-5-dimethylaminobenzoic acid	640	1.32×10^{-5}	5.6
Ni (II)	*p*-Acetylarsenazo	630	6.5×10^{-4}	6
Ni (II)	1-(2-Pyridylazo)-2-naphthol-6-sulfonic acid	570	5.6×10^{-4}	5–10
Ni (II)	2-(2-Imidazolylazo)phenol-4-sulfonic acid	510	2.7×10^{-4}	5.5
Ni (II)	5-(6-Methoxy-2-benzothiazoleazo)-8-aminoquinoline	623	1.28×10^{-5}	10
Ni (II)	2-(2-Benzothiazolylazo)-5-dimethylaminobenzoic acid	640	1.2×10^{-5}	8.5
Ni (II)	7-(4,5-Dimethyl-2-thiazolylazo)-8-hydroxyquinoline	560	1.12×10^{-5}	5.2
Ni (II)	*N*,*N*′-bis(3-methylsalicylidene)-*ortho*-phenylene diamine	640	1.2×10^{-5}	8.5

(Tablo.2.2.4.7.1. Ali Reza Fakhari at all. Talanta 2005 de yayınlanan makaleden alınmıştır.)

PHBMPBAB Nikel tayininde kullanılan diğer reaktiflerle karşılaştırıldığında nikel tayini için etkili bir reaktif olarak değerlendirilemeyeceği ortaya çıkmaktadır. Monomerinin başarılı olarak nikel tayininde kullanılabilmesine rağmen, aynı başarı polimer bileşiği için geçerli olmamıştır. Bu olası olarak monomerin polimere dönüşümünün C-O bağları üzerinden gerçekleşmesi ve nikel iyonunun bağlanacağı hidroksil gruplarının kapalı bulunmasından

kaynaklanabileceği düşünülebilir. Bu durum ise uygun çözücü, sıcaklık, baz ve uygun yükseltgen derişiminin belirlenerek C-C seçiciliğinin arttırılmasıyla sağlanabilir.

2.3. Test Mikroorganizmaları ve Test Bileşiklerinin Hazırlanması

Çalışılan test mikroorganizmaları Refik Saydam Hıfzısıhha (Ankara) merkezinden temin edildi. Bu çalışmada, Bacillus Subtilis ATCC 6633, Listeria Monocytogenes NCTC 5348, Pseudomena Aerugenosa ATCC 15442, Staphylococcus Aureus ATCC 25923 , Escherichia Coli ATCC 11229 bakterileri kullanıldı. Mikrobiyolojik çalışmada incelenecek test bileşikleri için tek konsantrasyon dozu (0.1mg/ml,) hazırlandı ve bu hazırlanan çözeltiden 25 µL boş antibiyotik emdirilmemiş disklere emdirildi. Tüm test bileşikleri dimetilsülfoksitte çözüldü. Test mikroorganizmaları Nutrient Broth içerisinde 37ºC'de 24 saat test mikroorganizmalarını aktive etmek amacıyla inkübe edildi. Besiyeri otoklav işleminden sonra sıcaklık 40-45ºC'ye geldiğinde Nutrient broth içerisinde zenginleştirilmiş test mikroorganizmalrından yeteri kadar tatbik edildi. Hazırlanan karışım hava kabarcıklarının oluşmamasına dikkat edecek şekilde yavaşça 100 mm çapındaki steril petri plaklarına yavaşça döküldü. Ortamın katılaşmasından sonra 25µL test bileşiklerinin emdirilmiş olduğu 6 mm çapındaki steril antibiyotik emdirilmemiş disklere tatbik edildi. Kontrol olarak dimetil sülfoksit kullanıldı.

3. SONUÇLAR VE TARTIŞMA

3.1. Bileşiklerin Oksidatif Polikondenzasyonu Reaksiyon Şartlarının Belirlenmesi

3.1.1. HMPMDA'in NaOCl ile Oksidatif Polikondenzasyonu

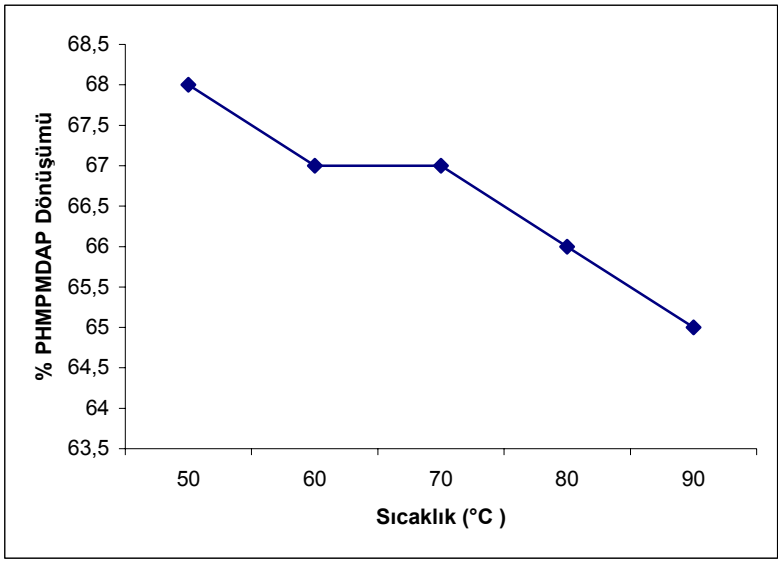
HMPMDA'in, bazik ortamda NaOCl ile oksidatif polikondenzasyon reaksiyonunda sıcaklığın artmasıyla beraber verim 60°C'ye kadar arttı ancak bu sıcaklığın üzerinde verimin azaldığı görüldü. 60°C'de sürenin artmasıyla da 3 saate kadar verimin arttığı açıkça gözlenmektedir. Ancak bu sürenin fazlasında verim az da olsa azaldı. Bu sebepten dolayı HMPMDA'in, optimum reaksiyon şartının 60^{o}C'de 1 saat olduğu sonucuna varıldı. Elde edilen ürün miktarları ve reaksiyon şartları Tablo 3.1.1.1.'de verildi.

Tablo 3.1.1.1. Bazik ortamda NaOCl (Deney No:1-9) ve Hava oksijeni (Deney No:10-19) ile HMPMDAP[a]'nın polikondenzasyon reaksiyon şartları

Deney No	$[KOH]_o$ (mol L^{-1})	$[NaOCl]_o$ (mol L^{-1}) hava O_2 (Litre/saat)	Sıcaklık. (^{o}C)	Süre, (Saat)	PHMPMDAP'nin % Verimi
1	0.014	0.014	50	1	68
2	0.014	0.014	60	1	67
3	0.014	0.014	70	1	67
4	0.014	0.014	80	1	66
5	0.014	0.014	90	1	65
6	0.028	0.028	50	1	70
7	0.014	0.028	50	1	40
8	0.028	0.028	50	3	65
9	0.028	0.028	50	5	62
10	0.014	8.5	50	1	27
11	0.014	8.5	60	1	38
12	0.014	8.5	70	1	34
13	0.014	8.5	80	1	30
14	0.014	8.5	90	1	23
15	0.014	8.5	60	3	44
16	0.014	8.5	60	5	26
17	0.014	8.5	60	10	21
18	0.014	8.5	60	15	17
19	0.014	8.5	60	25	8

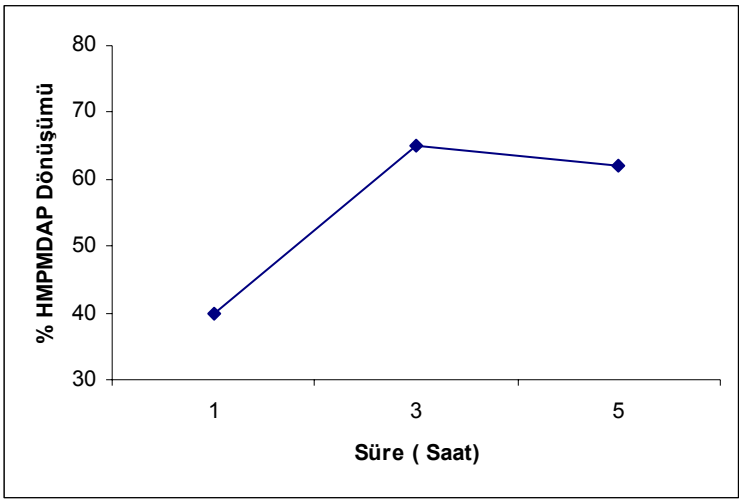
a = HMPMDAP'ın başlangıç konsantrasyonu 0.014 mol L^{-1}

NaOCl oksidantı için sıcaklık, zaman, KOH ve NaOCl'in başlangıç konsantrasyonun HMPMDA'in polimere dönüşümüne olan etkileri Şekil 3.1.1.1., 3.1.1.2., 3.1.1.3. ve 3.1.1.4.'de verildi. Polimer oluşumu bu dört parametreden de etkilenmektedir.



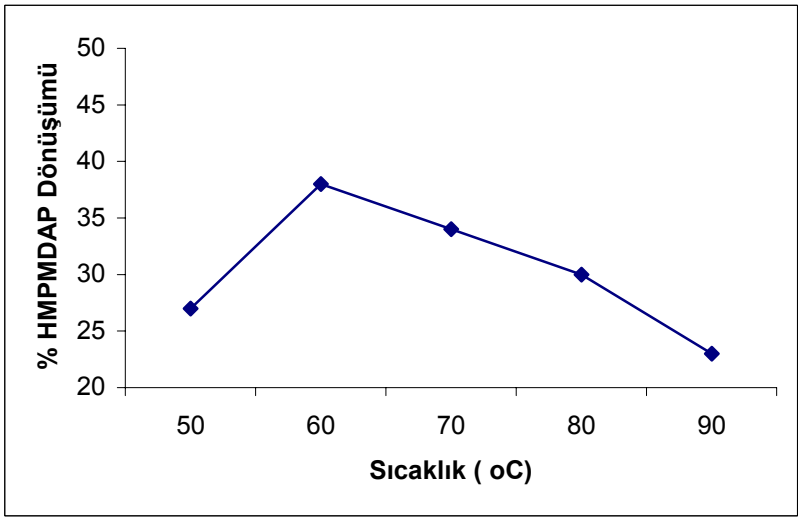
Şekil 3.1.1.1. Alkali ortamda reaksiyon sıcaklığının bir fonksiyonu olarak NaOCl oksidantı için HMPMDAP'ın dönüşümü üzerindeki etkisi

50 ile 90 ^{o}C arasında monomer ve baz derişimleri sabit kaldığında monomer dönüşümünün sıcaklığa bağılığı Şekil 3.1.1.1. verildi. Bu değerlere göre verimin en yüksek olduğu sıcaklık 50 ^{o}C olup sıcaklığın artmasına paralel olarak verimde bir azalma olduğu görüldü. Buna istinaden elde edilen ürünlerin renklerinde sıcaklık arttıkça sırasıyla açık kahverengi- koyu kahverengi ve siyah renk dönüşümü olduğu gözlendi. Bu artan sıcaklık değerlerinin yüksek molekül ağırlıklı polimerler oluşması lehinde olduğu şeklinde yorumlanabilir. Bu ise konjuge yapıda bulunan oksokrom OH gruplarının artmasından bağlanabilir. Bu verileri SEC analiz sonuçları da destekler.

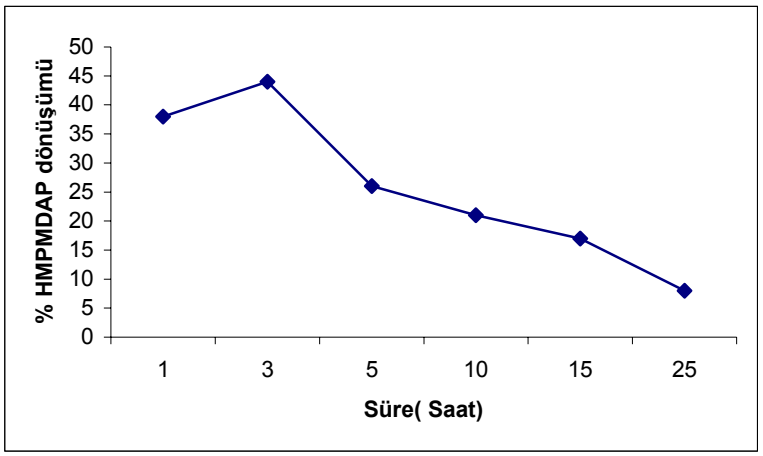


Şekil 3.1.1.2. Alkali ortamda reaksiyon süresinin bir fonksiyonu olarak NaOCl oksidantı için HMPMDAP'ın dönüşümü üzerindeki etkisi

Monomer dönüşümü için en uygun sıcaklık ve monomer konsantrasyonu tespit edildikten sonra çalışmanın diğer aşamasında reaksiyon süresinin monomer dönüşümündeki etkisi incelendi. Reaksiyon süresinin artması ile polimer verimlerinde azalma tespit edildi. Bu ilerleyen reaksiyon sürelerinde oluşan polimerik yapıların tekrar parçalanması yönünde olmasından kaynaklanabilir. 3 saatlik süre bu şartlarda monomer dönüşümü için en uygun süre olduğu tespit edildi. İlerleyen sürelerde monomer dönüşüm miktarı azalmasına karşın oluşan polimerin molekül ağırlığının arttığı ve çözünürlüğünün de buna paralel azaldığı ve elde edilen ürünlerin renklerinin ise koyulaşmaya başladığı gözlendi.

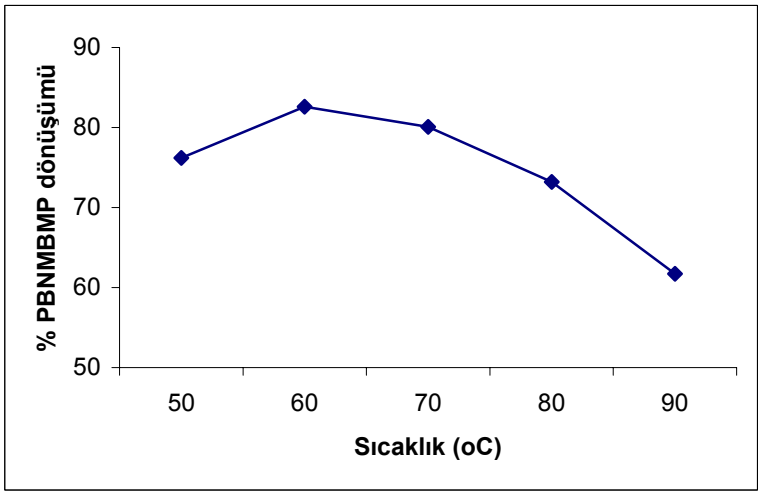


Şekil 3.1.1.3. KOH'un başlangıç konsantrasyonunun bir fonksiyonu olarak hava oksijeni ile HMPMDAP'ın dönüşümü üzerindeki etkisi



Şekil 3.1.1.4. Alkali ortamda hava oksijeni ile reaksiyon süresinin bir fonksiyonu olarak HMPMDAP'ın dönüşümü

Yükseltgen unsurların polimerizasyon reaksiyonlarına olan etkisinin değerlendirilmesi amacıyla hava oksijeni ile de çalışıldı ve elde edilen değerler karşılaştırılma yoluna gidildi. Bu amaçla verilen konsantrasyon aralığında monomer değişik sürelerle ısıtılmak suretiyle elde edilen verimler incelendi. Buna göre en yüksek verim yine 3 saatte olduğu tespit edildi. Elde edilen ürün dönüşümleri sodyum hipokloritin yükseltgen olduğu deney şartlarına göre daha az ve daha düşük molekül ağırlıklı ürünler elde edildi. Bu veriler bu polimerizasyonda sodyum hipokloritin hava oksijenine karşı daha etkili bir yükseltgen olduğu sonucuna götürmektedir.



Şekil 3.1.1.5. Alkali ortamda reaksiyon sıcaklığının bir fonksiyonu olarak NaOCl oksidantı için PBNMBMP'ın dönüşümü üzerindeki etkisi

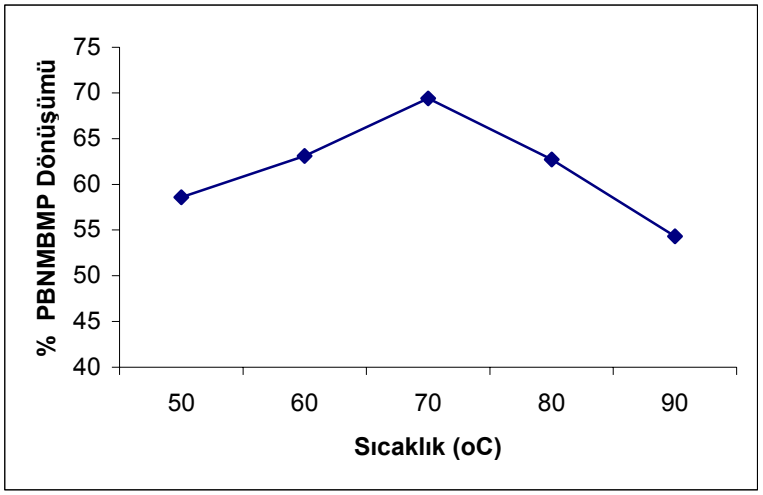
Tablo 3.1.1.2. Bazik ortamda NaOCl (Deney No:1-9) ve Hava oksijeni (Deney No:10-19) ile PBNMBMP'nın polikondenzasyon reaksiyon şartları

Deney No	$[KOH]_o$ (mol L^{-1})	$[NaOCl]_o$ (mol L^{-1})/ Hava O_2 (L/h)	Sıcaklık. (^oC)	Süre, (saat)	PBNMBMP'nin % Verimi
1	0.027	0.027	50	1	76.2
2	0.027	0.027	60	1	82.6
3	0.027	0.027	70	1	80.1
4	0.027	0.027	80	1	73.2
5	0.027	0.027	90	1	61.7
6	0.081	0.027	60	1	96.0
7	0.054	0.054	60	1	83.0
8	0.027	0.054	60	1	95.2
9	0.027	0.081	60	1	98.2
10	0.054	0.054	60	3	79.45
11	0.054	0.054	60	5	70.13
12	0.027	0.027	50	1	58.6
13	0.027	0.027	60	1	63.1
14	0.027	0.027	70	1	69.4
15	0.027	0.027	80	1	62.7
16	0.027	0.027	90	1	54.3
17	0.027	0.027	70	0.5	47.2
18	0.027	0.054	70	3	70.8
19	0.027	0.054	70	5	66.2
20	0.027	0.081	70	10	58.7
21	0.027	0.054	70	15	51.3
22	0.027	0.054	70	25	47.8

a = PBNMBMP'ın başlangıç konsantrasyonu 0.027 mol L^{-1}

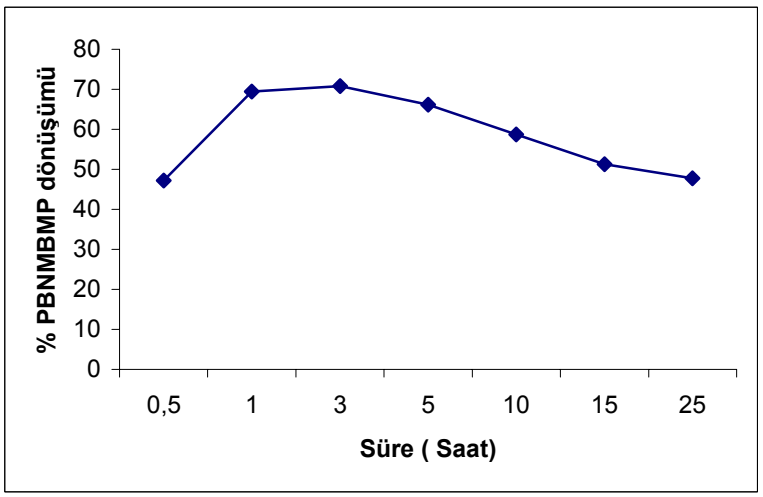
Benzer şartlar PBNMBMP'nin dönüşümü için incelenmiş ve elde edilen veriler Tablo 3.1.1.2.'de verildi. Bu değerler ve Şekil 3.1.1.5 incelendiğinde verimin diğer parametreler

aynı kalmak şatıyla 60 ^{o}C'de bir maksimum değere ulaştığı ve bunu takiben artan sıcaklıklarda azaldığı görüldü. $[KOH]_o$ =$[NaOCl]_o$ =0.027mol L^{-1} ve 1 saat süresinde bir optimum değere ulaştığı görülebilir.



Şekil 3.1.1.6. Alkali ortamda reaksiyon sıcaklığının bir fonksiyonu olarak hava oksijenin PBNMBMP'ın dönüşümü üzerine etkisi

PBNMBMP'nin dönüşümü üzerinde hava oksijeni de değişik sıcaklık değerlerinde benzer davranışlar göstermekle beraber optimum sıcaklığın 70 ^{o}C olduğu ve bu sıcaklık değerinde verimin % 69,4 olduğu belirlendi. Aynı sıcaklıkta sodyum hipoklorit ile elde edilen monomer verim ise %80,1 olarak bulundu. Tüm şartlar göz önüne alındığında yine sodyum hipoklorit hava oksijenine karşı daha etkili bir yükseltgen olduğu görüldü.



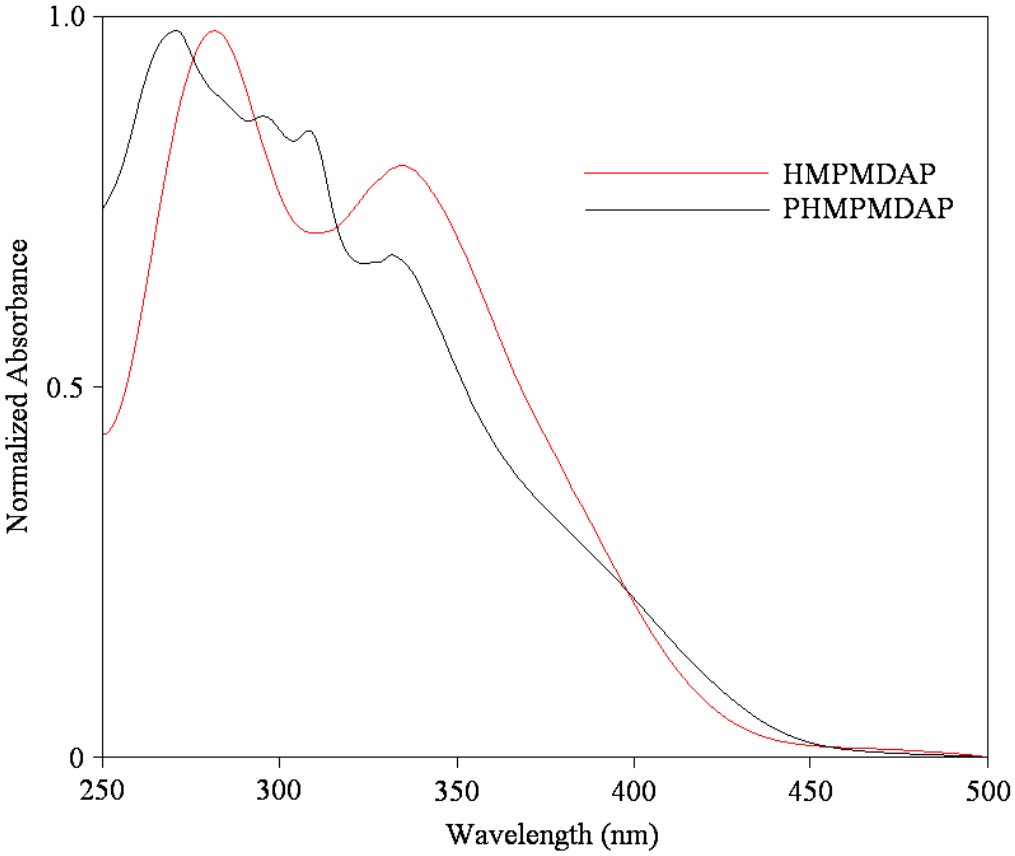
Şekil 3.1.1.7. Alkali ortamda reaksiyon süresinin bir fonksiyonu olarak hava oksijenin PBNMBMP'ın dönüşümüne etkisi

Bir saatten sonra artan reaksiyon süresi monomer dönüşümünün azalmasına sebep olduğu görüldü. Benzer yorumlar bu monomerin dönüşüm yüzdesi için yapılabilir. Reaksiyon şartları ve oluşan ürün yapıları göz önüne alındığında sadece amin grupları farklı olan vanilin monomerlerinden türetilen bu polimerlerden; HMPMDAP'nin ürünlerinin daha yüksek molekül ağırlıklı olduğu ve verimlerinin daha yüksek olduğu göze çarpar. SEC kromatogram sonuçlarından da bu durumun doğruluğu daha kolay gözlenebilir. Bu ise 2,3-diamino piridinin p-fenilen daiminden daha fazla oksidatif polimerizasyona yatkın olduğunu gösterir. Bundan önce piridinlerle yapılan çalışmalarda da piridin içeren monomerlerin dönüşüm yüzdesinin ve molekül ağırlığının daha yüksek olduğu sonucuna varılmış ve buna istinaden spektral analizlerinin yorumlanmasında BAZI sorunlar oluştuğu göze çarpmaktadır.

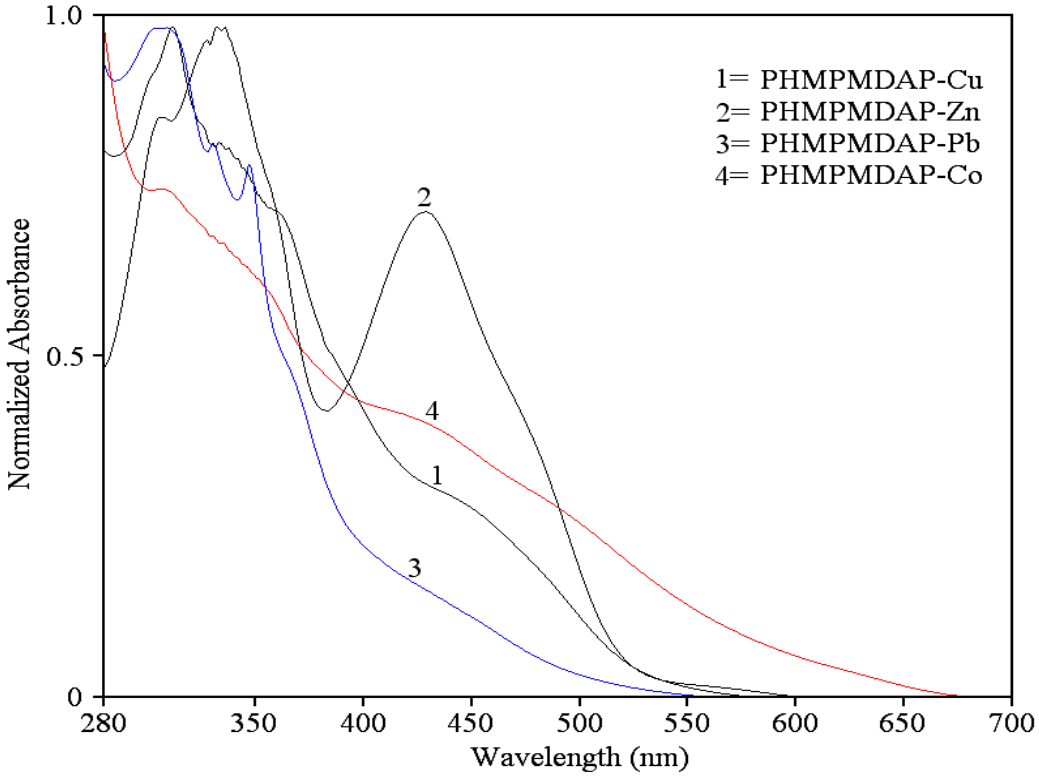
3.2. SENTEZLENEN MADDELERİN YAPI ANALİZLERİ

3.2.1. HMPMDAP ve PHMPMDAP'ın UV-Vis Spektrumları

HMPMDAP ve PHMPMDAP'ın UV-vis spektrumları sırasıyla Şekil 3.2.1.1., 3.2.1.2.'de verildi. HMPMDAP'nin UV-vis spektrumuna göre λ_{max} değerleri sırasıyla 223 ve 282 nm'de gözlenen değerler fenol ve C_5NH_3-N= gruplarının K bandını işaret etmektedir. 206 ve 335 nm'de gözlenen absorbans değerleri ise benzen ve C_5NH_3-N= gruplarına ait R bandını işaret etmektedir. Bu absorbans değerleri PHMPMDAP'nin UV-vis spektrumuna göre λ_{max} değerleri sırasıyla 227, 271, 295, 308 ve 332 nm'de gözlenmiştir. 227 ve 271 nm deki bantlar ise Kve R bantlarını gösterir. 332 nm'deki bant ise C_5NH_3-N= grubuna işaret eder. Azometin ve aromatik gruplara ait π–π^* geçişleri sırasıyla 350 ve 280 nm'de gözlendi.



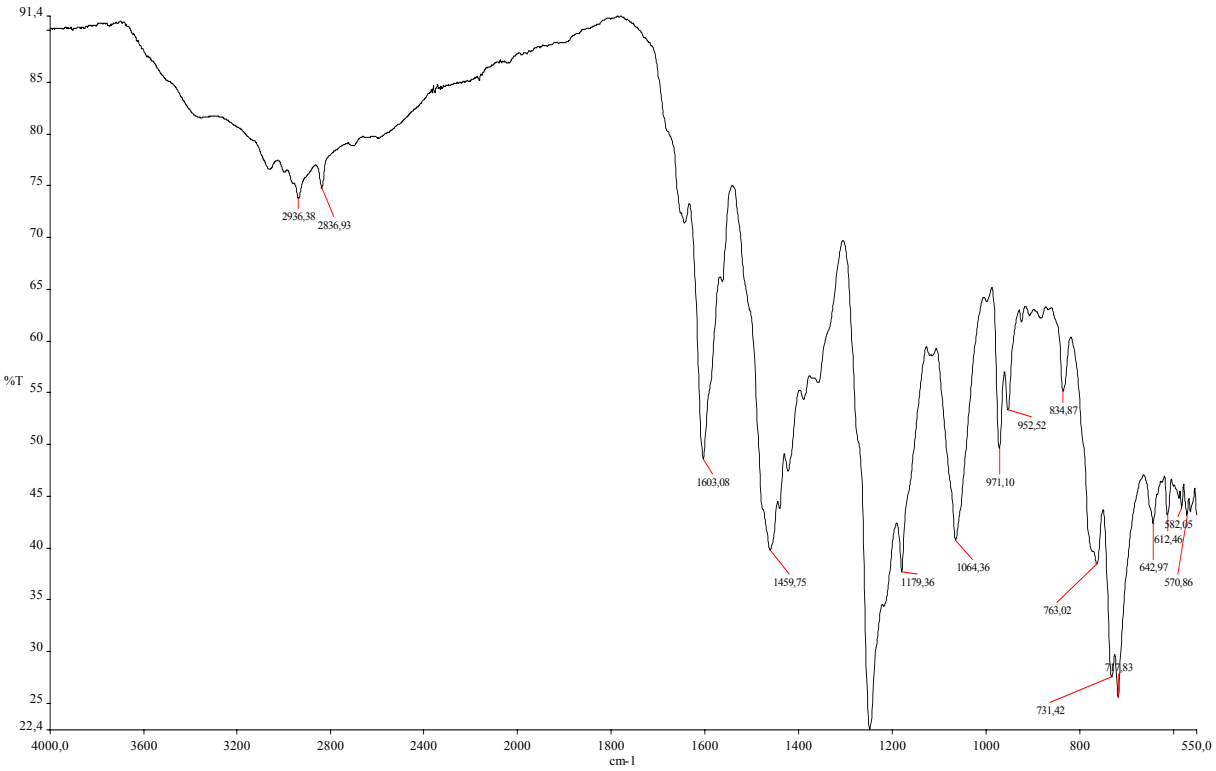
Şekil 3.2.1.1. HMPMDAP ve PHMPMDAP'ın UV-vis spektrumu



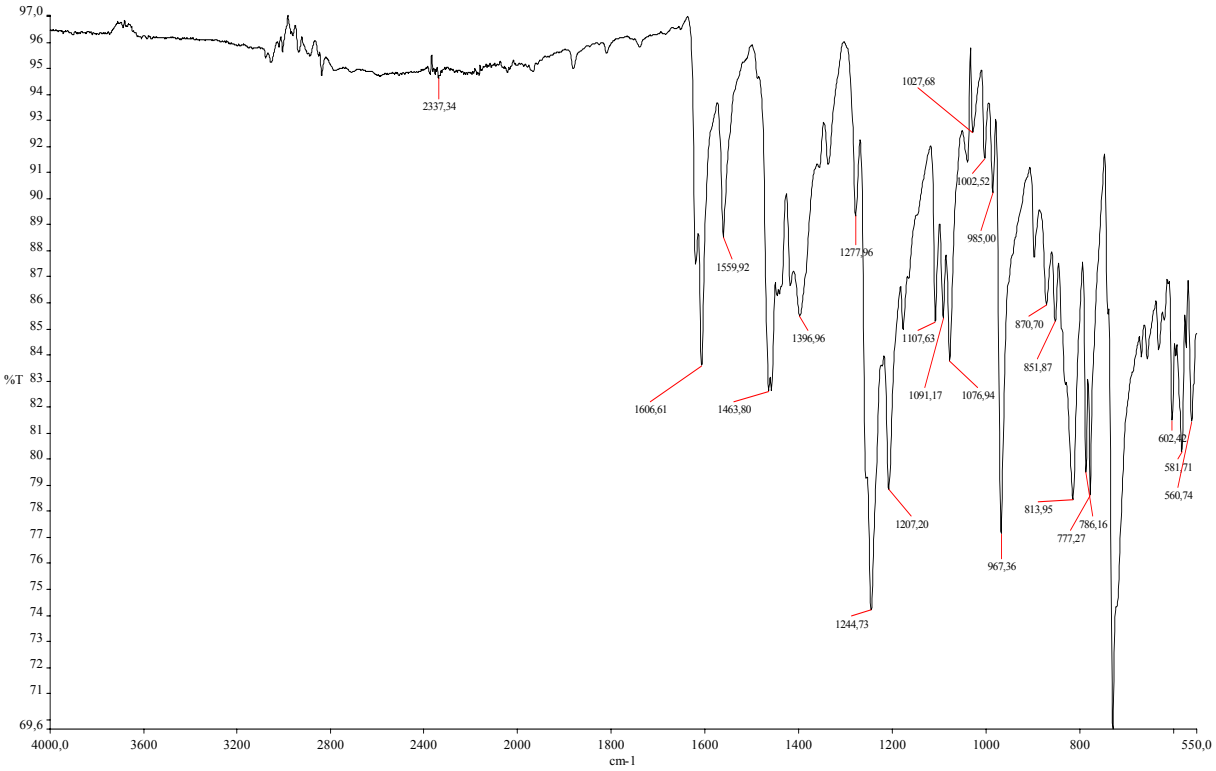
Şekil 3.2.1.2. Polimer–metal komplekslerinin UV-vis spektrumu

3.2.2. HMPMDAP ve PHMPMDAP'ın FT-IR Spektrumları

HMPMDAP'nin FT-IR spektrumunda (Şekil 3.2.2.1.), -OH grubuna ait karakteristik gerilme titreşimi 3378 cm^{-1} de, alifatik C-H gerilme titreşimi 2936 cm^{-1} de, Schiff bazları için karakteristik Ar-CH=N (azometin) gerilme titreşimi 1603 cm^{-1} de ve aromatik C=C gerilme titreşimleri ise 1460, 1440, 1423 cm^{-1} de gözlendi.



Şekil 3.2.2.1. HMPMDAP'ın FT-IR spektrumu.



Şekil 3.2.2.2. PHMPMDAP'ın FT-IR spektrumu

PHMPMDAP'nin FT-IR spektrumunda (Şekil 3.2.2.2.) -OH grubuna ait karakteristik gerilme titreşimi 3400 cm^{-1} de, alifatik C-H gerilme titreşimleri 2932 cm^{-1} de, Schiff bazları için karakteristik Ar-CH=N (Azometin) gerilme titreşimi 1620 cm^{-1} de ve aromatik C=C gerilme titreşimi ise 1606, 1560, 1463 cm^{-1} de gözlendi. FT-IR spektrumunda azometin grubuna ait pik monomerde 1603 cm^{-1} de gözlenirken polimerde 1620 cm^{-1} de gözlendi.

Monomer, polimer ve polimer-metal komplekslerinin FT-IR Spektrumuna ait veriler Tablo 3.2.2.1.'de ayrıntılı olarak verildi.

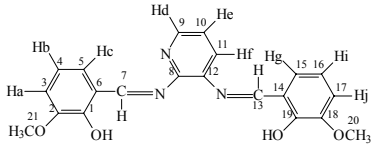
Tablo. 3.2.2.1. HMPMDAP, PHMPMDAP, PHMPMDAP-metal komplekslerinin FT-IR Spektrumuna ait veriler

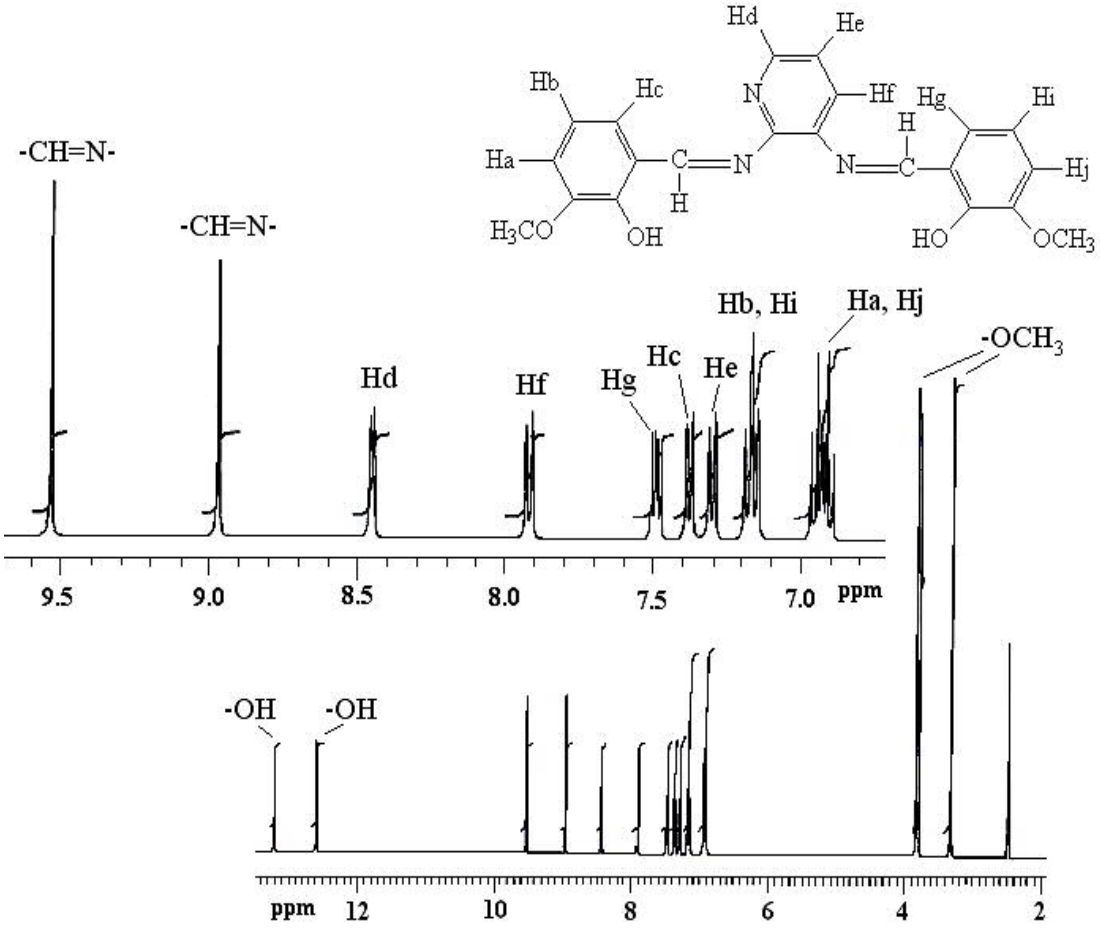
Bileşikler	Dalga Sayısı (cm^{-1})						
	-OH	-CH=N	-C=C	-C-O	$-CH_3$	Metal-O	Metal-N
HMPMDAP	3378	1603	1460, 1440, 1423	1244	2936	-	-
PHMPMDAP	3400	1620	1606, 1560, 1463	1245	2932	-	-
PHMPMDAP-Cu	3361	1603	1540, 1473, 1440	1240	2933	573	652
PHMPMDAP-Co	3339	1604	1560, 1542, 1420	1242	2923	575	664
PHMPMDAP-Fe	3198	1603	1541, 1475, 1423	1247	2930	594	645
PHMPMDAP-Pb	3235	1532	1465, 1432, 1404	1235	2923	563	656
PHMPMDAP-Zn	3297	1604	1565, 1538, 1469	1239	2928	560	632

3.2.3. HMPMDAP ve PHMPMDAP'ın ^{1}H ve ^{13}C-NMR Spektrumları

HMPMDAP'nin ^{1}H-NMR spektrumuna bakıldığında (Şekil 3.2.3.1.); spektrumdan beklenen karakteristik –OH, -CH=N- ve aromatik protonlar gözlendi. Buna göre; 12,64 ppm'de –OH (tekli, 1H), 13,24 ppm'de–OH (tekli, 1H) ve 8.98 ppm'de –CH=N- (tekli, 1H), 9.54 ppm'de –CH=N- (tekli, 1H), gözlenirken, aromatik halkaya ait protonlar ise 6,94-8,46 ppm'de gözlendi. Bu verilerden yararlanarak HMPMDAP'nin aşağıdaki yapı birimlerine sahip olduğu sonucuna varıldı (Tablo 3.2.3.1 ve Tablo 3.2.3.2).

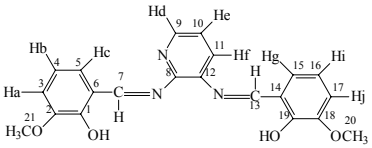
Tablo 3.2.3.1. HMPMDAP'nin ^{1}H-NMR spektrumu verileri

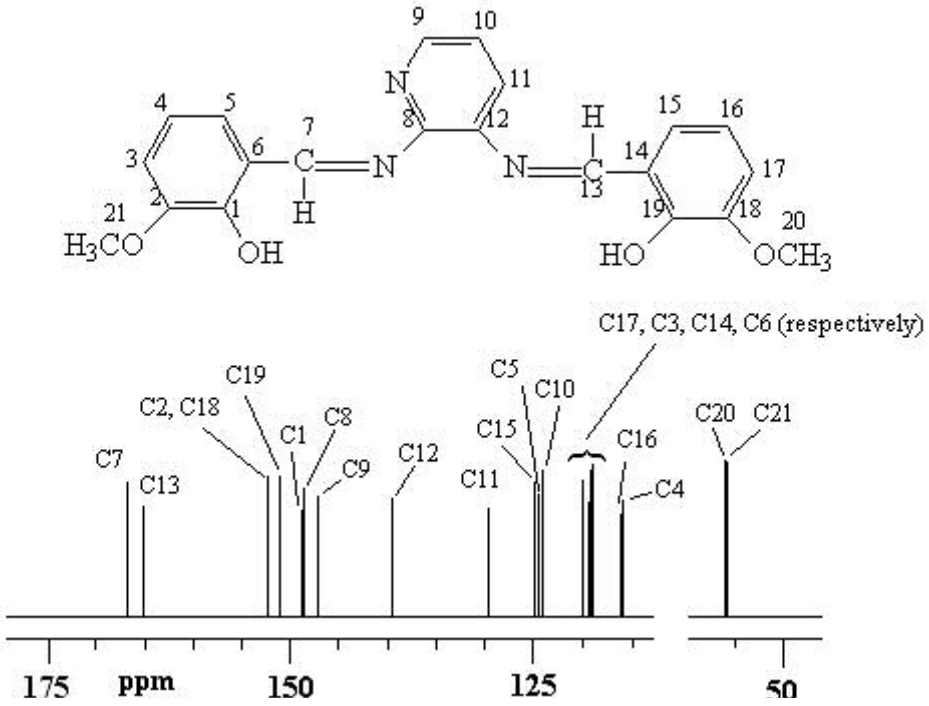
Yapı Birimi		**Fonksiyonel Gruplara Bağlı Hidrojenler**					
		-OH	-OH	-CH=N-	-CH=N-	Ha ve Hj	Hb ve Hi
		13,24 ppm 1H Tekli	12,62 ppm 1H Tekli	9.54 ppm 1H Tekli	8.98 ppm 1H Tekli	*6.94* ppm 2H İkili	7,18 ppm 2H Tekli
Hc	Hd	He	Hf	Hg	$OC\underline{H_3}$	$OC\underline{H_3}$	
7,38 ppm 1H İkili	8,46 ppm 1H İkili	7,29 ppm 1H Tekli	*7.93* ppm 1H İkili	*7.50* ppm 1H İkili	3.79 ppm 3H Tekli	3.84 ppm 3H Tekli	



Şekil 3.2.3.1. HMPMDAP'nin ^{1}H-NMR Spektrumu

Tablo 3.2.3.2. HMPMDAP'nin ^{13}C-NMR spektrumu verileri

Yapı Birimi			**Yapıdaki karbonların kayma değerleri (ppm)**						
			C_1	C2, C18-OCH_3-ipso	C_3	C4	C5	C6	C7
			148.50	150.94	119.49	116.18	124.46	119.17	166.40
C8	C9	C10	C11	C12	C13	C14	C15	C16	C17
148.40	147.13	124.02	129.60	139.38	164.79	119.28	124.88	116.38	119.95
C19-ipso	C20	C21							
152.24	56.20	56.09							

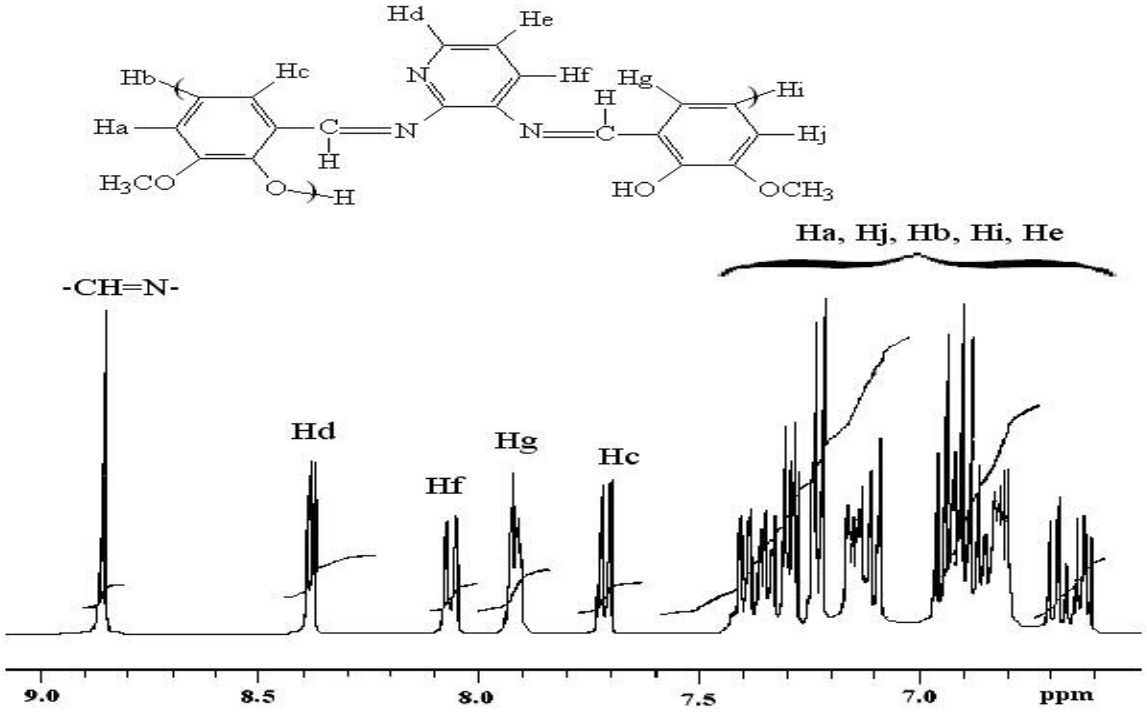


Şekil 3.2.3.2. HMPMDAP'in ^{13}C-NMR spektrumu

Şekil 3.2.3.2. HMPMDAP'nin ^{13}C-NMR spektrumu incelendiğinde 166.40 ppm ve 164.79 ppm'de azometin karbonlarına ait sinyaller; 148.50 ppm ve 152.24 ppm'de hidroksi gruplarının bağlı bulunduğu karbon atomlarına ait sinyaller; 56.20 ppm ve 56.09 ppm'de ise metoksi gruplarına ait karbon sinyalleri görülür. Diğer karbon sinyalleri Tablo 3.2.3.3.'de ayrıntılı olarak verildi.

Tablo 3.2.3.3. PHMPMDAP'nin ^{1}H-NMR spektrumu verileri

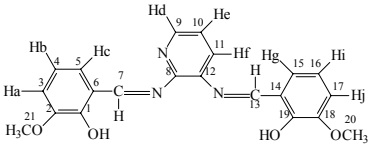
		-OH	-OH	-CH=N-	-CH=N-	Ha ve Hj	Hb ve Hi	He
		13,24 1H Tekli	12,62 1H Tekli	9.54 1H Tekli	8.98 1H Tekli	6.50 - 7.50 arasında 2H 2H 1H Çoklu pikler		
Hc	Hd	Hf	Hg	OCH_3	OCH_3			
7.70 1H İkili	8.38 1H İkili	8.07 1H İkili	7.90 1H İkili	3.82 3H Tekli	3.82 3H Tekli			

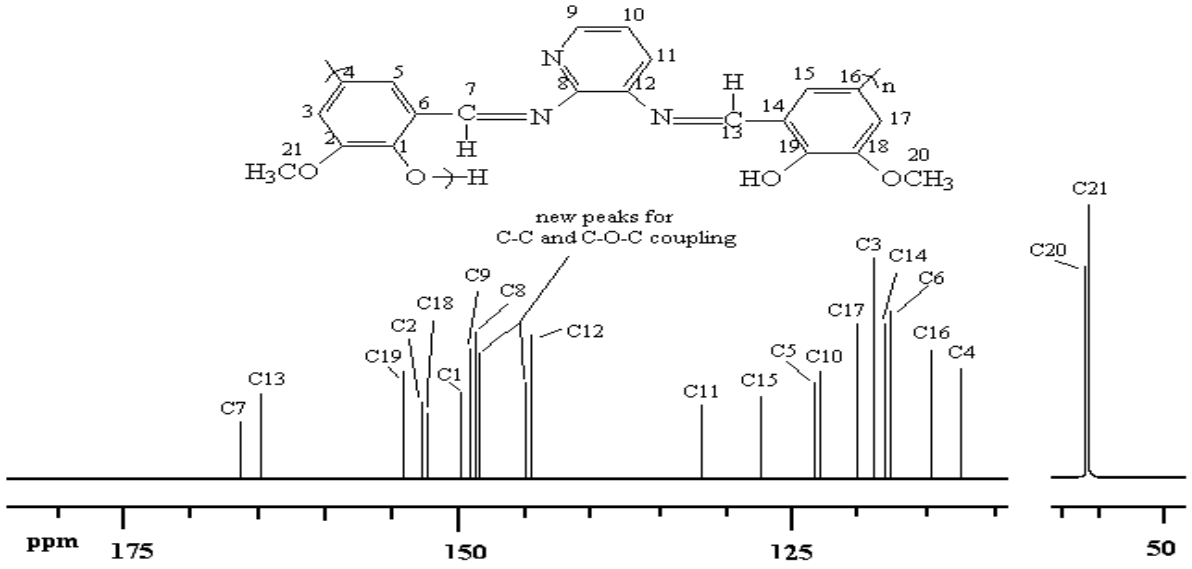


Şekil 3.2.3.3. PHMPMDAP'nin ^{1}H-NMR spektrumu

PHMPMDAP'nin ^{1}H-NMR spektrumunda 13,24 ppm ve 12,62 ppm'de –OH gruplarına ait protonlar; 9.54 ppm ve 8.58 ppm'de ise -CH=N gruplarına ait protonlar gözlenirken aromatik protonlar 6.50 - 7.50 ppm arasında çoklu pikler halinde görülmektedir (Tablo 3.2.3.4).

Tablo 3.2.3.4. PHMPMDAP'nin ^{13}C-NMR spektrumu verileri

Yapı Birimi			**Yapıdaki karbonların kayma değerleri (ppm)**						
			C_1	C2, OCH_3-ipso	C_3	C4	C5	C6	C7
			149.97	152.92	119.27	117.85	123.48	118.96	166.40
C8	C9	C10	C11	C12	C13	C14	C15	C16	C17
149.05	149.26	123.00	132.03	144.69	164.76	119.21	127.60	118.52	120.52
C18-OCH_3	C19	C20	C21	Yeni pik	Yeni pik				
152.34	154.33	56.80	56.05	148.62	145.23				

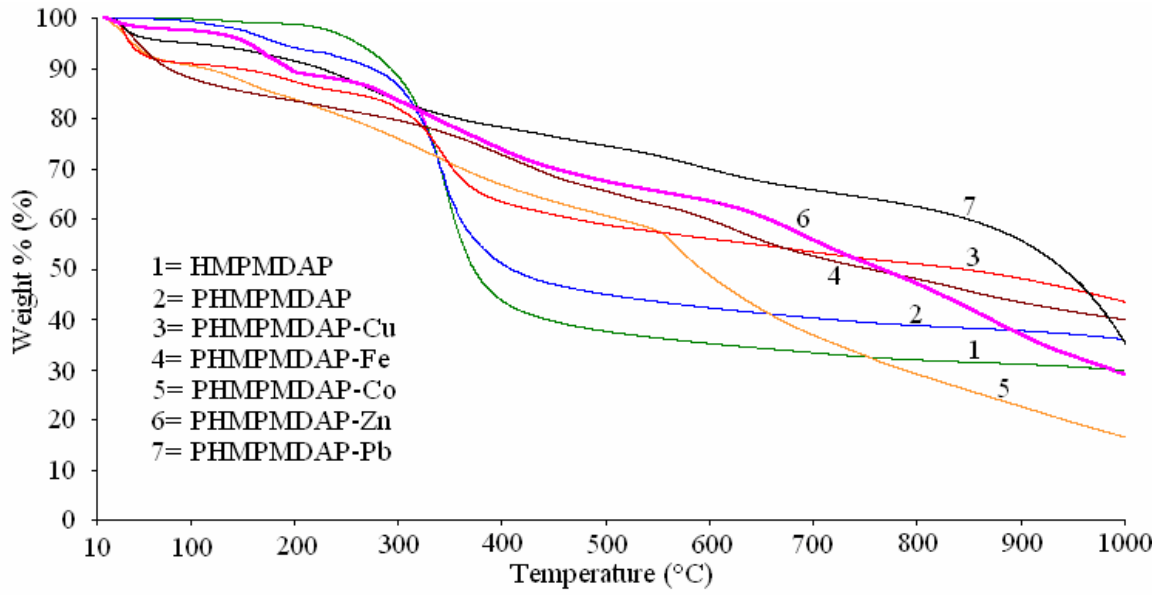


Şekil 3.2.3.4. PHMPMDAP'nin ^{13}C-NMR spektrumu

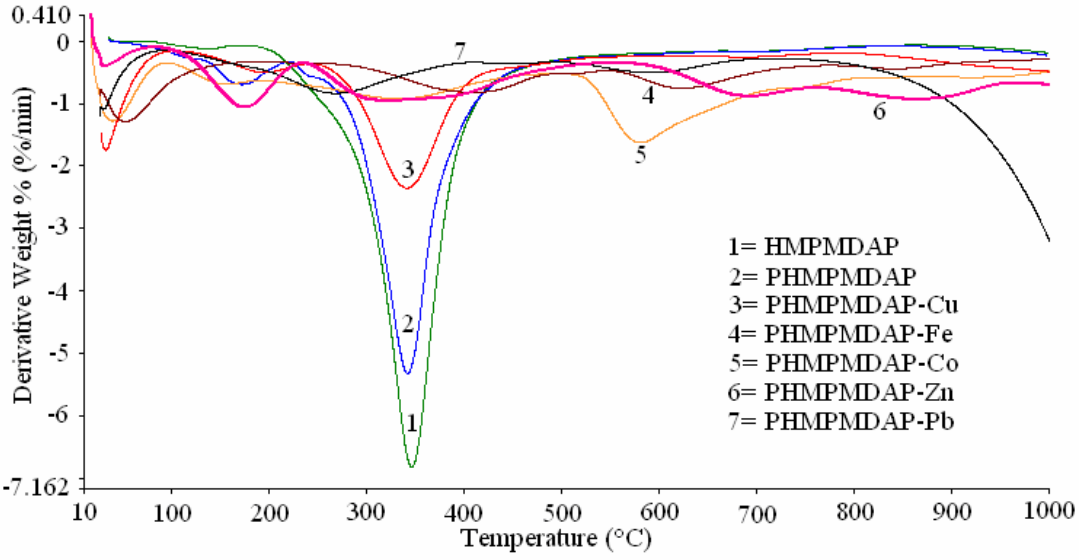
Tablo 3.2.3.4. PHMPMDAP'nin ^{13}C-NMR spektrumunda görülen her bir karbon atomunun sinyallerini göstermektedir. Bu verilere göre monomerin ^{13}C-NMR spektrumunda gözlenmeyen 148.62 ppm ve 145.23 ppm'de yeni C-C eşleşmesi ile oluşan sinyaller gözlenirken diğer karbon atomu sinyallerinde fazla bir kayma olmadığı görüldü.

3.2.4. HMPMDAP, PHMPMDAP ve onun Polimer-Metal Kompleks Bileşiklerinin DTA-TG Analizleri

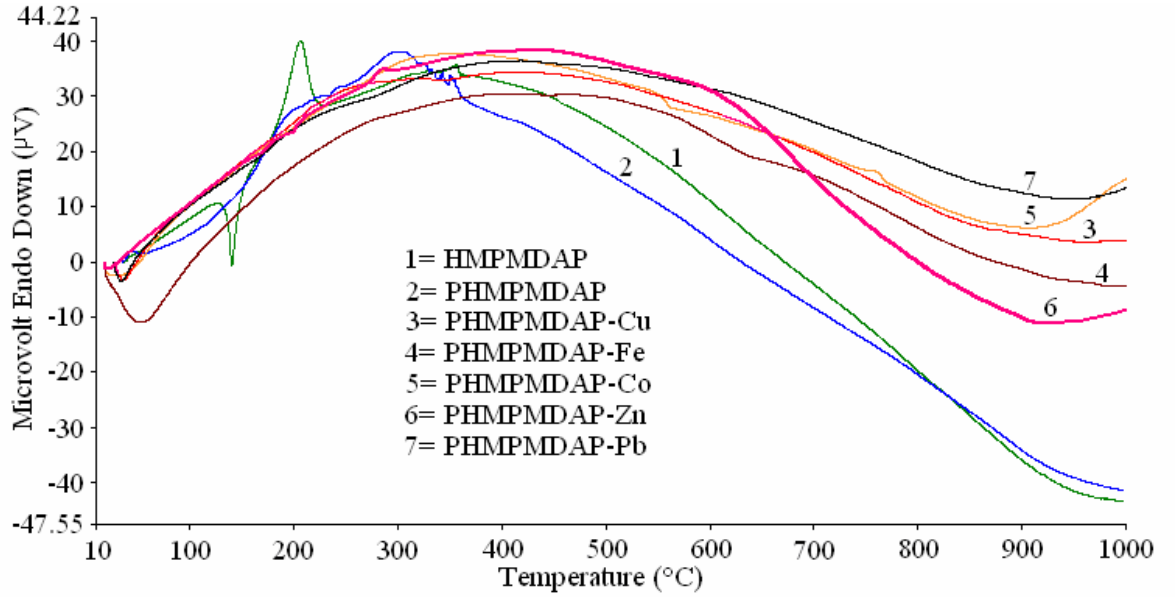
HMPMDAP ve PHMPMDAP'ın TGA-DTG-DTA termal analiz eğrileri Şekil 3.2.4.1. ve 3.2.4.2. ve 3.2.4.3'de verildi. Monomerin ve polimerin TG eğrilerinden ilk bozunma sıcaklıkları sırasıyla 296 ve 303°C olarak belirlendi. Hidrate su ise monomer ve polimerde sırasıyla 120 °C'ye kadar % 6 ve % 17 oranında gözlendi. 1000°C'deki % kütle kaybı ise monomer ve polimerde sırasıyla % 29,74 ve % 42,27 olarak hesaplandı. Bu sonuçlara göre polimer monomerden termal olarak daha kararlıdır denilebilir. Bu durum polimer moleküllerinde artan konjugasyona ve monomer birimleri arasında C-C bağının oluşmasına atfedilebilir. TGA bileşiklerinde görülen polimer metal komplekslerinin monomer ve polimerlere göre yüksek bozunma sıcaklığı, polimer ve metal iyonları arasında metal-oksijen ve metal-azot bağlarının oluştuğunu gösterir. TGA ve DTG eğrileri incelendiğinde 100- 225 ºC'de su moleküllerinin bozunmasına ait eğriler görülür. 50–150 ºC arası bozunmalar polimerdeki kristalize suyun eliminasyonunu, 150–200 ºC'deki bozunmalar ise koordine olarak bağlanmış su moleküllerinin eliminasyonunu gösterir. Bu ise bulunan ve hesaplanan elementel analiz değerleri arasındaki farkı gösterir. TG analizleri sonucu polimer metal komplekslerinin 1000 C'deki termal dayanıklılıkları şu şekildedir: PHMPMDAP-Cu> PHMPMDAP-Fe> PHMPMDAP-Pb> PHMPMDAP-Zn> PHMPMDAP-Co. Tüm bileşiklerin termal analiz sonuçları Tablo 3.2.4.1.'de verildi.



Şekil 3.2.4.1. HMPMDAP, PHMPMDAP ve PHMPMDAP metal komplekslerinin TGA eğrileri



Şekil 3.2.4.2 HMPMDAP, PHMPMDAP ve PHMPMDAP metal komplekslerinin DTG eğrileri



Şekil 3.2.4.3. HMPMDAP, PHMPMDAP ve PHMPMDAP metal komplekslerinin DTA eğrileri

Tablo 3.2.4.1. HMPMDAP, PHMPMDAP ve onun polimer-metal kompleks bileşiklerinin termal analiz sonuçları

	TGA					DTA	
Bileşikler	[a]T_{on}	[b]$W_{max.}T$	20% kütle kaybı	50% kütle kaybı	% kalıntı 1000°C'de	exo	endo
HMPMDAP	296	345	323	375	29.74	206	141
PHMPMDAP	303	340	345	506	42.27	300	-
PHMPMDAP-Cu	304	342	374	-	58.06	-	-
PHMPMDAP-Zn	282	329, 690, 863	458	880	40.90	-	-
PHMPMDAP-Fe	332	407, 621, 841	538	-	56.87	-	-
PHMPMDAP-Pb	193	267, 592	466	968	41.57	-	-
PHMPMDAP-Co	290	332, 581	457	737	32.19	-	-

[a]İlk bozunma sıcaklığı [b]Maksimum kütle kaybının gözlendiği sıcaklık

3.2.5. HMPMDAP, PHMPMDAP ve PHMPMDAP-Metal Komplekslerinin UV-vis Spektrofotometresi Ölçümlerinden Optik Bant Boşluklarının Hesabı

3-bis[(2-hidroksi-3-metoksifenil) metilen]diaminopiridin ve oligomerinin ve oligomer-metal komplekslerinin Şekil 3.2.1.1. ve 3.2.1.2'de yer alan absorbsiyon spektrumları kullanılarak hesaplanan optik band boşluğu değerleri Tablo. 3.2.5.1.'de verildi. Optik bant boşluğu (E_g) değerleri HMPMDAP, PHMPMDAP, PHMPMDAP-Cu, PHMPMDAP-Co, PHMPMDAP-Zn ve PHMPMDAP-Pb bileşikleri için sırasıyla 2.94, 2.80, 2.36, 2.05, 2.40 ve 2.45 bulundu. Bu değerlere göre PHMPMDAP-Co'ın E_g değerinin monomer, polimer ve polimer-metal komplekslerinden daha düşük olduğu gözlendi.

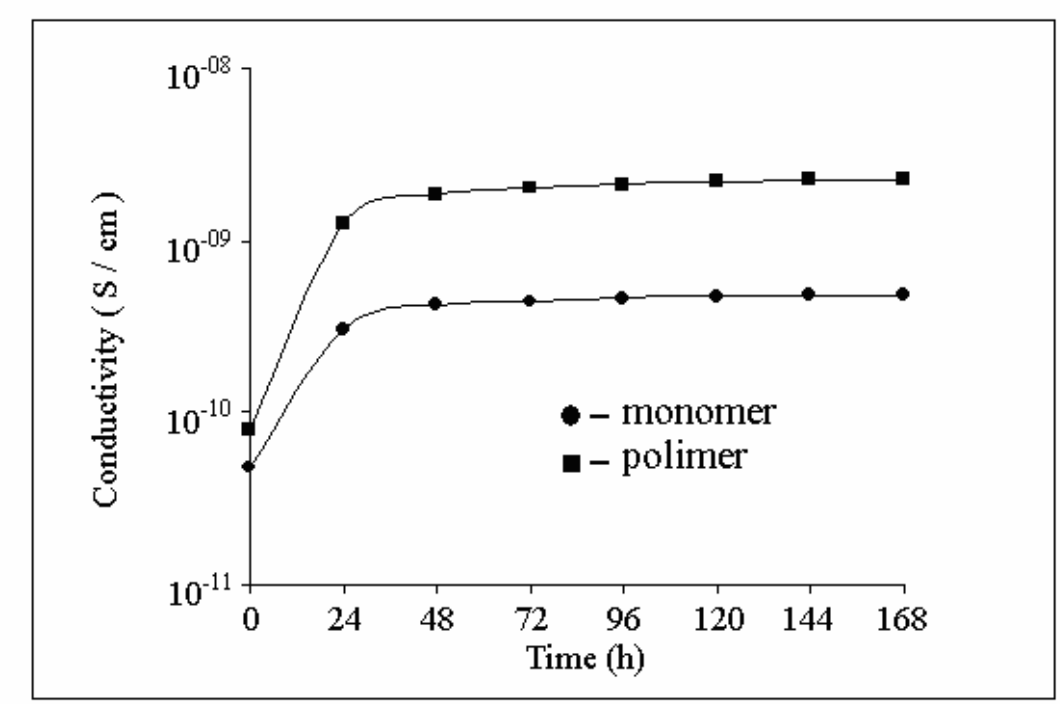
Tablo 3.2.5.1. PHMPMDAP, PHMPMDAP ve PHMPMDAP-metal komplekslerinin E_g (eV), λ_{max} (nm) ve λ_{onset} (nm) değerleri

Ürünler	λ_{max} (nm)	E_g (eV)	λ_{onset} (nm)
HMPMDAP	206, 223, 282, 335	2.94	422.45
PHMPMDAP	227, 271, 295, 308, 332	2.80	443.57
PHMPMDAP-Cu	262, 312, 358, 437	2.36	526.27
PHMPMDAP-Co	268, 306, 418	2.05	605.85
PHMPMDAP-Zn	258, 307, 332, 429	2.40	517.50
PHMPMDAP-Pb	261, 309, 330, 347	2.45	506.94

3.2.6. Elektriksel İletkenlik Ölçümleri

Elektriksel özelliklerini incelemek için, sentezlenen maddelerin, 1687.2 kg/cm^2 basınç altında peletleri hazırlandı. Peletler üzerine belirlenen sürelerle iyot dop edildi. İyotla dop işlemi, bir desikatörde oda sıcaklığında ve atmosferik basınç altında peletlerin iyot buharlarına maruz bırakılması şeklinde gerçekleştirildi.

HMPMDAP, PHMPMDAP iyot ile dop edilmeden önceki iletkenlik değerleri 6.89 x10^{-11} ve 9.01 x 10^{-11} S.cm^{-1} değerlerinde olduğu görüldü. İyotla dop edilmeye başladıktan sonra ve iyotla dop süresi arttıkça iletkenlik ilk gün sonunda keskin bir şekilde arttı, sonra ilerleyen günlerde iletkenlik artışında bir azalma gözlendi ve iletkenlik değeri 10^{-9} S/cm değerinde hemen hemen sabit kalmışdığı görüldü. (Şekil 3.2.6.1. ve Tablo 3.2.6.1. ve Tablo 3.2.6.2).



Şekil 3.2.6.1. İyot ile doplanmış HMPMDAP, PHMPMDAP'ın 25 °C'deki iletkenlik eğrileri

Şekilde de görüldüğü gibi iletkenlikte 24 saat sonunda keskin bir artış gözlendi. Yaklaşık 90 saat doplamadan sonra iletkenlik sabit kaldığı görüldü. En yüksek iletkenlik değeri, PHMPMDAP için 3.67x 10^{-9} S/cm olarak bulundu. Dopant miktarına bağlı olarak iletkenliğin artması, polimerler ile iyot molekülleri arasında yük-transfer olayının süreklilik kazanması ile açıklanabilir.

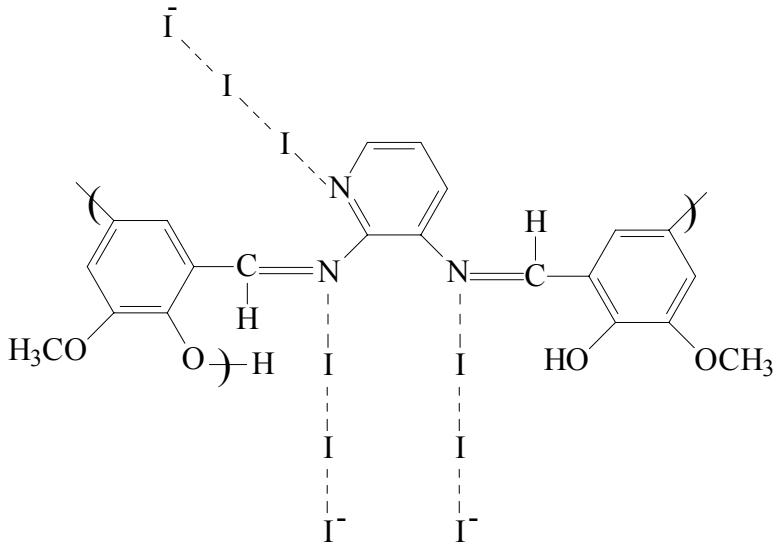
Tablo 3.2.6.1. İyot ile doplanmış HMPMDAP, PHMPMDAP'ın 25 °C'deki iletkenlik değerleri (x10^{-11} S.cm^{-1})

zaman(s)	Monomer	Polimer
0	6.89	9.01
24	47.8	111
48	61.1	278
72	63.3	311
96	65.6	333
120	66.7	344
144	66.7	367
168	66.7	367

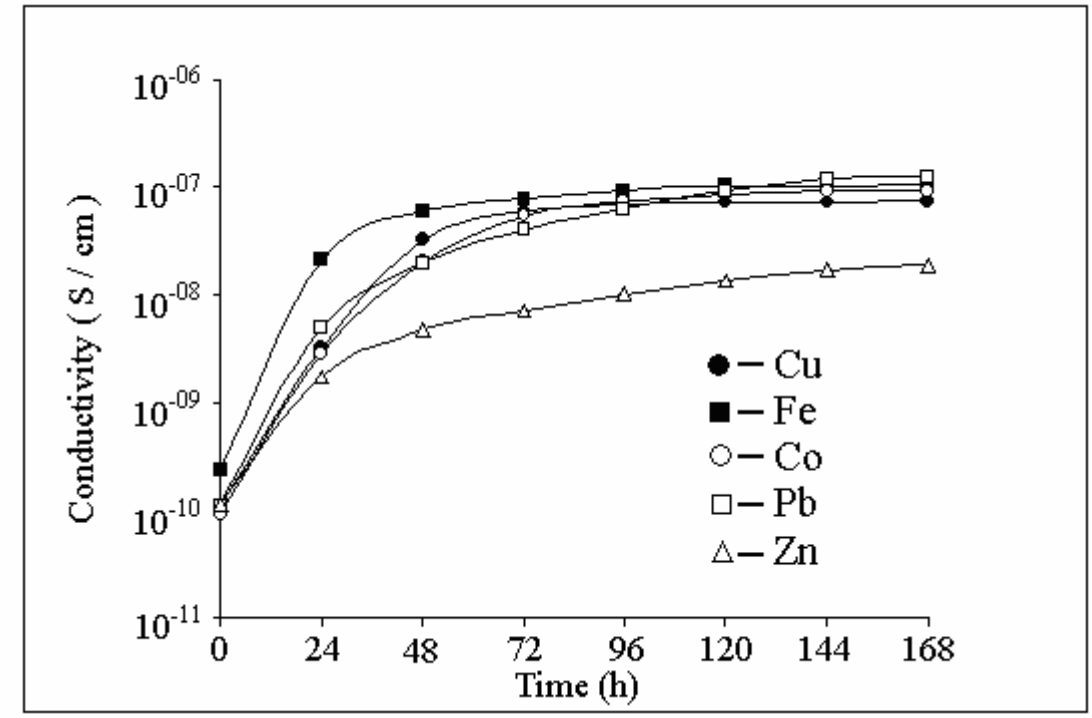
Tablo 3.2.6.2. İyot ile doplanmış PHMPMDAP-metal komplekslerinin 25 °C'deki iletkenlik değerleri ($x10^{-10}$ $S.cm^{-1}$).

Süre (saat)	**Bakır**	**Demir**	**Kobalt**	**Kurşun**	**Çinko**
0	1.103	2.293	0.933	1.103	1.136
24	31.98	212.4	28.85	50.20	17.62
48	331.5	605.9	205.5	199.9	47.29
72	609.9	795.9	548.8	414.7	72.30
96	698.5	958.4	762.7	625.1	103.6
120	721.9	1040	866.0	935.1	138.9
144	740.8	1069	933.4	1202	170.6
168	750.6	1078	955.3	1249	193.5

Diaz *et al.* (1999), Schiff bazı polimerlerin iyotla dop edilmesi ile ilgili olarak bir iletkenlik mekanizması önermiştir. Azot molekülleri çok elektronegatif bir element olduğu için iyot molekülleri ile koordinasyona girme kapasitesine sahiptir.



Polimerlerin iyotla dop edilmesi süresince iyot moleküllerinin yapıya yukarıda gösterilen şekilde belirtildiği gibi koordine olduğu belirtilmiştir (Diaz ve ark.).



Şekil 3.2.6.2. PHMPMDAP-metal komplekslerinin 25 °C'deki iletkenlik eğrileri

PHMPMDAP-Cu, PHMPMDAP-Co, PHMPMDAP–Zn, PHMPMDAP–Pb, PHMPMDAP-Fe komplekslerinin iletkenlik değerleri sırasıyla $7.51x\ 10^{-8}$, $9.55\ x\ 10^{-8}$, $1.94\ x\ 10^{-8}$, $1.25\ x\ 10^{-7}$ and $1.08\ x\ 10^{-7}$ S/cm olarak ölçüldü. Bu değerlere göre en büyük iletkenlik değeri kurşun kompleksinde görüldü.

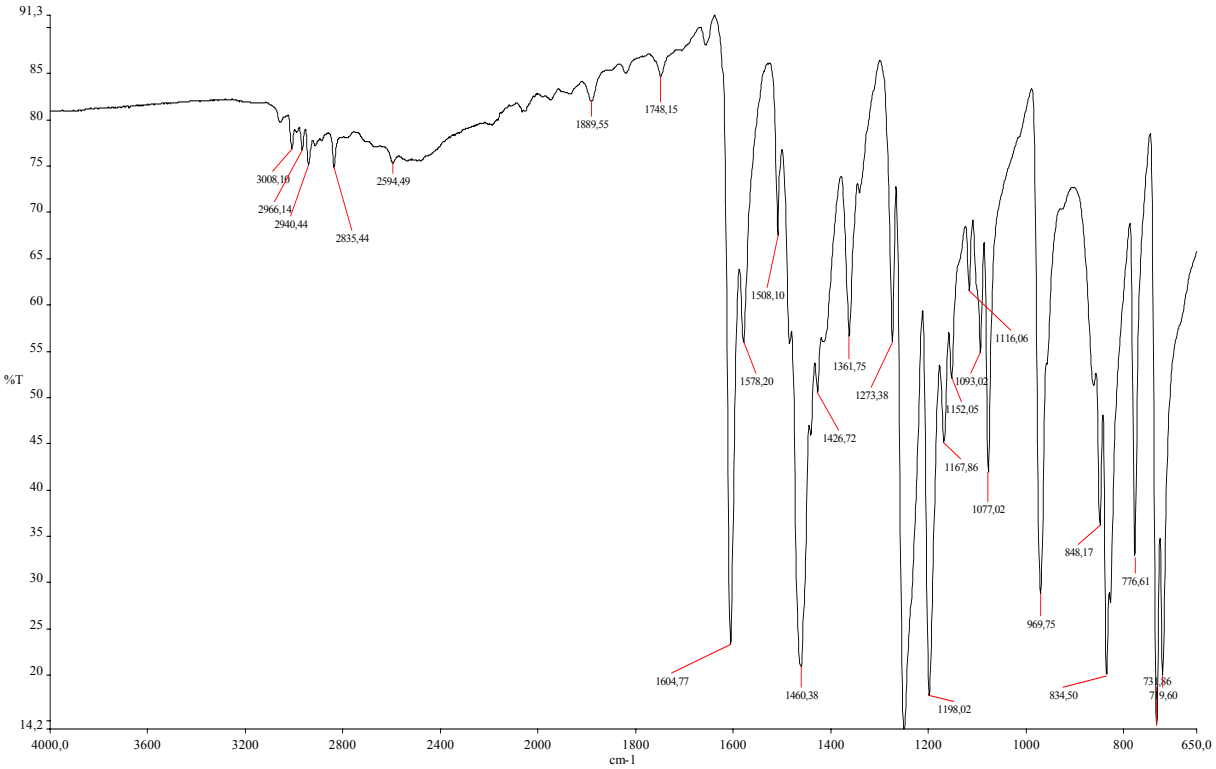
Sonuçlardan görüldüğü gibi polimerin elektriksel iletkenliği monomerden yüksektir. Bu durum polimerdeki konjugasyonun artmış olmasına bağlanabilir. Artan konjugasyon iletkenliğin artmasına sebep olduğu literatür kaynakları ile desteklenir. Polimer metal komplekslerinin iletkenlik eğrileri incelendiğinde ufak detaylar gözardı edilirse eğriler hemen hemen birbirinin aynısıdır. Bununla birlikte metalin organik polimere katılması iletkenliğinin artmasına sebep olmuştur.

Elektriksel iletkenlik sonuçları, sentezlenen tüm bileşiklerin tipik yarı iletken özelliğe sahip olduğunu göstermektedir.

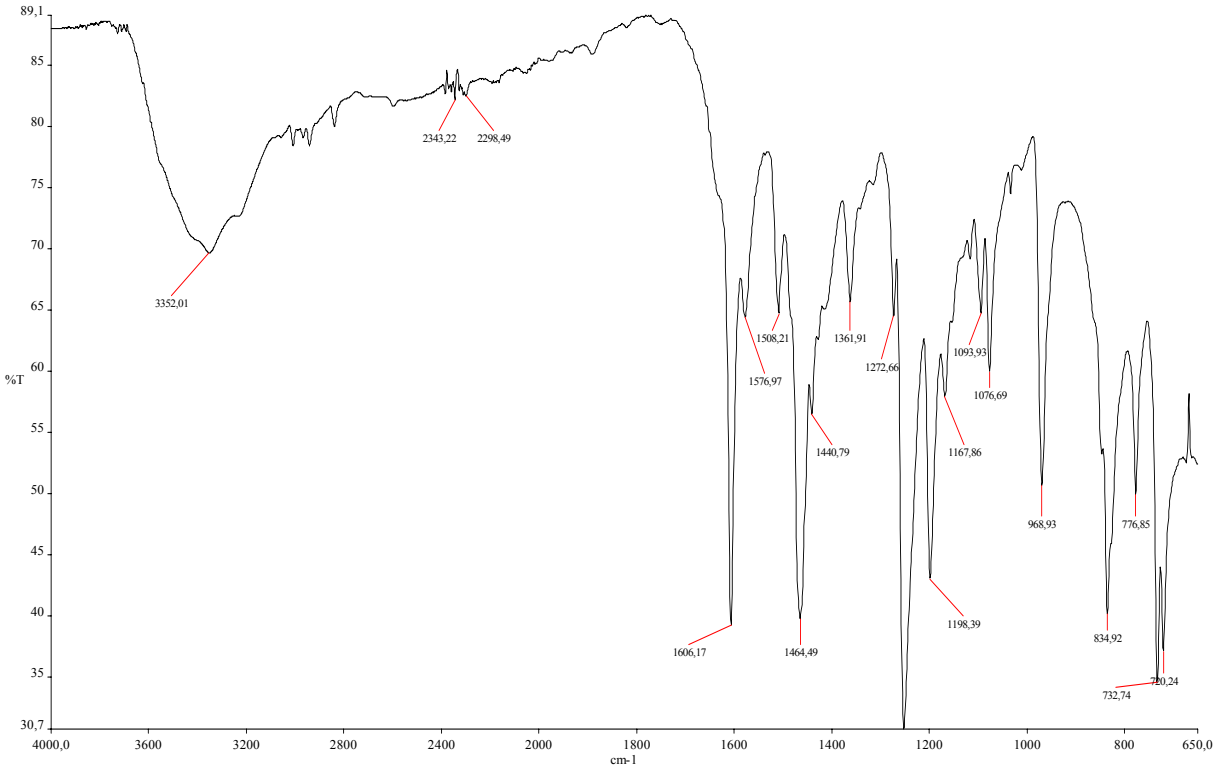
3.3.1. PBNMBMP ve OPBNMBMP FT-IR Spektrumu

PBNMBMP ve OPBNMBMP'nin FT-IR spektrumlarında (Şekil 3.3.1.1. ve Şekil 3.3.1.2), -OH grubuna ait karakteristik gerilme titreşimi 3352 cm^{-1} de, Schiff bazları için karakteristik Ar-CH=N (Azometin) gerilme titreşimi 1606 cm^{-1} de ve aromatik C=C gerilme titreşimi ise 1576 ve 1508 ve 1464 cm^{-1} de gözlendi. Monomerde ise OH grubuna ait karakteristik

gerilme titreşimi 3342 cm^{-1} de, Ar-CH=N (Azometin) gerilme titreşimi 3342 cm^{-1} de ve aromatik C=C gerilme titreşimi ise 1578 ve 1508 ve 1460 cm^{-1} de gözlendi. Azometin ve diğer fonksiyonlu grupların dalga boyundaki kayma değerleri konjugasyonun oluştuğunu göstermektedir.



Şekil 3.3.1.1. PBNMBMP'nin FT-IR spektrumu



Şekil 3.3.1.2. OPBNMBMP'nin FT-IR spektrumu

Tablo 3.3.1.1. PBNMBMP ve OPBNMBMP, OPBNMBMP-Cu bileşiklerine ait FT-IR spektral verileri

Bileşikler	Dalga sayısı (cm^{-1})					
	-OH	-CH=N	-C=C	-C-O	Metal-O	Metal-N
PBNMBMP	3377	1604	1578, 1508, 1460	1249	-	-
OPBNMBMP	3352	1606	1576, 1508, 1464	1252	-	-
OPBNMBMP-Cu	3453	1604	1583, 1541, 1497	1234	570	645

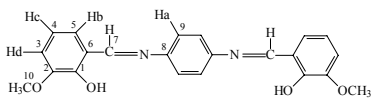
3.3.2. PBNMBMP ve OPBNMBMP'nin ^{1}H-NMR Spektrumu

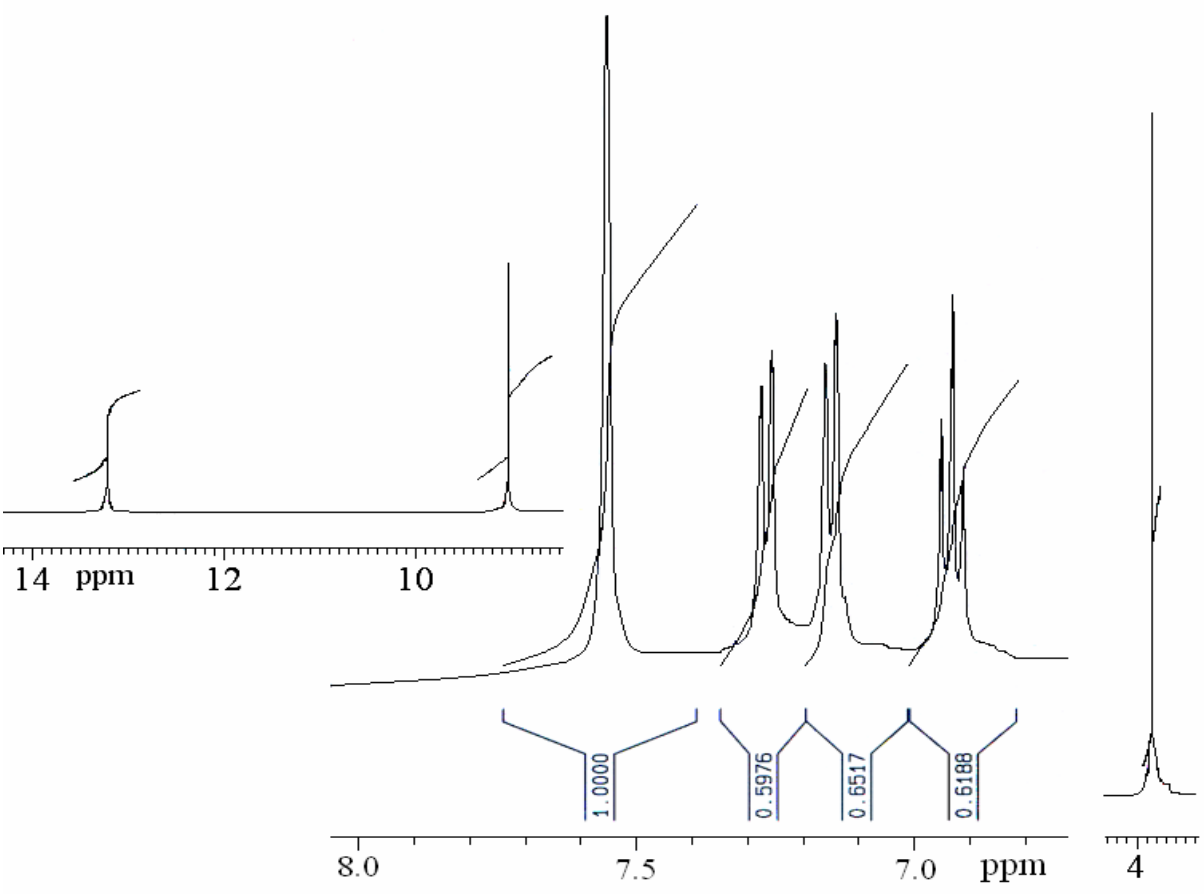
3.3.2.1. PBNMBMP'ın ^{1}H-NMR Spektrumu

PBNMBMP'nin ^{1}H-NMR spektrumuna bakıldığında (Şekil 3.3.2.1.); spektrumdan beklenen karakteristik –OH, ve -CH=N gruplarına ait protonlar 13,21 ppm, 9,03 ppm' de gözlenirken -aromatik protonlar 6,93 ppm ile 7,55 ppm arasında gözlendi. Yapının simetrik olduğu ^{1}H-

NMR spektrumundan da kolaylıkla görülebilir. Fonksiyonlu gruplara bağlı hidrojenler Tablo 3.3.2.1. ve Şekil 3.3.2.1.'de verildi. Bu verilerden yararlanarak PBNMBMP'in aşağıdaki yapı birimlerine sahip olduğu sonucuna varıldı.

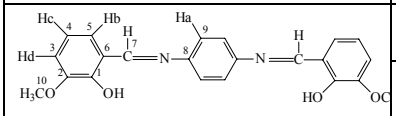
Tablo 3.3.2.1. PBNMBMP'ın ^{1}H-NMR spektrumu verileri

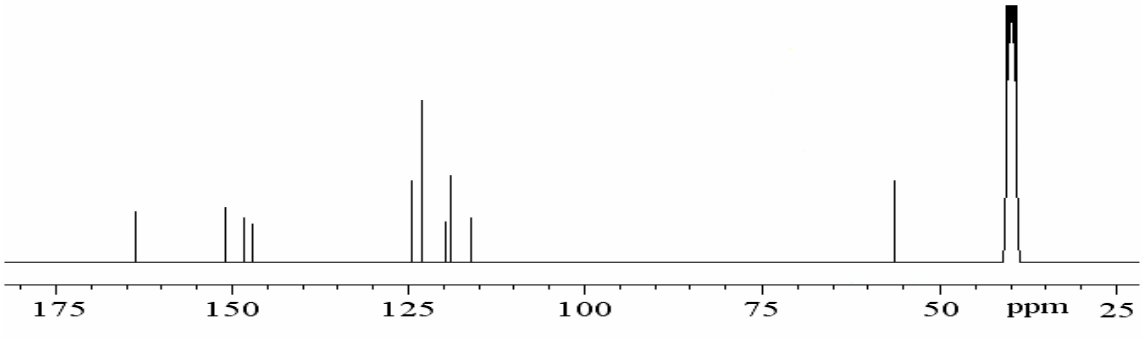
Yapı Birimi		**Fonksiyonel Gruplara Bağlı Hidrojenler**					
		-OH	-CH=N-	Ha	Hb	Hc	Hd
		13,21 ppm 1H Tekli	9,03 ppm 1H Tekli	7,55 ppm 4H Tekli	7,27 ppm 1H İkili	6,93 ppm 1H Üçlü	7,15 ppm 1H İkili
-OCH_3							
3,84 ppm 3H Tekli							



Şekil 3.3.2.1. PBNMBMP'ın ^{1}H-NMR spektrumu

Tablo 3.3.2.2 PBNMBMP'ın ^{13}C-NMR spektrumu verileri

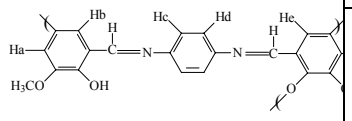
Yapı Birimi			**Yapıdaki karbonların kayma değerleri (ppm)**						
			C_1	C2-ipso	C_3	C4	C5	C6-ipso	C7
			151.01	148.38	116.10	119.14	124.37	119.74	163.77
C8-ipso	C9	C10							
146.97	123.02	56.36							



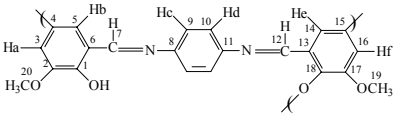
Şekil 3.3.2.2. PBNMBMP'ın ^{13}C-NMR spektrumu

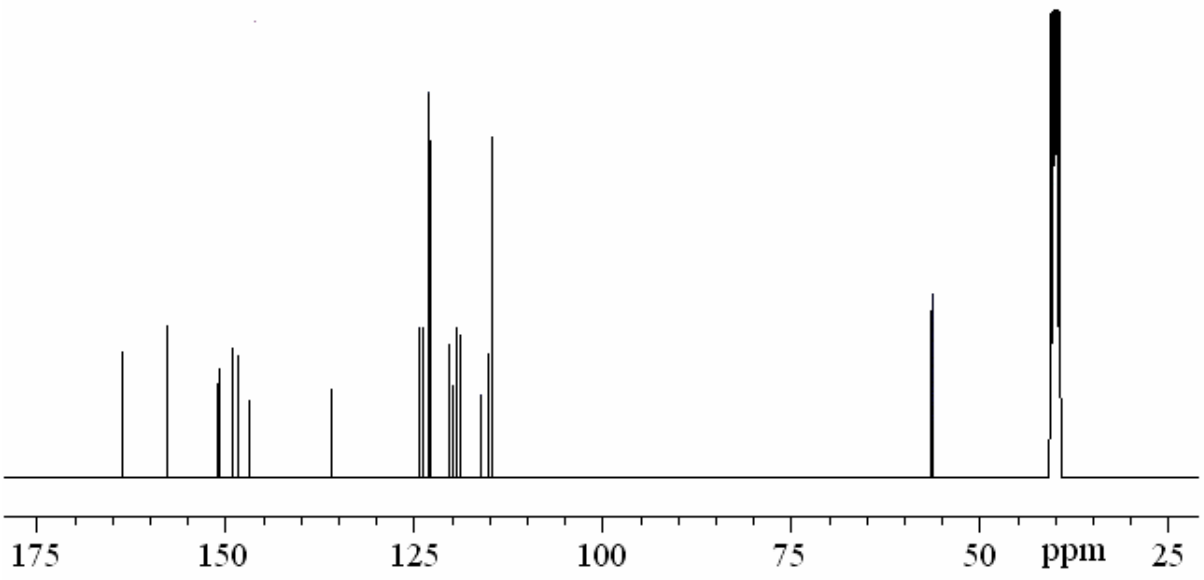
PBNMBMP'ın ^{13}C-NMR spektrumu'na bakıldığında ilk önce 151.01 ppm'de hidroksi grubunun bağlı olduğu C atomuna ait ^{13}C-NMR sinyali , 148.38 ppm'de metoksi grubunun C atomuna ait ^{13}C-NMR sinyali, 163.77 ppm'de azometin grubunun bağlı olduğu C atomuna ait ^{13}C-NMR sinyalleri , 116.10 ile 146.97 ppm arası aromatik karbonlara ait ^{13}C-NMR sinyalleri gözlenmektedir. Metksi grubunun karbonu ise 56.36 ppm'de görülmektedir.

Tablo 3.3.2.3. OPBNMBMP'nin ^{1}H-NMR spektrumu verileri

	-OH	-OH	-CH=N	-CH=N	Ha	Hb	Hc
	13,91H Tekli	13,20 1H Tekli	9,03 1H Tekli	8,85 1H Tekli	7,04 1H, İkili	7,26 1H, İkili	7,55 2H İkili
Hd	He	Hf	Terminal, H	Terminal, H	OC $\underline{H_3}$	OC$\underline{H_3}$	
6,63 2H İkili	7,22 1H İkili	6,86 1H, Üçlü	6.93 1H Üçlü	7,14 1H Üçlü	3,84 3H Tekli	3,81 3H Tekli	

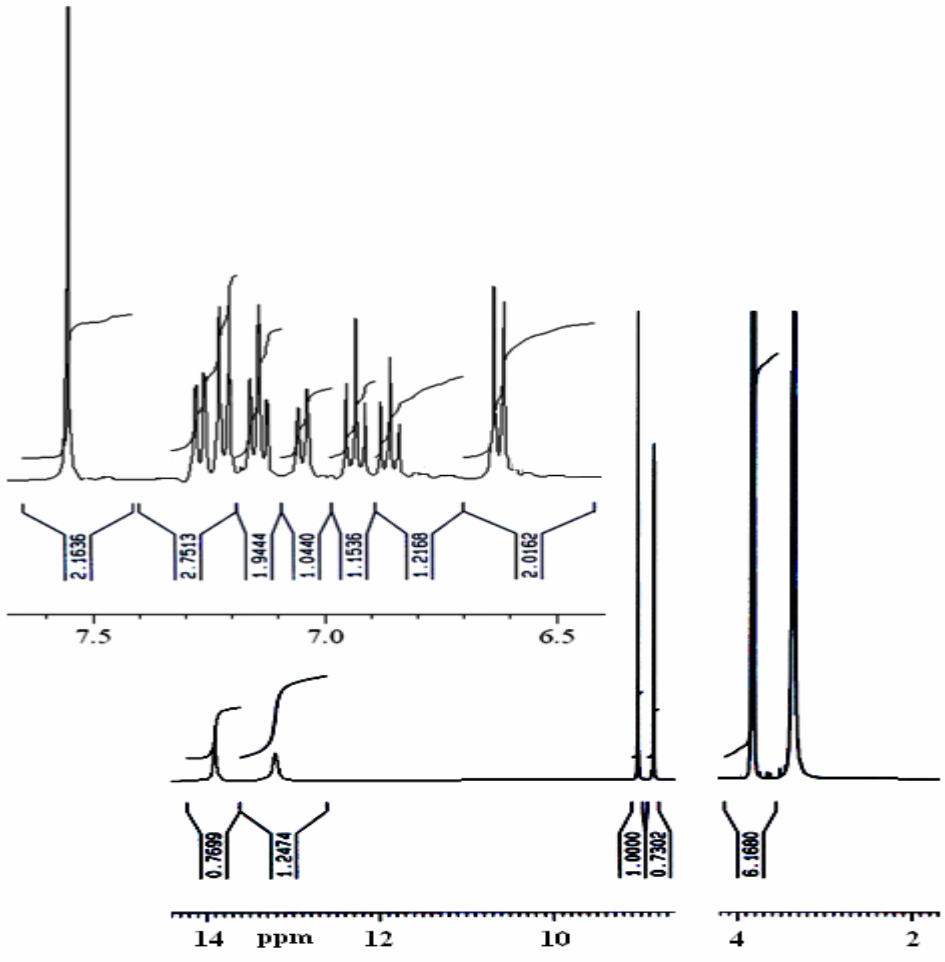
Tablo 3.3.2.4. OPBNMBMP'ın ^{13}C-NMR spektrumu verileri

Yapı Birimi			**Yapıdaki karbonların kayma değerleri (ppm)**						
			C1-ipso	C2-C17-ipso	C3	C4-ipso	C5	C6-ipso	C7
			151.02	149.21	114.60	119.15	136.03	119.75	163.77
C8-ipso	C9	C10	C11-ipso	C12	C13-ipso	C14	C15-ipso	C16	C18-ipso
148.38	122.88	123.03	148.26	157.83	119.99	124.38	123.82	118.72	150752
C19	C20	Yeni pik	Yeni pik						
56.36	56.27	115.00	116.10						



Şekil 3.3.2.3. OPBNMBMP'ın ^{13}C-NMR spektrumu

Şekil 3.3.2.3.incelendiğinde OPBNMBMP'ın nin ^{13}C-NMR spektrumu sinyallerinin sayısında artış olduğu görülmektedir. Bu ise monomerdeki simetri yapısının polimerde bozulmasından kaynaklanır. Ayrıca 115.00 ve 116.00 ppm'de monomerin ^{13}C-NMR spektrumunda gözlenmeyen C-C eşleşmesine ait yeni karbon sinyalleri görülmektedir. Tablo 3.3.2.4.'de ise her bir karbon atomuna ait sinyaller ayrıntılı olarak verildi.



Şekil 3.3.2.4. OPBNMBMP'ın ^{1}H-NMR spektrumu

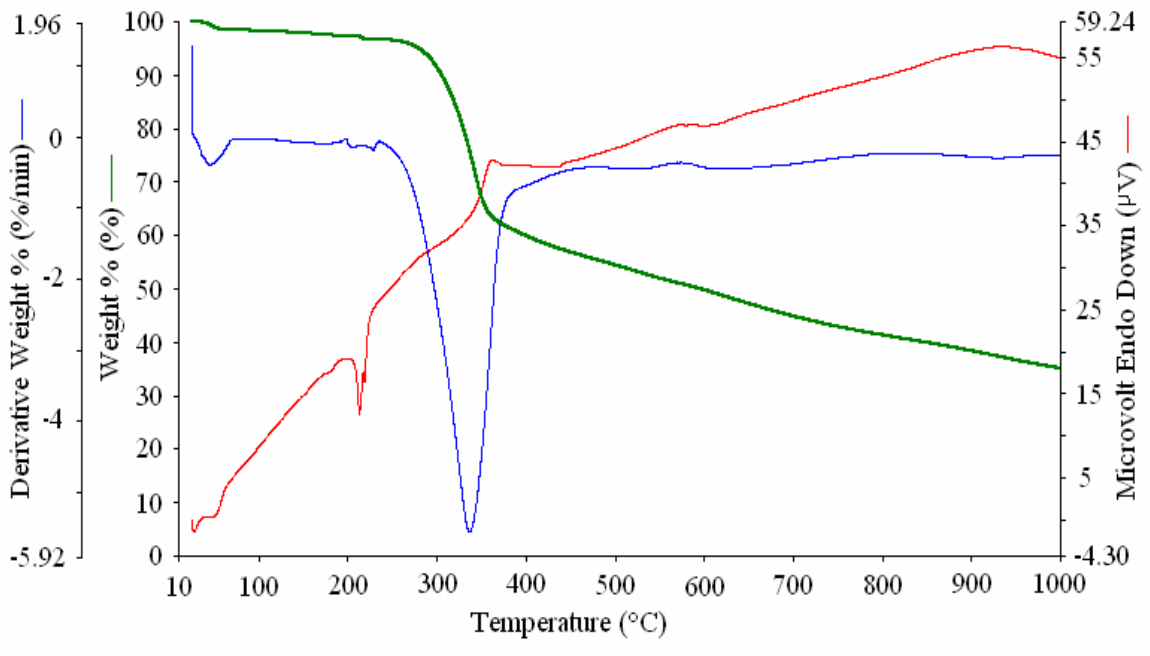
Şekil 3.3.2.4.'de OPBNMBMP'ın ^{1}H-NMR spektrumu incelendiğinde ve 12-14 ppm arasındaki hidroksil gruplarının integrasyon alanı gözönüne alındığında polimerleşmenin başlıca C-C bağlanması şeklinde gerçekleştiğini aynı zamanda C-O üzerinde de polimerizasyonun az da olsa gerçekleştiği görülebilmektedir. Yine spektrumda 6-8 ppm arası aromatik halkaya ait hidrojen pikleri; 8.85 ile 9.03 ppm'de ise azometin gruplarına ait pikler görülmektedir.

3.3.3. PBNMBMP ve OPBNMBMP'nin DTA-TG Analizleri

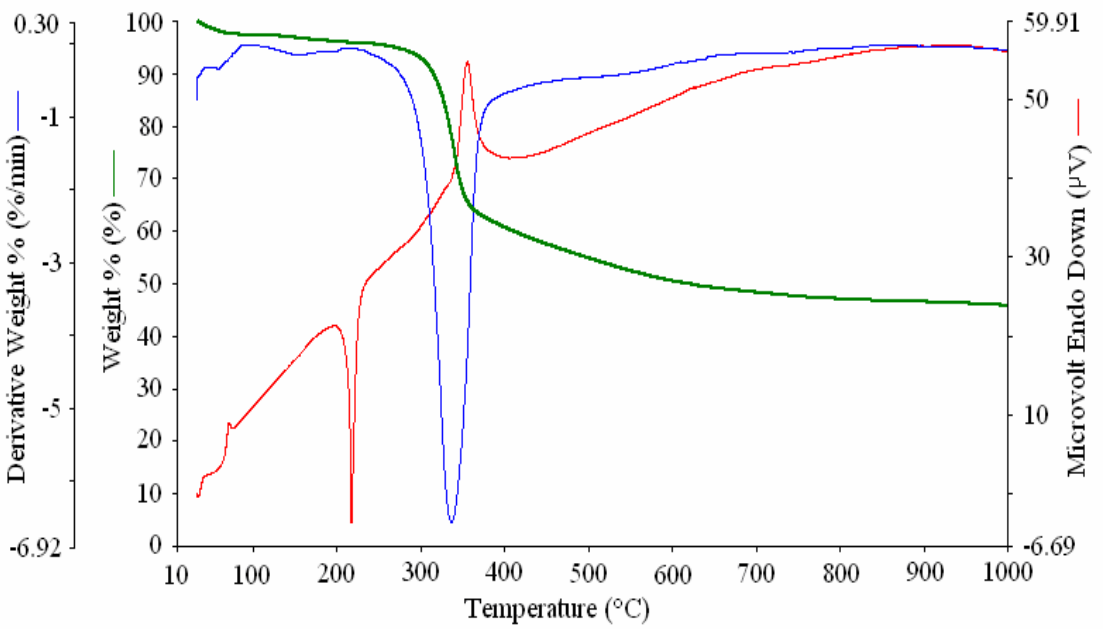
Poli(Schiff baz)larının yüksek sıcaklıklara karşı davranışları yapılan birçok çalışma ile incelenmiştir (Patel ve Patil, 1981, Karampurwala ve ark., 1981, Ragimov ve ark., 1989, Kaya ve ark., 2001, Cianga, 2006).

Bu çalışmada, sentezlenen monomer ve oligomerlerin azot ortamında termal dayanıklılıkları araştırıldı. Analizler N_2 atmosferi altında 20-1000°C'de aralığında ve 10°C/dak ısıtma hızında yapıldı. PBNMBMP ve OPBNMBMP'nin TG-DTG-DTA termal analiz eğrileri Şekil 3.3.3.1 ve 3.3.3.2'de verildi. Monomer ve oligomerin TG eğrilerinden ilk bozunma sıcaklığı değerleri sırasıyla 299 ve 312°C olarak belirlendi. Bu değerlere göre oligomerin başlangıç bozunma sıcaklığı monomerden daha yüksektir. Ayrıca, absorpsiyon halindeki su molekülleri 50-100°C arası sıcaklıklarda, kristal yapıdaki su molekülleri ise 100-150°C arası sıcaklıklarda yapıdan uzaklaştırılabilmektedir (Kaya *et al.* 2006). 50-100°C arası sıcaklıkta gözlenen %3-4'lük kütle kaybının absorbe haldeki su moleküllerinin uzaklaşmasından kaynaklanmaktadır.

Kütle kaybının %20 olduğu sıcaklık oligomerde 338 ^{o}C, monomerde 332 ^{o}C olarak gözlenirken, kütle kaybının %50 olduğu sıcaklık da sırasıyla oligomer ve monomer için 918 ve 653 ^{o}C olarak gözlendi. 1000°C'deki % kütle kaybı ise oligomerde 50,23 monomerde ise 62,20 olarak bulundu. Bu değerlere göre oligomer, monomere göre termal olarak daha kararlıdır denilebilir. Bu kararlılık oligomerdeki konjugasyonun artması ile ilişkilendirilebilir. Ana zinciri sigma-bağları ile bağlanmış ve yan dallarında Schiff baz grupları içeren poli(2-H-4-ABPI) bileşiği, 700°C'de kütlesinin tamamını kaybetmiştir (Kaliyappan et al. 2004). Ana zincirinde -CH=N- grubu bulunan poli(Schiff baz)ları ise 300-400°C gibi yüksek sıcaklıklarda bozunmaya başlamalarına karşın, 700°C'ye ulaşıldığında kütlelerinin tamamını kaybettikleri gözlenmiştir. Yüksek molekül kütlelerine sahip olmalarına rağmen, geride hiç karbon artık bırakmamaktadırlar. TG ve DTA analizlerine göre; sentezlenen bileşikler sıcaklık ve bozunmaya karşı yüksek kararlılık göstermiştir. Bu bilgiler ışığında sentezlenen bileşikler termal kararlılık ve grafit materyal özellikleri taşımaktadır. Bu özellikler teknolojik kullanım açısından önemlidir (Ionova, 1981).



Şekil 3.3.3.1. PBNMBMP TG-DTG-DTA eğrisi



Şekil 3.3.3.2. OPBNMBMP TG-DTG-DTA eğrisi

3.3.4 Çözünürlük

Sentezlenen bileşiklerin çözünürlük testleri çeşitli çözücüler içerisinde yapıldı. Testler 0,1mg/1 ml konsantrasyonunda gerçekleştirildi. Çözünürlük test sonuçları Tablo 3.3.4.1 ve Tablo 3.3.4.2.'de verildi. HMPMDAP; DMF, THF, DMSO, etanol, etil asetat, metanol, kloroform, heksan, aseton, der.H_2SO_4 ve sulu KOH'da çok iyi çözünmektedir. Toluende ise

kısmen çözünmektedir. PHMPMDAP ise DMF, THF, DMSO, der.H_2SO_4 ve sulu KOH'da çözünmektedir. Etanol, etil asetat, metanol, kloroform, heksan, aseton ve toluende ise çözünmemektedir.

Tablo 3.3.4.1. Sentezlenen monomer ve polimerlerin çözünürlük testleri

	DMF	**THF**	**DMSO**	**Etanol**	**Etil asetat**	**Metanol**	**Kloroform**	**Heksan**	**Aseton**	**Toluen**	**KOH(aq)**	***Der. H_2SO_4***
HMPMDAP	+	+	+	+	+	+	+	+	+	Δ-	+	+
PHMPMDAP	+	+	+	-	-	-	-	-	-	-	+	+
PBNMBMP	+	+	+	+	Δ+	Δ+	Δ+	Δ+	Δ+	Δ+	+	+
OPBNMBMP	+	+	+	Δ+	-	Δ+	-	-	δ-	-	+	+

+ : çözünmekte *Δ+ : sıcaklık etkisi ile çözünmekte*

δ- : kısmen çözünmekte *Δ-:sıcaklık etkisi ile çözünmemekte* *- : çözünmemekte*

Sentezlenen polimerlerin, reaksiyon sonunda reaksiyona girmeden kalan monomerlerden ayrılmasında çözünürlük farkından yararlanıldı. Reaksiyona girmeyen monomerler bu çözünürlük farkından yararlanılarak, yani monomeri çözen, polimeri çözmeyen bir çözücü yardımıyla ortamdan uzaklaştırıldı. Monomerlerle polimerlerin farklı çözücülerde çözünmesi de polimerizasyon reaksiyonunun gerçekleştiğinin bir kanıtıdır. Metal komplekslerinin çözünürlükleri ise monomer ve polimere oranla belirgin derecede düştüğü görüldü. Metal komplekleri için çözünürlük değerleri tabloda verilmiştir.

Tablo 3.3.4.2. Sentezlenen polimer- metal komplekslerinin çözünürlük testleri

	DMF	**THF**	**DMSO**	**Etanol**	**Etil asetat**	**Metanol**	**Kloroform**	**Heksan**	**Aseton**	**Toluen**	**KOH(aq)**	***Der. H_2SO_4***
PHMPMDAP Cu	Δ+	-	δ-	-	-	-	-	-	-	-	-	+
PHMPMDAP -Co	Δ+	-	δ-	-	-	-	-	-	-	-	-	+
PHMPMDAP Zn	Δ+	-	δ-	-	-	-	-	-	-	-	-	+
PHMPMDAP –Ni	Δ+	-	δ-	-	-	-	-	-	-	-	-	+
OPBNMBMP –Pb	Δ+	-	δ-	-	-	-	-	-	-	-	-	+

+ : çözünmekte *Δ+ : sıcaklık etkisi ile çözünmekte*

δ- : kısmen çözünmekte *Δ-:sıcaklık etkisi ile çözünmemekte* *- : çözünmemekte*

3.3.5. Sentezlenen Bileşiklerin SEC Analizleri

Sentezlenen bileşiklerin molekül ağırlığı dağılımı Shimadzu marka 10AVP model kromatografi cihazı kullanılarak gerçekleştirildi. Hareketli faz olarak DMF (0.4 ml/dak) ve dedektör olarak da refraktif indeks dedektör (RID) kullanıldı. Elde edilen sonuçlar Tablo 3.3.5.1. ve Tablo 3.3.5.2'de verildi. NaOCl oksidantı ile elde edilen OPBNMBMP oligomerinin büyüklükçe ayırma kromatografisine (SEC) göre; sayıca ortalama molekül ağırlığı (M_n), ağırlıkça ortalama molekül ağırlığı (M_w) ve heterojenlik indeksi değerleri sırası ile 1300 g mol^{-1}, 1500 g mol^{-1} ve 1,154 olarak hesaplandı. Aynı değerler hava oksijeni kullanıldığında sırası ile 1500g mol^{-1}, 1900 g mol^{-1} ve 1,267 olarak hesaplanmıştır. Bu değerler 50°C'de 1saat ve $[BNMBMP]_0=[KOH]_0=[NaOCl]_0$=0.027 mol/L, derişimlerinde ve hava oksijeni için $[BNMBMP]_0=[KOH]_0$=0.027 mol/L at 50°C de 1saat sonucundaki analiz verilerine göre belirlendi.

Tablo 3.3.5.1. OPBNMBMP'nin sayıca ortalama molekül ağırlığı (M_n), ağırlıkça ortalama molekül ağırlığı (M_w), polidispersite indeks (PDI) ve % değerleri

	Molekül Ağırlığı Dağılım Parametreleri													
	Toplam			Fraksiyon I				Fraksiyon II				Fraksiyon III		
Bileşikler	M_n	M_w	PDI	M_n	M_w	PDI	%	M_n	M_w	PDI	%	M_n	M_w	PDI
%														
OPBNMBMP[1]	1500	1900	1.267	1100	1600	1.455	95	38600	45400	1.176	5	-	-	-
OPBNMBMP[2]	1300	1500	1.154	900	1050	1.167	90	1900	2100	1.105	5	60000	66500	1.108
5														

1= Hava oksijeni oksidantı.; 2= NaOCl oksidantı

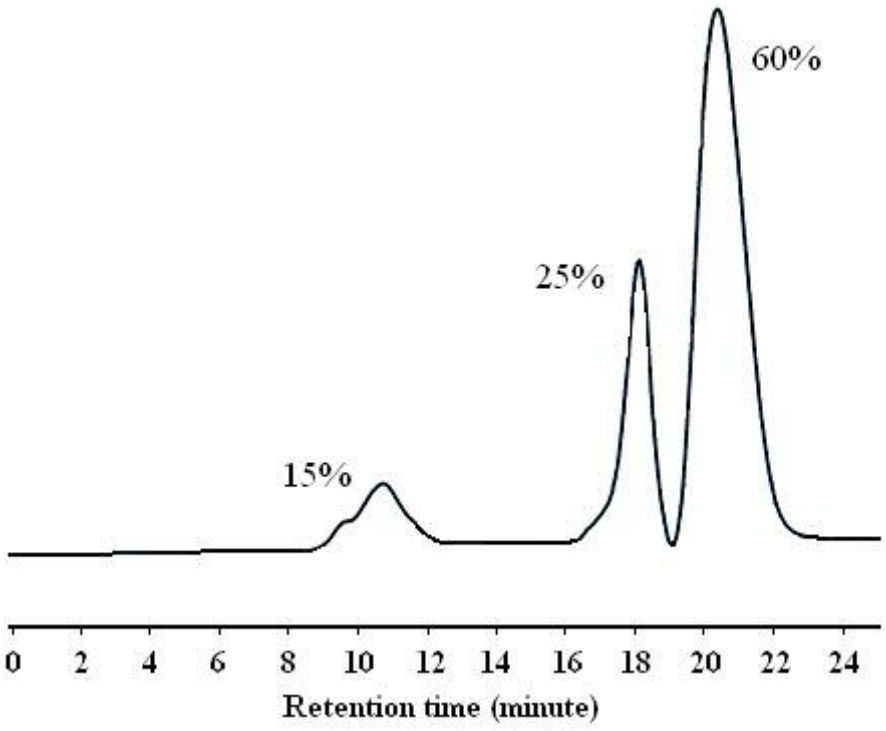
NaOCl oksidantı ile elde edilen PHMPMDAP oligomerinin büyüklükçe ayırma kromatografisine (SEC) göre; sayıca ortalama molekül ağırlığı (M_n), ağırlıkça ortalama molekül ağırlığı (M_w) ve heterojenlik indeksi değerleri sırası ile 6200 g mol^{-1}, 6900 g mol^{-1} ve 1,113 olarak hesaplandı. Aynı değerler hava oksijeni kullanıldığında sırası ile 5400 g mol^{-1}, 7700 g mol^{-1} ve 1,426 olarak hesaplandı. Yükseltgen olarak hidrojen peroksit kullanıldığında

sırası ile 4100 g mol^{-1}, 16200 g mol^{-1} ve 3.951 olarak hesaplandı. Bu değerler 50°C'de 1 saat ve $[HMPMDAP]_0=[KOH]_0=[NaOCl]_0$=0.014 mol/L, derişimlerinde ve hava oksijeni için $HMPMDAP]_0=[KOH]_0$=0.014 mol/L at 60°C de 1 saat sonucundaki analiz verilerine göre belirlendi.

Tablo 3.3.5.2. PHMPMDAP 'nin sayıca ortalama molekül ağırlığı (M_n), ağırlıkça ortalama molekül ağırlığı (M_w), polidispersite indeks (PDI) ve % değerleri

	Molekül Ağırlığı Dağılım Parametreleri														
	Toplam			Fraksiyon I				Fraksiyon II				Fraksiyon III			
Bileşikler	M_n	M_w	PDI	M_n	M_w	PDI	%	M_n	M_w	PDI	%	M_n	M_w	PDI	%
PHMPMDAP[1]	6200	6900	1.113	7500	9000	1.200	60	9300	11500	1.237	20	62000	64800	1.045	20
PHMPMDAP[2]	4100	16200	3.951	600	900	1.500	60	19800	79800	4.030	40	-	-	-	-
PHMPMDAP[3]	5400	7700	1.426	750	1000	1.333	45	8000	12900	1.613	45	123500	169800	1.375	10

1= Hava oksijeni oksidantı.; 2= NaOCl oksidantı , 3=Hidrojen peroksit oksidantı



Şekil 3.3.5.1. PHMPMDAP'ın SEC Kromatogramı

Bu değerlerden ve yürütülen reaksiyon sonuçları göz önüne alındığında şu çıkarımlar elde edildi. Reaksiyon sıcaklıkları ve süreleri arttığında yüksek molekül ağırlıklı bileşikler meydana geldiği görüldü. Bu durum olası olarak ortamda bulunan radikallerin tekrar reaksiyon ortamında bulunan oligomerlere katılmasından kaynaklanır. Yüksek molekül ağırlıklı bileşikler oluşmasına karşın ürün yüzdeleri azaldı. Genellikle yükseltgen materyal olarak sodyumhipoklorit kullanılan reaksiyonlarda ürün dönüşüm yüzdeleri fazla olmakla beraber molekül ağırlıkları düşüktür. Buna karşılık yükseltgen olarak hidrojen peroksit kullanılan deneylerde ise molekül ağırlıkları artmaktadır. Molekül ağırlıklarının artışı SEC analizlerine paralel olarak ürün renginin koyu renklere bürünmesinden de anlaşılabilir. Koyu kahverengiden siyah renge doğru kayan renkler yüksek molekül ağırlığına işaret eder. Bu durum olası olarak yapıda bulunan OH gruplarının monomerden fazla olması ve görünür bölgede absorbsiyon vermesi esasına bağlanabilir. Buna ilaveten bileşiklerin aynı şartlardaki çözünürlüklerinin azalması da bu düşünceyi destekler.

3.3.6. Sentezlenen Bileşiklerin Anti-mikrobiyal Özelliklerinin İncelenmesi

Sentezlenen maddelerin antimikrobiyal özelliklerini incelemek için bu maddelerin DMF'de (1,0 mg/1,0 mL) çözeltileri hazırlandı. Bu maddelerin antimikrobiyal aktivitesi disk diffüzyon metodu kullanılarak test edildi. Bu çözeltilerden 25 μL mikropipet yardımıyla alınarak, 6 mm çapındaki boş steril antibiyotik disklere (Schleicher & Shüll No: 2668, Almanya) emdirildi. Kontrol olarak da DMSO emdirilmiş diskler kullanıldı. Sentezlenen monomer ve polimerin tek konsantrasyondaki dozları test mikroorganizmalarına karşı farklı inhibisyon zonları gösterdikleri gözlendi ve sonuçlar Tablo 3.3.6.1.'de verildi.

Tablo 3.3.6.1. Sentezlenen bileşiklerin anti-mikrobial etkileri

Sıra Nu.	**Maddenin Adı**	***Bakteriler*** *(İnhibisyon Zonu, mm)*				
		E. coli	***S.aureus***	***P. auregenosa***	***B. subtilis***	***L. monoyctoges***
1	HMPMDAP	12	8	12	12	*0*
2	OHMPMDAP	18	8	0	12	*8*
3	PBNMBMP	14	15	8	10	*8*
4	OPBNMBMP	8	8	14	16	*12*
5	HMPMDAP -Cu	0	0	8	0	*0*
6	HMPMDAP -Co	0	0	0	0	*0*
7	HMPMDAP-Pb	0	0	0	0	*0*
8	HMPMDAP -Ni	0	0	8	0	*0*
9	*HMPMDAP -Zn*	*0*	*0*	*0*	*0*	*0*

Polimer-metal komplekslerinin DMSO'da tam olarak çözünmemesine rağmen çözünebilen kısımları ile antimikrobiyal çalışmaları yürütüldü. Bu ise bize metal komplekslerinin antimikrobiyal özelliği hakkında bilgi vermesi açısından önemlidir. Tablodan da görüldüğü gibi metal kompleksleri seçilen mikroorganizmalara karşı önemli bir direnç göstermemektedir. Sadece nikel ve bakır kompleksinin *P. Auregenosa* bakterisine karşı zayıf direnç gösterdiği belirlendi.

HMPMDAP bileşiği *L. Monoyctoges* bakterisi dışında diğer bakterilere karşı direnç gösterirken, OHMPMDAP bileşiği monomerine oranla *E.Coli* bakterisine karşı daha fazla direnç gösterdi. Bu bileşikler *S. Aureus* ve *B. Subtilis* bakterilerine karşı da yapılan testte hemen hemen aynı etkiyi gösterdiler.

PBNMBMP ve OPBNMBMP tüm bakterilere karşı direç göstermekle beraber; PBNMBMP bileşiği *E. Coli* ve *S.aureus* bakterilerine karşı monomerlere nazaran daha fazla direnç gösterdi. Diğer bakterilere karşı ise bu bileşiğin polimerinin daha etkili olduğu gözlendi.

4. SONUÇLAR

Yapılan bu çalışmada HMPMDAP ve PBNMBMPnin oksidatif polikondenzasyon reaksiyon şartları ve oluşan ürünlerin özellikleri incelendi. HMPMDAP'ın değişik sıcaklıklarda ve reaksiyon sürelerinde, bazik sulu ortamda hava oksijeni ve NaOCl ile etkileşerek koyu kahve renkli radikaller oluşturduğu gözlemlendi. Reaksiyon şartları ve oksidantların türü değiştikçe dönüşüm ürünlerinin miktarının değiştiği gözlemlendi. Reaksiyon şartları ve oluşan ürün yapıları göz önüne alındığında sadece amin grupları farklı olan vanilin monomerlerinden türetilen bu polimerlerden; HMPMDAP'nin ürünlerinin daha yüksek molekül ağırlıklı olduğu ve dönüşüm oranlarının daha yüksek olduğu göze çarpar. SEC kromatogram sonuçlarından da bu durumun doğruluğu daha kolay gözlenebilir. Bu ise 2,3-diamino piridinin, p-fenilen daiminden daha fazla oksidatif polimerizasyona yatkın olduğunu gösterir. Bundan önce piridinlerle yapılan çalışmalarda da piridin içeren monomerlerin dönüşüm yüzdesinin ve molekül ağırlığının daha yüksek olduğu sonucuna varılmış ve buna istinaden spektral analizlerinin yorumlanmasında sorunlar oluştuğu göze çarpmıştır.

Bileşiklerin termal kararlılıkları incelendiğinde monomerlerine nispeten polimerlerin termal bozunmaya karşı daha dayanıklı olduğu belirlendi. Literürde Daimin ve dialdehit bileşiklerinden polikondenzasyon yöntemi ile elde edilen poliazometin bileşiklerininden her iki polimerin de daha fazla termal kararlılık gösterdikleri 1000°C'deki kalıntı miktarlarına bakılarak rahatlıkla söylenebilir. Optik ve elektriksel özellikleri bileşiklerin tipik birer yarı iletken olduklarını ve doplanma ajanları ile doplanan bileşiklerin iletkenliklerinin artığı belirlendi. Monomer ve polimerler ve polimer metal-komplekslerinin Bacillus Subtilis ATCC 6633, Listeria Monocytogenes NCTC 5348, Pseudomena Aerugenosa ATCC 15442, Staphylococcus Aureus ATCC 25923 , Escherichia Coli ATCC 11229 bakterilerine karşı aktiviteleri incelendi. Ayrıca PHMPMDAP bileşiği nikel iyonunun spektrofotometrik olarak tayininde yeni bir ligand olarak kullanıldı. Sonuçlar diğer kullanılan reaktiflerler karşılaştırıldı.

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6. PROJE ÖZET BİLGİ FORMU

Proje Kodu: TBAG-105T428

Proje Başlığı: Oligo-2-[(2-hidroksi-6-metoksi-benziliden)aminopridin-3-il-iminometil-3-metoksifenol] ve Oligo-4[(2-hidroksi-6-metoksifenilmetilen)aminofeniliminometil-3metoksifenol]'ün sentezi, karakterizasyonu, termal, anti-mikrobiyal, iletkenlik özellikleri ve gıdalara uygulanması

Proje Yürütücüsü ve Yardımcı Araştırmacılar: Prof. Dr. İsmet KAYA
Doktora Öğr. Ali BİLİCİ, Doktora Öğr. Murat GÜL, Habibe BAĞCI, Mehmet DİLER, Mustafa KÖSEOĞLU

Projenin Yürütüldüğü Kuruluş ve Adresi: Çanakkale Onsekiz Mart Üniversitesi Fen-Edebiyat Fakültesi Kimya Bölümü, 17020 Çanakkale

Destekleyen Kuruluş(ların) Adı ve Adresi:

Projenin Başlangıç ve Bitiş Tarihleri: 01.05.2006-01.05.2008

Öz:

Bu çalışmada, *o*-vanilin ile 2,3 diaminopridin ve *p*-fenilendiaminin kondenzasyon reaksiyonundan Schiff bazları elde edildi. Sentezlenen monomerler NaOCl, H_2O_2 ve hava oksijeni ile bazik ortamda polimerlerine dönüştürüldü. Prosesin temel değerleri ve optimum reaksiyon koşulları belirlendi. Sentezlenmiş ürünlerin yapıları element analizi, FT-IR, ^{1}H-NMR, ^{13}C-NMR ve UV-vis spektrumlarındaki verilerinden faydalanarak belirlendi. ^{1}H-^{13}C-NMR verilerine göre; polimerizasyon, monomerlerin -OH gruplarına göre, *para* ve oksifenilen konumlarından gerçekleşmektedir. Büyüklükçe ayırma kromatografisine (SEC) göre, PHMPMDAP'in sayıca ortalama molekül ağırlığı (M_n), ağırlıkça ortalama molekül ağırlığı (M_w) ve heterojenlik indeksi değerleri hava oksijeni, NaOCl ve H_2O_2 yükseltgenlerine göre sırası ile 6200, 4100 ve 5400g mol^{-1}, 6900, 16200 ve 7700 g mol^{-1} ve 1,113, 3,951, 1,426 olarak hesaplandı. SEC analizlerine göre, OPBNMBMP'in sayıca ortalama molekül ağırlığı (M_n), ağırlıkça ortalama molekül ağırlığı (M_w) ve heterojenlik indeksi değerleri NaOCl ve hava oksijeni oksidantlarıyla elde edilen ürünler açısından sırası ile 1300 g mol^{-1}, 1500 g mol^{-1}: 1900, 1500 g mol^{-1} ve 1.267 ve 1,154 olarak hesaplandı. Ayrıca, DTA ve TG analizleri sentezlenen polimerlerin monomerlerine göre termal bozunmaya karşı daha dayanıklı olduğunu gösterdi. Polimerlerin dört nokta prob tekniği ile iletkenlik özellikleri incelendi. Monomer, polimer ve polimer-metal komplekslerinin bazı seçilmiş bakterilere karşı anti-mikrobial aktiviteleri

belirlendi.Ayrıca sentezlenen PHMPMDAP bileşiği gıdalarda nikel iyonunun spektrofotometrik olarak tayini için yeni bir ligand olarak denendi ve elde edilen çalışma sonuçları değerlendirildi.

Anahtar Kelimeler: Oksidatif polikondenzasyon, Schiff bazı oligomer, anti-mikrobial aktivite, yarı iletkenlik, termal kararlılık.

Projeden Kaynaklanan Yayınlar:

Makaleler:

1- İ. Kaya and A. Bilici, Synthesis, characterization, thermal Analysis and band gap of oligo-2-methoxy-6-[(4-methylphenyl)imino]methylphenol, *Journal of Applied Polymer Science*, **104** (5) 3417-3426 (2007).

2- İ. Kaya and M.Yıldırım, Synthesis and characterization of novel polyphenol species derived from bis(4-aminophenyl)ether: Substituent effects on thermal behavior, electrical conductivity, solubility, and optical band gap, *Journal of Applied Polymer Science*, 110 (1), 539-549 (2008).

3- İ. Kaya and A. Aydın, Synthesis, characterization, thermal stability, conductivity and band gaps of monomer and oligo-4-[(thien-2-yl-methylene)]amino phenol, *E-Polymer*, 071, 1-14 (2008).

4- İ. Kaya, A. Bilici and M.Gül, Schiff base substitute polyphenol and its metal complexes derived from *o*-vanillin with 2, 3-diaminopyridine: Synthesis, characterization, thermal and conductivity properties, *Polymers for Advanced Technology*, 19, 1154-1163 (2008).

5- İ. Kaya and A. Bilici, Synthesis, characterization, thermal analysis and electrical properties of poly-4-[1-(4-hydroxyphenyl)ethylidenamino]phenol, *Polimery*, 2, (2009).

6- İ. Kaya and A. Aydın, Synthesis, characterization, thermal degradation and electrical conductivity of oligo-2-[(thien-2-yl-methylene)]aminophenol and oligomer-metal complexes, *Chinese Journal of Polymer Science*, accepted for publication.

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Ekler

Ek:1

Synthesis, Characterization, Thermal Analysis, and Band Gap of Oligo-2-Methoxy-6-[(4-methylphenyl)-imino]methylphenol

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ABSTRACT: The oxidative polycondensation reaction conditions of 2-methoxy-6-[(4-methylphenyl)imino]methylphenol (2M-4-MPIMP) by using oxidants such as air O_2, H_2O_2 and NaOCl were studied in an aqueous alkaline medium between 30 and 90°C. The structures of synthesized monomer and oligomer were confirmed by FTIR, UV–vis, ^{1}H NMR, ^{13}CNMR, and elemental analysis. The characterization was made by TG–DTA, size exclusion chromatography (SEC), and solubility tests. At the optimum reaction conditions, the yield of oligo (O)-2M-4-MPIMP was 68% for air O_2 oxidant, 68% for H_2O_2 oxidant, and 82% for NaOCl oxidant. According to the SEC analysis, the number–average molecular weight (M_n), weight–average molecular weight (M_w), and polydispersity index (PDI) values of O-2M-4-MPIMP were found to be 695, 1000 g mol^{-1} and 1.439, using air O_2, and 670, 795 g mol^{-1} and 1.187, using NaOCl, and 645, 790 g mol^{-1} and 1.225, using H_2O_2, respectively. TG–DTA analyses were shown to be stable of O-2M-4-MPIMP against thermal decomposition. The weight losses of 2M-4-MPIMP and O-2M-4-MPIMP were found to be 98.46% and 89.54% at 1000°C, respectively. Also, electrical conductivity of the O-2M-4-MPIMP was measured, showing that the polymer is typical semiconductor. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of monomer and oligomer were determined from the onset potentials for *n*-doping and *p*-doping, respectively. Optical energy gaps (E_g) of 2M-4-MPIMP and O-2M-4-MPIMP were calculated from UV–vis measurements. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3417–3426, 2007

Key words: oxidative polycondensation; oligo-2-methoxy-6-[(4-methylphenyl)imino]methylphenol; air O_2, NaOCl; H_2O_2; thermal analysis; conductivity and band gap

INTRODUCTION

Polymers with highly conjugated chains have attracted much attention in the last few years because they are materials of academic interest and also they are promising candidates for a wide variety of applications such as electronics,[1] optoelectronics,[2] and photonics.[3] Numerous articles have been published having polymers as a main subject conjugated systems of type polyacetylenes, polyphenylenes, polyphenylene vinylenes, polypyrrole, polythiophene, or polyaniline.[1,4] The oxidative polycondensation method is simply the reaction of compounds including —OH groups and active functional groups (—NH_2, —CHO, and —COOH) in their structure with the oxidants such as NaOCl, H_2O_2, an air oxygen in the aqueous alkaline, and acidic medium.[5] Another class of this family, unfortunately less examined, is that of polyimines (PIs), which are also known as polymeric Schiff bases, polymers that are synthesized by a polycondensation reaction between an amine or hydrazine with an aldehyde or diketone.[6–9] The PIs have attracted much attention not only as high performance fiber and film-forming polymers with remarkable thermal stability, high strength, and high modulus[10–14] but also as particularly promising electronic materials with semiconducting properties[15–17] nonlinear optical properties,[18] and ability to form chelates.[19]

In this article, we have investigated the effects of different parameters such as temperature, reaction time, and initial concentration of NaOCl and H_2O_2 for the oligo-2-methoxy-6-[(4-methylphenyl)imino]-methylphenol (2M-4-MPIMP). We have characterized 2M-4-MPIMP and O-2M-4-MPIMP by using FTIR, UV–vis, ^{1}H NMR, ^{13}C NMR, elemental analysis, TG–DTA, and size exclusion chromatography (SEC) techniques. The electrical conductivity of the oligomer was measured after doping with I_2. Also, electrochemical (E'_g) and optical (E_g) energy gaps of the monomer and oligomer were determined from cyclic voltammetry (CV) and UV–vis measurements.

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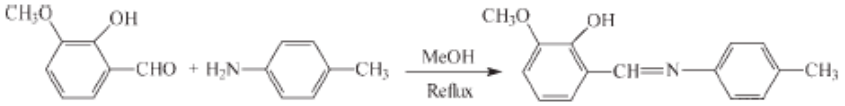


Scheme 1 Synthesis of 2-methoxy-6-[(4-methylphenyl)imino]methylphenol.

MATERIALS AND METHODS

Materials

Methanol, *p*-toluidine, *o*-vanillin, dioxane, ethanol, 1-butanol, acetonitrile, benzene, toluene, ethyl acetate, heptane, hexane, CCl_4, $CHCl_3$, tetrahydrofurane, THF, *N*,*N*′-dimethylformamide, DMF, dimethylsulfoxide, DMSO, H_2SO_4 (98%), NaOH, H_2O_2 (30% aqueous solution), KOH, and hydrochloric acid (HCl, 37%) were supplied from Merck Chemical (Germany) and they were used as received. Sodiumhypochloride (NaOCl), 30% aqueous solution, was supplied from Paksoy Chemical (Turkey). 2M-4-MPIMP was synthesized from condensation reaction of *o*-vanillin with *p*-toluidine and recrystallized in methanol.

Preparation of 2M-4-MPIMP

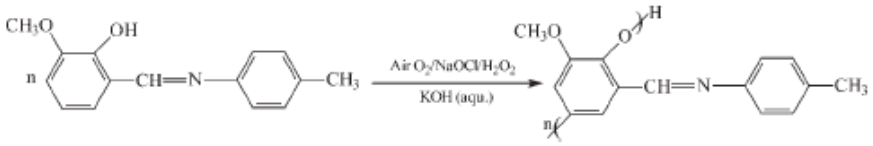
2M-4-MPIMP was prepared by the condensation of *o*-vanillin (1.52 g, 0.01 mol) with *p*-toluidine (1.07 g, 0.01 mol) in methanol (50 mL) achieved by boiling the mixture under reflux for 2 h at 70°C (Scheme 1). The precipitated 2M-4-MPIMP was filtered, recrystallized from methanol, and dried in a vacuum desiccators (yield 96%).

Calcd. for 2M-4-MPIMP: C, 74.69; H, 6.22; N, 5.81. Found: C, 74.55; H, 6.15; N, 5.70. UV–vis (λ_{max}): 203, 225, 276, and 316 nm. FTIR (cm^{-1}): ν (O—H) 3261 s, ν (C—H phenyl) 3029 m, ν (C—H aliphatic) 2920 s, ν (C=N) 1616 s, ν (OCH_3) 1456 s, ν (C=C phenyl) 1595, 1575, 1509 s, ν (C—O) 1255 s. ^{1}H NMR (DMSO): δ, ppm, 13.35 (s, 1H, —OH), 8.93 (s, 1H, —C*H*=N—), 7.33 (d, 2H, Ar—Haa′), 7.28 (d, 2H, Ar—Hbb′), 7.13 (d, 1H, Ar—Hc), 6.91 (t, 1H, Ar—Hd), 7.23 (d, 1H, Ar—He), 3.84 (s, 3H, —OCH_3), 2.35 (s, 3H, —CH_3). ^{13}C NMR (DMSO): ppm, 151.06 (C_1-ipso-OH), 148.37 (C_2-ipso-OCH_3), 118.99 (C_3—H), 115.95 (C_4—H), 124.33 (C_5—H), 119.69 (C_6-ipso), 163.16 (C_7—H), 145.67 (C_8-ipso), 121.66 (C_9—H), 130.43 (C_{10}—H), 137.01 (C_{11}-ipso), 56.36 (C_{12}—OCH_3), 21.08 (C_{13}—CH_3).

Synthesis of oligo-2M-4-MPIMP with NaOCl, air O_2, and H_2O_2 in aqueous alkaline medium

O-2M-4-MPIMP was synthesized through oxidative polycondensation of 2M-4-MPIMP with solution of NaOCl (30%, in water), air O_2, and H_2O_2 (30%, in water) oxidants, respectively, (Scheme 2).[20] The 2M-4-MPIMP (2.41 g 0.01 mol) was dissolved in an aqueous solution of KOH (10%, 0.01 mol) and placed into a 50-mL three-necked round-bottomed flask. It was fitted with a condenser, thermometer, and stirrer and at addition to funnel containing NaOCl or H_2O_2. After heating to room temperature, NaOCl and H_2O_2 were added drop by drop over about 30 min and mixture was heated between 30 and 90°C. The reaction mixtures were stirred at various temperatures and durations (Tables I and II). Air O_2 was passed into an aqueous solution of KOH (%20) before being sent through the reaction tube to prevent water loss in the reaction mixture and the neutralizing of CO_2 in the air to KOH (Scheme 2). The mixture was neutralized with HCl 0.01 mol (37%) at room temperature. Unreacted monomer was separated from the reaction products by washing with methanol. The mixture was filtered and washed with hot water (3 × 25 mL) for separating from mineral salts and then dried in the oven at 110°C.

Calcd. for O-2M-4-MPIMP.C, 75.00; H, 5.83; N, 5.83. Found: C, 74.40; H, 5.55; N, 5.72. UV–vis (λ_{max}): 207, 228, 274, and 325. FTIR (cm^{-1}): ν (O—H) 3357 s, ν (C—H phenyl) 3050 m, ν (C—H aliphatic) 2920 s, ν (C=N) 1622 s, ν (OCH_3) 1079 s,ν (C=C phenyl) 1596, 1574, 1509 s, ν (C—O) 1252 s. ^{1}H NMR (DMSO): δ, ppm, 13.40 (s, 1H, —OH), 8.95 (s, 1H, —CH=N—), 7.33 (d, 2H, Ar—Haa′), 7.27 (d, 2H, Ar—Hbb′), 7.12 (d, 1H, Ar—Hc), 6.90 (t, 1H, end group, Ar—Hd), 7.23 (d, 1H, Ar—He), 3.85 (s, 3H,



Scheme 2 Synthesis of oligo-2-methoxy-6-[(4-methylphenyl)imino]methylphenol.

TABLE I
The Oxidative Polycondensation Reaction Parameters of 2-Methoxy-6-[(4-methylphenyl)imino]methylphenol[a] with NaOCl in Aqueous KOH

Sample no.	$[KOH]_0$ (mol L^{-1})	NaOCl (mol L^{-1})	Temp. (°C)	Times (h)	The yield of O-2-M-4-MPIMP (%)
1	0.01	0.01	40	3	63
2	0.01	0.01	50	3	71
3	0.01	0.01	60	3	77
4	0.01	0.01	50	3	80
5	0.01	0.01	80	3	82
6	0.01	0.01	90	3	74
7	0.01	0.01	80	1	67
8	0.01	0.01	80	5	77
9	0.01	0.01	80	10	73
10	0.01	0.01	80	15	70
11	0.01	0.01	80	25	57
12	0.01	0.02	40	3	44
13	0.01	0.02	50	3	49
14	0.01	0.02	60	3	53
15	0.01	0.02	70	3	58
16	0.01	0.02	80	3	60
17	0.01	0.02	90	3	57
18	0.01	0.02	80	1	31
19	0.01	0.02	80	3	25
20	0.01	0.02	80	5	48
21	0.01	0.02	80	10	34
22	0.01	0.02	80	15	28
23	0.01	0.02	80	25	26

[a] The initial concentration of 2-M-4-MPIMP was used as 0.01 mol L^{-1}.

$-OCH_3$), 2.33 (s, 3H, $-CH_3$). ^{13}C NMR (DMSO): ppm, 151.08 (C_1-ipso-OH), 148.37 (C_2-ipso-OCH_3), 119.69 (C_3—H), 118.98 (C_4-ipso), 129.68 (new peak of C—C coupling system), 124.34 (C_5—H), 115.93 (C_6-ipso), 163.13 (C_7—H), 145.65 (C_8-ipso), 121.65 (C_9—H), 130.42(C_{10}—H), 137.00 (C_{11}-ipso), 56.35 (C_{12}—OCH3), 21.08 (C_{13}—CH3).

Electrochemical properties

CV measurements were carried out with a CH Instruments 660B Electrochemical Analyzer at a potential scan rate of 20 mV/s. All the experiments were performed in a dry box under Ar atmosphere at room temperature. The electrochemical potential of Ag was calibrated with respect to the ferrocene/ferrocenium (Fc/Fc^+) couple. The half-wave potential ($E^{1/2}$) of (Fc/Fc^+) measured in 0.1*M* tetrabutylammonium hexafluorophosphate ($TBAPF_6$) acetonitrile solution is 0.39 V vs. Ag wire or 0.38 V versus supporting calomel electrote (SCE). The voltammetric measurements were carried out for 2M-4-MPIMP and O-2M-4-MPIMP in acetonitrile and DMSO, respectively. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the 2M-4-MPIMP and O-2M-4-MPIMP were determined from the onset potentials of the *n*-doping (ϕ'_n) and *p*-doping (ϕ'_p), respectively, as shown in literature.[21]

Optical properties

The optical band gaps (E_g) of monomer and oligomer compounds were calculated from their absorption edges. Ultraviolet–visible (UV–vis) spectra were measured by PerkinElmer Lambda 25. The absorption spectra of monomer and oligomer were recorded by using methanol and DMSO, respectively, at 25°C.

Electrical properties

Conductivity was measured on a Keithley 2400 Electrometer. The pellets were pressed on hydraulic press developing up to 1687.2 kg/cm^2. Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in a desiccator.[22]

TABLE II
The Oxidative Polycondensation Reaction Parameters of 2-Methoxy-6-[(4-methylphenyl)imino]methylphenol[a] with H_2O_2 (Sample Number: 1–15) and Air O_2 (Sample Number: 16–26) in Aqueous KOH

Sample no.	$[KOH]_0$ (mol L^{-1})	H_2O_2 (mol L^{-1}) or Air O_2 (L h^{-1})	Temp. (°C)	Time (h)	The Yield of O-2-M-4-MPIMP (%)
1	0.01	0.01	40	3	43
2	0.01	0.01	50	3	49
3	0.01	0.01	60	3	62
4	0.01	0.01	70	3	68
5	0.01	0.01	80	3	60
6	0.01	0.01	90	3	57
7	0.01	0.01	70	1	27
8	0.01	0.01	70	5	48
9	0.01	0.01	70	10	41
10	0.01	0.01	70	15	36
11	0.01	0.01	70	25	33
12	0.01	0.02	40	3	27
13	0.01	0.02	50	3	28
14	0.01	0.02	50	1	21
15	0.01	0.02	50	5	24
16	0.01	8.5	30	3	52
17	0.01	8.5	40	3	64
18	0.01	8.5	50	3	68
19	0.01	8.5	60	3	43
20	0.01	8.5	70	3	42
21	0.01	8.5	80	3	30
22	0.01	8.5	90	3	29
23	0.01	8.5	50	1	37
24	0.01	8.5	50	5	44
25	0.01	8.5	50	10	33
26	0.01	8.5	50	15	18

[a] The initial concentration of 2-M-4-MPIMP was used as 0.01 mol L^{-1}.

Solubility and characterization techniques

O-2M-4-MPIMP was dark brown at powder form and it was completely soluble in organic solvents such as DMF, THF, DMSO, aqueous alkaline, and conc. H_2SO_4, but it was partly soluble in methanol, ethanol, and 1-buthanol. O-2M-4-MPIMP was any insoluble in heptane, hexane, benzene, toluene, ethyl acetate, acetonitrile, $CHCl_3$, CCl_4, and dioxane. The solubility tests were done by using 1 mg sample and 1 mL solvent at 25°C. The infrared spectra was measured by PerkinElmer FTIR spectrum one. The FTIR spectra were recorded using ATR attachment (4000–550 cm^{-1}). UV–vis spectra of 2M-4-MPIMP and O-2M-4-MPIMP were determined by using methanol and DMSO. Elemental analysis was carried out with a Carlo Erba 1106. 2M-4-MPIMP and O-2M-4-MPIMP were characterized by using ^1H and ^{13}C NMR spectra (Bruker AC FT–NMR spectrometer operating at 400 and 100.6 MHz, respectively) and recorded by using deuterated DMSO-d_6 as a solvent at 25°C. Tetramethylsilane was used as an internal standard. Thermal data were obtained by using a PerkinElmer Diamond Thermal Analysis system. The TG–DTA measurements were made between 15 and 1000°C (in N_2, rate 10°C/min). The number–average molecular weight (M_n), weight–average molecular weight (M_w), and polydispersity index (PDI) were determined by SEC techniques of Shimadzu. For SEC, investigations were used a SGX (100 Å and 7-nm diameter loading material) 3.3 mm i.d. × 300 mm columns; eluent: DMF (0.4 mL/min), polystyrene standards. A refractive index detector (at 25°C) was used to analyze the oligomer.

RESULTS AND DISCUSSION

The investigation of synthesis conditions of O-2M-4-MPIMP

2M-4-MPIMP is not oxidized at the normal condition in the neutral aqueous and organic medium by air O_2, H_2O_2 (30% aqueous solution), and NaOCl (30% aqueous solution). When 2M-4-MPIMP interacted by oxidizes such as air O_2, H_2O_2, and NaOCl, it immediately precipitated phenoxy radicals with brown adding to alkaline solution. The conditions of oxidative polycondensation reaction of 2M-4-MPIMP with 30% NaOCl solution in aqueous alkaline medium are given in Table I. The yield of O-2M-4-MPIMP was 82% at the NaOCl medium for 3 h at 80°C. The yield of O-2M-4-MPIMP was 63% at the reaction conditions such as $[KOH]_0 = [2M\text{-}4\text{-}MPIMP]_0 = [NaOCl]_0 = 0.01$ mol/L at 40°C for 3 h. At the same conditions (at 80°C and 3 h), when molar amount of NaOCl oxidant increased in two coating, total yield of 2M-4-MPIMP changed from 82 to 60%. That is, increasing of oxidant amount decreased in the yield of O-2M-4-MPIMP.

The oxidative polycondensation reaction conditions of 2M-4-MPIMP with 30% H_2O_2 solution in aqueous alkaline medium are given in Table II. The yield of O-2M-4-MPIMP was 68% at optimum conditions such as $[2M\text{-}4\text{-}MPIMP]_0 = [KOH]_0 = [H_2O_2]_0 = 0.01$ mol/L at 70°C for 3 h. At the same conditions, when molar amount of alkaline increased in two coating, total yield of 2M-4-MPIMP changed from 62% to 15%. The yield of O-2M-4-MPIMP was 27% at the reaction conditions such as $[2M\text{-}4\text{-}MPIMP]_0 = [KOH]_0 = [H_2O_2]_0 = 0.01$ mol/L at 70°C for 1 h. According to these values, yield of O-2M-4-MPIMP decreased increasing of reaction temperatures and time. The oxidative polycondensation reaction conditions of 2M-4-MPIMP with air O_2 oxidant in an aqueous alkaline medium are given in Table II. At the oxidative polycondensation reaction of 2M-4-MPIMP, when air O_2 passed into 8.5 L/h rate at the reaction medium at 30°C for 3 h, the yield of product was 52%. The yield of O-2M-4-MPIMP was 68% at optimum conditions such as $[2M\text{-}4\text{-}MPIMP]_0 = [KOH]_0 = 0.01$ mol/L and 8.5 L h^{-1} rate at 50°C for 3 h. As is seen from Table I and II, in these reactions the yield of the oligomer was dependent upon temperature, times, and initial concentrations of alkaline and oxidants. At the same conditions, the yield of O-2M-4-MPIMP with NaOCl was higher than that of air O_2 and H_2O_2.

TABLE III
The Number–Average Molecular Weight (M_n), Weight–Average Molecular Weight (M_w), Polydispersity Index (PDI) and % Values of O-2-M-4-MPIMP

	Molecular weight distribution parameters														
	Total			Fraction I				Fraction II				Fraction III			
Compounds	M_n	M_w	PDI	M_n	M_w	PDI	%	M_n	M_w	PDI	%	M_n	M_w	PDI	%
O-2-M-4-MPIMP[a]	695	1000	1.439	560	1100	1.964	96	21300	23140	1.086	4	–	–	–	–
O-2-M-4-MPIMP[b]	670	795	1.187	790	1000	1.266	96	14695	15380	1.047	4	–	–	–	–
O-2-M-4-MPIMP[c]	645	790	1.225	630	965	1.532	76	2170	2810	1.295	19	20840	22050	1.058	5

[a] Air O_2 oxidant.
[b] NaOCl oxidant.
[c] H_2O_2 oxidant.

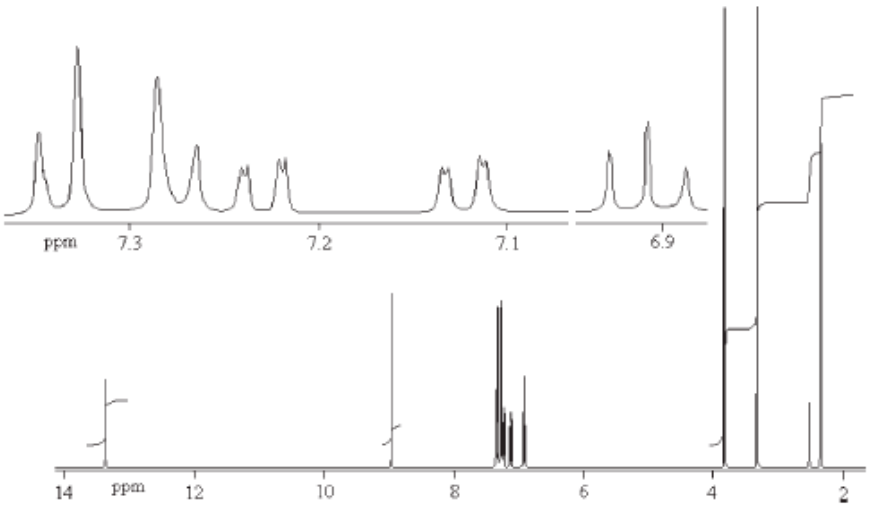


Figure 1 ^{1}H NMR spectrum of 2-methoxy-6-[(4-methylphenyl)imino]methylphenol.

Structure of O-2M-4-MPIMP

According to SEC chromatograms, the values of number–average molecular weight (M_n) and weight–average molecular weight (M_w) of O-2M-4-MPIMP were calculated according to a polystyrene standard calibration curve and are given in Table III. It is seen that, two fractions observed in oligomer by air O_2 and NaOCl oxidants but three fractions determined for H_2O_2 oxidant. An important section of products had little molecular weight distribution.

The UV–vis spectra of 2M-4-MPIMP and O-2M-4-MPIMP were similar to one together. However, at the spectra of 2M-4-MPIMP, K bands of phenol, and C_6H_5—N= were observed in 205 and 225 nm, respectively. Benzene band of 2M-4-MPIMP and strength R band of —CH=N— groups were observed in 276 and 316 nm, respectively. λ_{max} values of O-2M-4-MPIMP were observed in 207, 228, 274, and 325 nm. UV–vis spectra of O-2M-4-MPIMP, K, and R bands were observed in 274 and 325 nm, respectively. Because of conjugated band systems, azomethine group of oligomer shifted to higher field.

At the FTIR spectra of oxidative polycondensation, product of 2M-4-MPIMP are only different by reduction of band strength and peak numbers from the FTIR spectra of 2M-4-MPIMP. At the FTIR spectra of 2M-4-MPIMP and O-2M-4-MPIMP, bands of —OH, —CH=N, and aliphatic —CH_3 groups were observed in 3261, 1616, and 2920 cm^{-1}; 3357, 1622, and 2925 cm^{-1}, respectively. To identify the structures of monomer and oligomer, the ^{1}H NMR spectra were recorded in DMSO-d_6. ^{1}H NMR and ^{13}C NMR spectra of the 2M-4-MPIMP and O-2M-4-MPIMP are given in Figures 1–4, respectively. At the ^{1}H NMR spectra of 2M-4-MPIMP and

Figure 2 ^{13}C NMR spectrum of 2-methoxy-6-[(4-methylphenyl)imino]methylphenol.

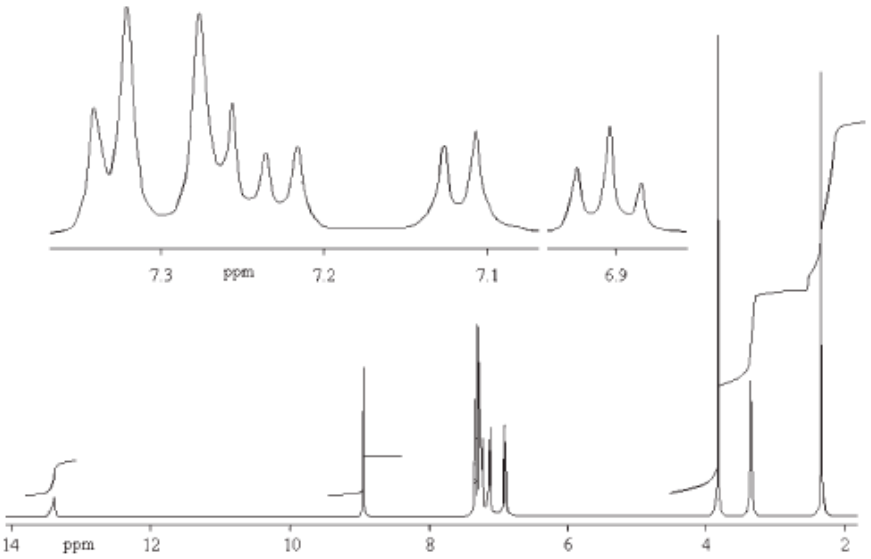


Figure 3 ^{1}H NMR spectrum of oligo-2-methoxy-6-[(4-methylphenyl)imino]methylphenol.

O-2M-4-MPIMP, the signals of —OH, —CH=N, and —OCH_3 groups were observed in 13.35, 8.93, and 3.84 ppm and 13.40, 8.95, and 3.85 ppm, respectively. It is seen from Figure 4 that because of C—C coupling system, a new peak is observed in 129.68 ppm. The ^{13}C NMR spectrum of O-2M-4-MPIMP has been demonstrated C—C and C—O—C coupling systems.[20] Interconversion combinations of radical units and formation of dimer, trimer, tetramer, and pentamer units are proposed as follows (Scheme 3). The SEC results spectral data and the results of FTIR, ^{1}H NMR, and ^{13}C NMR spectra of the O-2M-4-MPIMP have supported together.

Thermal analyses of 2M-4-MPIMP and O-2M-4-MPIMP

TG/DTA curves of monomer and oligomer were given in Figures 5 and 6. The initial degradation temperature, 50 and 98.46% weight loss of 2M-4-MPIMP found to be 209, 233, and 1000°C, respectively. According to DTG curve, thermal degradation of 2M-4-MPIMP was formed at one step. T_{max} value of 2M-4-MPIMP was observed in 250°C. According to DTA analysis, exothermic peaks observed in 100, 260, and 672°C. The initial degradation temperature,

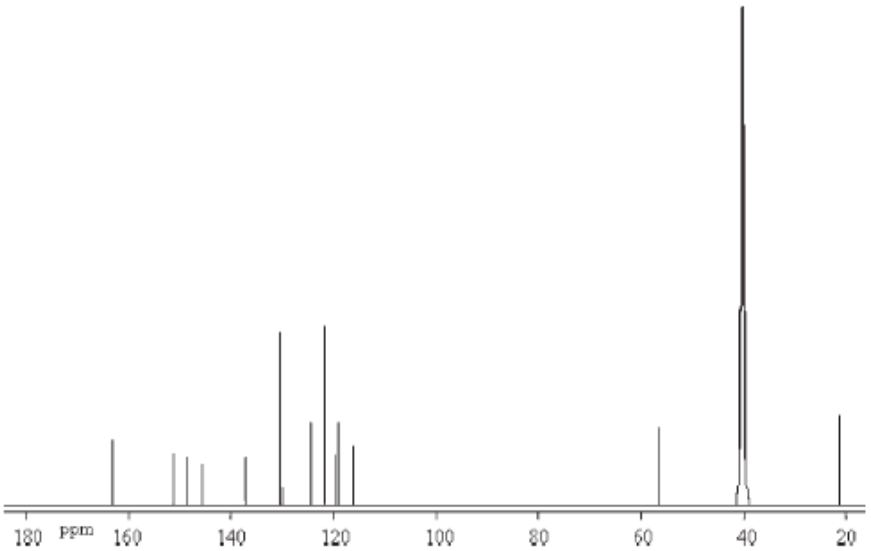
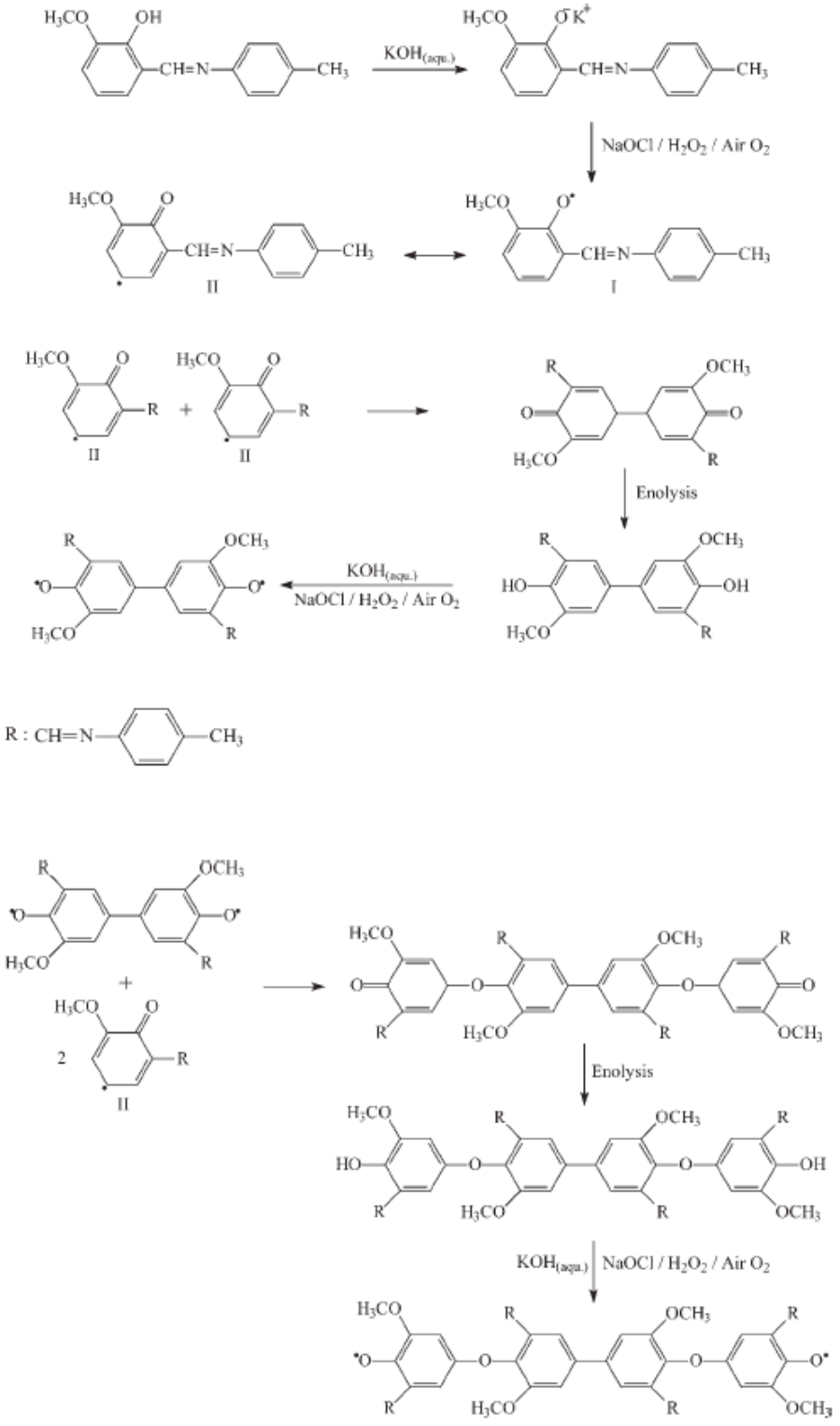
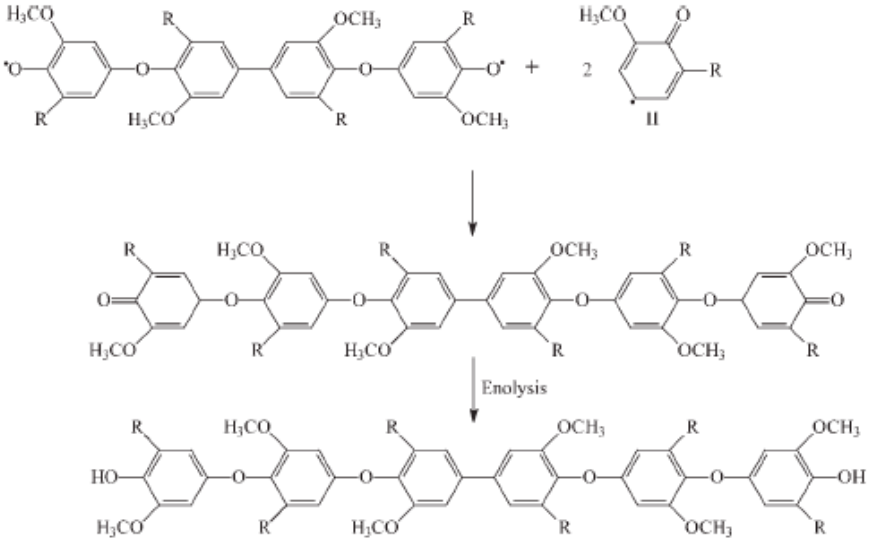


Figure 4 ^{13}C NMR spectrum of oligo-2-methoxy-6-[(4-methylphenyl)imino]methylphenol.



Scheme 3 The reaction mechanism of oligomer.



Scheme 3 (*Continued from previous page*)

50 and 89.54% weight loss of O-2M-4-MPIMP found to be 214, 257, and 1000°C, respectively. According to DTG curve, T_{max} value of O-2M-4-MPIMP was observed in 255°C According to DTA analysis, exothermic peaks observed in 83, 256, and 760°C. Because of long conjugated band systems, oligomer demonstrated higher resist against high temperature than monomer. According to TG analysis, although initial degradation temperature of O-2M-4-MPIMP was lower than monomer, it was more stable than monomer through to temperature and thermal decomposition. Carbines residue was formed at high amount such as 10.46% at 1000°C. Because of long conjugated band systems, oligomer demonstrated partly higher resist against high temperature than monomer. The high thermal stability of O-2M-4-MPIMP demonstrated to be formed of C—C and C—O—C coupling systems.

Electrochemical properties of 2M-4-MPIMP and O-2M-4-MPIMP

The voltammetric measurements of 2M-4-MPIMP and O-2M-4-MPIMP were carried out in acetonitrile

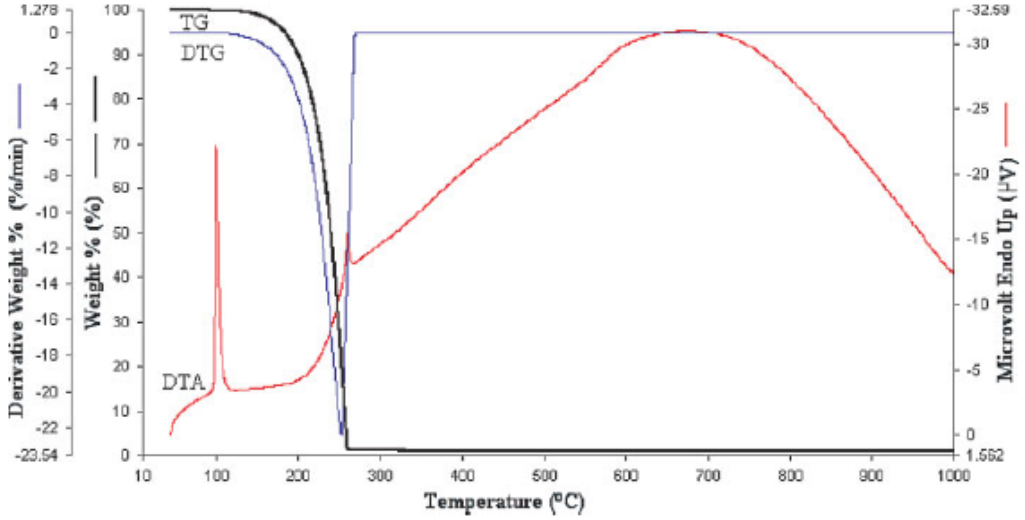


Figure 5 TG–DTG–DTA curves of 2-methoxy-6-[(4-methylphenyl)imino]methylphenol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

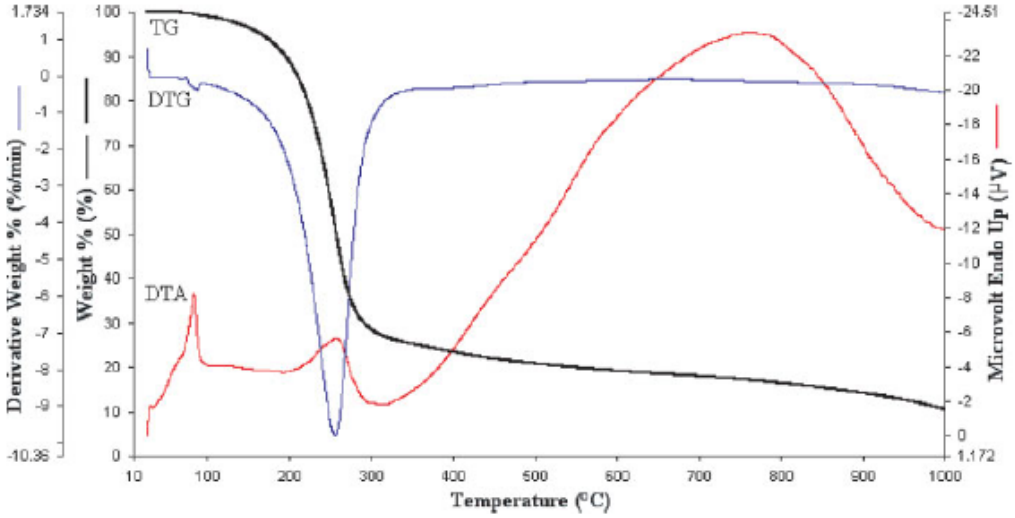


Figure 6 TG–DTG–DTA curves of oligo-2-methoxy-6-[(4-methylphenyl)imino]methylphenol. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and DMSO, respectively. The HOMO and LUMO energy levels of the 2M-4-MPIMP and O-2M-4-MPIMP were determined from the onset potentials of the *n*-doping (ϕ_n') and *p*-doping (ϕ_p'), respectively (Fig. 7). The HOMO and LUMO energy levels and electrochemical energy gaps[21] (E_g'), ($E_g' = \Delta\phi = \phi_p' - \phi_n'$) of 2M-4-MPIMP and O-2M-4-MPIMP were found to be −6.03, −6.12; −2.67, −2.75; 3.45 and 3.27 eV, respectively.

The absorption spectra of 2M-4-MPIMP and O-2M-4-MPIMP were recorded by using methanol and DMSO at 25°C (Fig. 8) and λ_{max} and E_g values of 2M-4-MPIMP and O-2M-4-MPIMP were found to be 318 and 334 nm and 3.25 and 3.08 eV, respectively.

O-2M-4-MPIMP has conductivities of $10^{-8} - 10^{-7}$ S/cm. When doped with iodine, their conductivities could be increased by about eight orders of magnitude (up to 10^{-3} S/cm). Figure 9 show the results of O-2M-4-MPIMP doped with iodine at various times at 25°C. Although the structure of O-2M-4-MPIMP differs, little significant difference in conductivity was observed. This effect may possibly be because of all actually belonging to the same class of oligomer. In the doping of O-2M-4-MPIMP with iodine, it was found that the conductivity of O-2M-4-MPIMP first increases greatly with doping time, but then tends to level-off. The maximal (or saturated) conductivity was 1.07×10^{-5} S/cm (shown in Fig. 9). The increasing conductivity could indicate that a charge-transfer complex between O-2M-4-MPIMP and dopant iodine is continuously formed. Consequently, Figure 9 not only shows the conductivity/doping

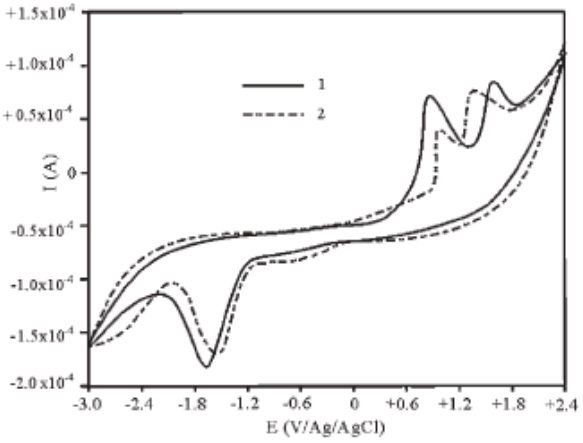


Figure 7 Cyclic voltammograms of 2M-4-MPIMP (1) and O-2M-4-MPIMP (2).

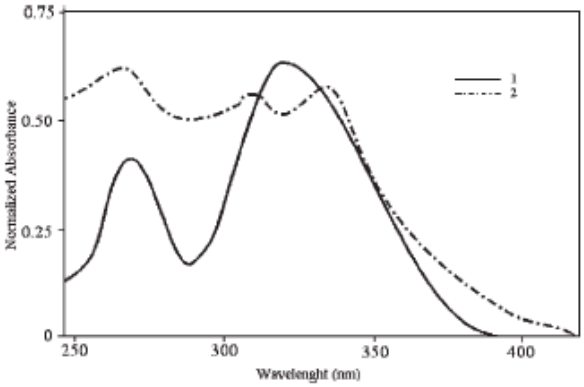


Figure 8 Absorption spectra of 2M-4-MPIMP (1) and O-2M-4-MPIMP (2).

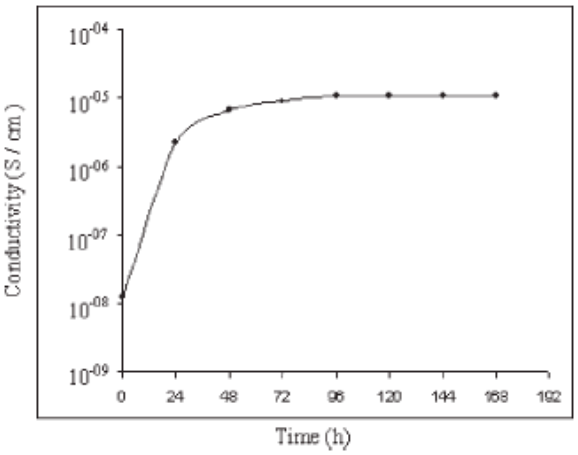
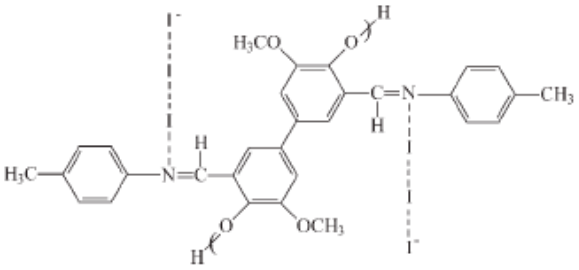


Figure 9 Electrical conductivity of I_2-doped O-2M-4-MPIMP versus doping time at 25°C.

time relationship but also indicates how quickly the doping reaction takes place. Our experiments showed that a longer doping time is needed to obtain the maximal conductivity. As a result, the conductivity/doping time curve varies with doping conditions. To exclude the influence of doping conditions, the conductivity of doped O-2M-4-MPIMP has been related with doping extent (shown in Fig. 9). Diaz et al. had been suggested the conductivity mechanisms of Schiff base polymers for doping with iodine.[23] Nitrogen is a very electronegative element and it is capable of coordinating an iodine molecule. On the nitrogen atom coordination of iodine with Schiff base, polymers and pyridine solutions had been suggested at the literatures as follows (Scheme 4).[24–26]

CONCLUSIONS

O-2M-4-MPIMP with Schiff base substitute is synthesized by oxidants such as air O_2, H_2O_2, and NaOCl in an aqueous alkaline medium. The yield of O-2M-4-MPIMP was found to be 68, 68, and 82% for air O_2, H_2O_2, and NaOCl oxidants, respectively. At the oxidative polycondensation reaction of 2M-4-MPIMP, NaOCl demonstrated to higher activity than H_2O_2 and air O_2. The ^{13}C NMR data have demonstrated to unite from *para*-carbons of phenol ring each other of formation oligomer from oxidative polycondensation of 2M-4-MPIMP. Thermal analysis results have demonstrated to be enough resistance against thermal degradation of synthesized oligomer. The carbines residue of O-2M-4-MPIMP was found at high amount such as 10.46% at 1000°C. Properties of monomer and oligomer with potential low-band gap characteristics were determined. The band gap value of monomer was higher than oligomer. This is



Scheme 4 Coordination of iodine during O-2M-4-MPIMP doping.

a result of the azomethine group that is an electron donor. This increases the HOMO more than the LUMO and therefore lowers the band gap. The observed band gaps are sufficiently low to make this oligomer highly promising for photovoltaic applications.

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Synthesis and Characterization of Novel Polyphenol Species Derived from Bis(4-aminophenyl)Ether: Substituent Effects on Thermal Behavior, Electrical Conductivity, Solubility, and Optical Band Gap

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ABSTRACT: In this study, four different Schiff bases namely 4,4′-oxybis[*N*-(2-hydroxybenzilidene)aniline] (2-HBA), 4,4′-oxybis[*N*-(4-hydroxybenzilidene)aniline] (4-HBA), 4,4′-oxybis[*N*-(3,4-dihydroxybenzilidene)aniline] (3,4-HBA), and 4,4′-oxybis[*N*-(4-hydroxy-3-methoxybenzilidene)aniline] (HMBA) were synthesized. These Schiff bases were converted to their polymers that have generate names of poly-4,4′-oxybis[*N*-(2-hydroxybenzilidene)aniline] (P-2-HBA), poly-4,4′-oxybis[*N*-(4-hydroxybenzilidene)aniline] (P-4-HBA), poly-4,4′-oxybis[*N*-(3,4-dihydroxybenzilidene) aniline] (P-3,4-HBA), and poly-4,4′-oxybis[*N*-(4-hydroxy-3-methoxybenzilidene)aniline] (PHMBA) via oxidative polycondensation reaction by using NaOCl as the oxidant. Four different metal complexes were also synthesized from 2-HBA and P-2-HBA. The structures of the compounds were confirmed by FTIR, UV-vis, ^{1}H and ^{13}C NMR analyses. According to ^{1}H NMR spectra, the polymerization of the 2-HBA and 4-HBA largely maintained with C—O—C coupling, whereas the polymerization of the 3,4-HBA and HMBA largely maintained with C—C coupling. The characterization was made by TG-DTA, size exclusion chromatography and solubility tests. Also, electrical conductivity of the polymers and the metal complex compounds were measured, showing that the synthesized polymers are semiconductors and their conductivities can be increased highly via doping with iodine ions (except PHMBA). According to UV–vis measurements, the optical band gaps (E_g) were found to be 3.15, 2.06, 3.23, 3.02, 2.61, 2.47, 2.64, 2.42, 2.83, 2.77, 2.78, and 2.78 for 2-HBA, P-2-HBA, 4-HBA, P-4-HBA, 3,4-HBA, P-3,4-HBA, HMBA, PHMBA, 2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co, respectively. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 539–549, 2008

Key words: oxidative polycondensation; polyazomethine ether; thermal analysis; conductivity; optical band gap

INTRODUCTION

Polyazomethines (PAMs) and their derivatives have attracted much attention because of their useful properties such as high thermal stability, excellent mechanical strength, and good optoelectronic properties.[1–4] However, many synthesized PAMs, especially aromatic derivatives have low solubility in many organic solvents. With the aim of obtaining soluble PAMs many kinds of them have been previously prepared such as poly(azomethine ether)s,[5] poly(acrylate-azomethine)s,[6] poly(azomethine carbonate)s,[7] poly(amide-azomethine-ester)s,[8] poly(azomethine sulfone)s,[9] etc. Additionally, PAMs containing methoxy substituent have been presented with good solubility and also high thermal stability.[10] Oligophenols and their —CH=N— containing derivatives have been synthesized by oxidative polycondensation method and presented in the literature with their several useful properties.[11–15] Using of water medium makes this method environmental harmless. Also, using of cheap oxidants such as NaOCl, H_2O_2, and air O_2 is another advantage of this method. Additionally, because the synthesized products have good properties such as paramagnetism, semiconductivity, electrochemical cell, and resistance to high energy, this class of PAMs has become more attractive for researchers. During the last decade, Kaya and coworkers have studied this class of PAMs with thermal, electrochemical, optical, and electrical properties.[16–18] The synthesized products were also investigated as an antimicrobial agent.[19] It is seen that the synthesized PAMs have semiconductivity due to their polyconjugated bond systems.[20,21] Also, they have high thermal stability because of their highly aromatic structures.

For these reasons, we aimed to synthesize new soluble, semiconductive poly(azomethine ether)s via

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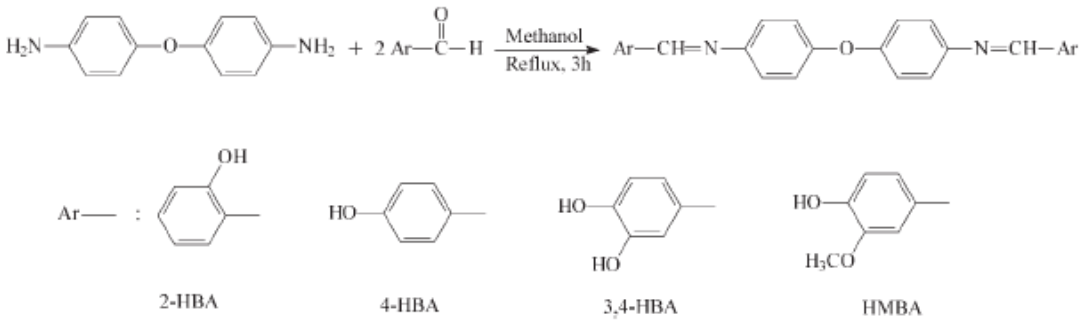


Scheme 1 Synthesis of the monomers.

oxidative polycondensation reaction. Also, we determined the changes of thermal, optical, and electrical characteristics related to different structures of the polymers. For this purpose, in the first part of this article, we synthesized a series of azomethine ether monomers containing —OH and/or —OCH_3 groups in different positions of aromatic ring. Then, we converted these monomers to poly (azomethine ether) derivatives via oxidative polycondensation reaction with using NaOCl as the oxidant. Also, to obtain higher electroconductive materials, we synthesized copper and cobalt complexes from 4,4′-oxybis[*N*-(2-hydroxybenzilidene)aniline] and poly-4,4′-oxybis[*N*-(2-hydroxybenzilidene)aniline].

In the second part, we determined the solubility properties of the synthesized monomers and polymers in different organic solvents to learn how easy these products are used in various applications. Then, we characterized the monomers, polymers, and the metal complex compounds by using UV–vis, ^{1}H and ^{13}C NMR, FTIR, and size exclusion chromatography (SEC) techniques. Also, thermal stabilities of the products were studied by TG-DTA techniques. Optical band gaps (E_g) were calculated from their absorption edges. Electrical properties of doped and undoped polymers and the metal complexes were determined by four-point probe technique at the room temperature and atmospheric pressure. In addition, an important increase of the conductivity was attained when iodine was employed as a doping agent.

MATERIALS AND METHODS

Materials

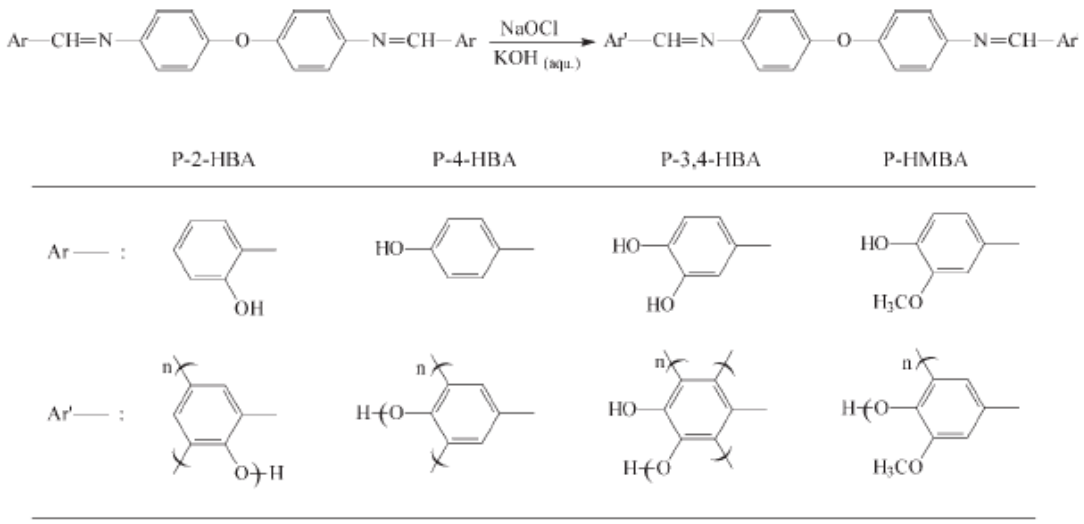
Bis(4-aminophenyl)ether, salicylaldehyde, 4-hydroxybenzaldehyde, 3,4-dihydroxy benzaldehyde, vanillin (4-hydroxy-3-methoxybenzaldehyde), $Cu(AcO)_2$ H_2O, $Co(AcO)_2$ $4H_2O$, methanol, ethanol, ethyl acetate, acetonitrile, acetone, $CHCl_3$, tetrahydrofurane, THF, dimethylformamide, DMF, dimethylsulfoxide, DMSO, H_2SO_4, KOH, and HCl (37%) were supplied from Merck Chemical (Germany) and they were used as received. Sodium hypo chloride (NaOCl), (30% aqueous solution) was supplied from Paksoy Chemical (Turkey).

Synthesis of the monomers

The Schiff base monomers abbreviated as 2-HBA, 4-HBA, 3,4-HBA, and HMBA were synthesized by the condensation reaction of bis(4-aminophenyl)ether with salicylaldehyde, 4-hydroxybenzaldehyde, 3,4-dihydroxybenzaldehyde, and 4-hydroxy-3-methoxybenzaldehyde, respectively. Reactions were made as follows: Bis(4-aminophenyl)ether (0.2 g, 0.001 mol) was placed into a 250-mL three-necked round-bottom flask which was fitted with condenser, thermometer, and magnetic stirrer, and 60 mL methanol was added into the flask as a solvent. Reaction mixture was heated at boiling temperature of methanol and bis(4-aminophenyl)ether was solved. A solution of excess amount of aldehyde (0.366 g, 0.003 mol for salicylaldehyde and 4-hydroxybenzaldehyde; 0.414 g, 0.003 mol for 3,4-dihydroxybenzaldehyde, and 0.456 g, 0.003 mol for 4-hydroxy-3-methoxybenzaldehyde) in 20 mL methanol was added into the flask. Reactions were maintained for 3 h under reflux (Scheme 1). The precipitated Schiff bases were filtered, recrystallized from methanol, and dried in vacuum desiccators (yields: 94, 96, 46, and 93%, for 2-HBA, 4-HBA, 3,4-HBA, and HMBA, respectively).

Synthesis of the polymers

The synthesized monomers were converted to their polymer derivatives through oxidative polycondensation reactions in an aqueous alkaline medium using NaOCl (30%) as the oxidant (Scheme 2), as in the literature.[21] Reactions were made in 250 mL three-necked round-bottom flasks which were fitted



Scheme 2 Synthesis of the polymers.

with condenser, thermometer, and magnetic stirrer. When the monomers interacted with NaOCl in alkaline medium, phenoxy radicals precipitated immediately with brown color. The oxidative polycondensation reaction conditions and the yields of polymer are shown in Table I.

Synthesis of the metal complex compounds of 2-HBA and P-2-HBA

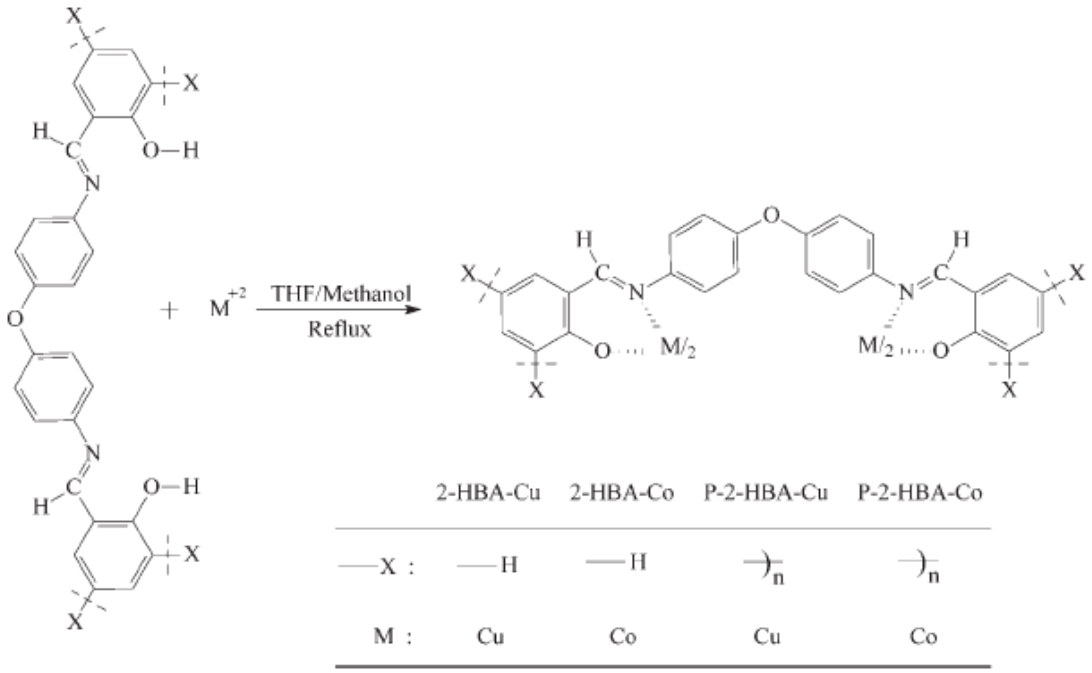
A solution of $Cu(AcO)_2$ H_2O (0.160 g, 8×10^{-4} mol) and $Co(AcO)_2$ $4H_2O$ (0.200 g, 8×10^{-4} mol) in methanol (10 mL) was added to a solution of 2-HBA (0.204 g, 5×10^{-4} mol) and P-2-HBA (0.200 g) in tetrahydrofurane (40 mL). The mixtures were heated at 70°C and reactions were maintained for 5 h under reflux (Scheme 3). The precipitated monomer and polymer complexes were filtered, washed with cold methanol/THF (1 : 1), and dried in vacuum oven (yields: 94, 86, 21, and 38% for 2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co complexes, respectively).

Characterization techniques

The infrared spectra were measured by Perkin–Elmer FTIR Spectrum one. The FTIR spectra were recorded using universal ATR sampling accessory (4000–550 cm^{-1}). Ultraviolet–visible (UV–vis) spectra were measured by Perkin-Elmer Lambda 25. UV–vis spectra of the synthesized compounds were determined by using methanol for the monomers and DMSO for the polymers and the complexes. The synthesized monomers and polymers were characterized by using ^1H and ^{13}C NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) and recorded by deuterated DMSO-d_6 as a solvent at 25°C. Tetramethylsilane was used as internal standard. Thermal data were obtained by using Perkin-Elmer Diamond Thermal Analysis. The TG-DTA measurements were made between 20 and 1000°C (in N_2, rate 10°C/min). The number average molecular weight (M_n), weight average molecular weight (M_w), and polydispersity index (PDI) were determined by SEC techniques of Shimadzu. For SEC investigations a SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. × 300 mm columns was used; eluent: DMF/Methanol (v/v, 4/1, 0.4 mL/min), polystyrene standards. A refractive index detector was used to analyze the products at 25°C. Electrical conductivities were measured on a Keithley 2400 Electrometer using four-point probe technique. The pellets were pressed

TABLE I
The Oxidative Polycondensation Reaction Conditions and the Yields of Polymers

Polymer	Temp. (°C)	Reaction time (h)	$[Monomer]_0$ (mol/L)	$[NaOCl]_0$ (mol/L)	$[KOH]_0$ (mol/L)	Yield of polymer (%)
P-2-HBA	90	10	0.007	0.044	0.315	94
P-4-HBA	90	10	0.010	0.067	0.085	67
P-3,4-HBA	90	10	0.019	0.071	0.045	92
PHMBA	90	10	0.013	0.071	0.045	95



Scheme 3 Synthesis of the metal complex compounds of monomer and polymer.

on a hydraulic press developing up to 1687.2 kg cm^{-2}. Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in a desiccator.[20] The optical band gaps (E_g) of the synthesized compounds were calculated from their absorption edges.

RESULTS AND DISCUSSION

Solubility properties

All of the synthesized monomers have light colors. But the colors of their polymer derivatives are dark brown. The solubility tests were done in different solvents by using 1 mg sample and 1 mL solvent at 25°C and the results are shown in Table II.

As shown in Table II the monomers are more soluble in many solvents compared with their polymers. They are all soluble in conc. H_2SO_4, DMF, and DMSO. Although the monomers are completely soluble in THF none of their polymers is soluble. Therefore, THF was used to separate unreacted monomers from the synthesized polymers after the polymerizations. Although chloroform is a good solvent for P-2-HBA and PHMBA to separate from their unreacted monomers it can not be used for P-4-HBA and P-3,4-HBA with same purpose.

TABLE II
Solubility Tests of the Monomer and Polymer Compounds

	Compounds							
Solvent	2-HBA	4-HBA	3,4-HBA	HMBA	P-2-HBA	P-4-HBA	P-3,4-HBA	PHMBA
$CHCl_3$	+	−	−	+	−	−	−	−
Acetone	−	+	+	+	−	−	−	−
Ethyl acetate	−	−	±	−	−	−	−	−
Ethanol	−	−	±	−	−	−	−	−
Acetonitrile	−	−	±	−	−	−	−	−
THF	+	+	+	+	−	−	−	−
DMF	+	+	+	+	+	+	+	+
DMSO	+	+	+	+	+	+	+	+
H_2SO_4	+	+	+	+	+	+	+	+

+, soluble; −, insoluble; ±, partially soluble.

TABLE III
The Number Average Molecular Weight (M_n), Weight Average Molecular Weight (M_w), Polydispersity Index (PDI), and % Values of the Oxidative Polycondensation Products of 2-HBA, 4-HBA, 3,4-HBA, and HMBA

	Molecular weight distribution parameters													
	Total			Fraction I				Fraction II				Fraction III			
Compounds	M_n	M_w	PDI	M_n	M_w	PDI	%	M_n	M_w	PDI	%	M_n	M_w	PDI	%
P-2-HBA	2,400	2,850	1.188	750	950	1.267	75	9,500	14,300	1.505	10	39,000	42,900	1.100	15
P-4-HBA	4,900	5,400	1.102	700	900	1.286	80	11,200	11,900	1.063	10	130,000	144,000	1.108	10
PHMBA	23,400	25,700	1.098	650	900	1.385	30	11,600	13,000	1.121	35	189,000	206,600	1.093	35
P-3,4-HBA	31,200	41,700	1.337	600	850	1.417	10	11,000	11,400	1.036	25	139,800	188,400	1.348	65

However, with exception of 2-HBA the synthesized monomers are soluble in acetone whereas their polymers are not (see Table II). These all mean that the synthesized poly(azomethine ethers) have higher resistant to solubility in many organic solvents with comparison to their monomers.

Structures of the synthesized compounds

According to the SEC chromatograms, the values of number–average molecular weight (M_n), weight average molecular weight (M_w), and PDI of P-2-HBA, P-4-HBA, P-3,4-HBA, and PHMBA were calculated according to a Polystyrene standard calibration curve and given in Table III. According to the SEC analysis, the number–average molecular weight (M_n), weight–average molecular weight (M_w), and PDI values were found to be 2400, 2850 g mol^{-1} and 1.188 for P-2-HBA, 4900, 5400 g mol^{-1} and 1.102 for P-4-HBA, 23,400, 25,700 g mol^{-1} and 1.098 for PHMBA, and 31,200, 41,700 g mol^{-1} and 1.337 for P-3,4-HBA, respectively. According to these results, P-3,4-HBA and PHMBA have quite high molecular weights and lower PDI values when compared to the previously presented oligophenol derivatives,[15–19] while the others' are similar with literature values. HMBA contains —OCH_3 substituent in the structure, and this substituent likely makes this monomer more soluble. So, during the growing up of the polymer chains, PHMBA keeps the solubility for a long time and consequently longer polymer molecules are obtained. Also, 3,4-HBA has two —OH groups where the radicalic polymerization begins. This supplies the molecule radicalic stability during the oxidative polycondensation and so high molecular weight depending on the high ratio of the intermolecular combinations of 3,4-HBA units.

The FTIR spectra of the oxidative polycondensation products of 2-HBA, 4-HBA, 3,4-HBA, and HMBA are different by broadening and shifting of the peaks from the FTIR spectra of the monomers. Also the numbers of the peaks of the polymers are less than the monomers. To identify the structures of the monomers and the polymers, ^{1}H NMR and ^{13}C NMR spectra were recorded in DMSO-d_6. To identify the metal complex compounds, the UV–vis and FTIR spectra were recorded. At the FTIR spectra of 2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co the new peaks indicating metal—N and metal—O coordinations were observed between 550 and 700 cm^{-1}. The results of UV-vis, FTIR, ^{1}H NMR, and ^{13}C NMR analyses were shown in Table IV.

Coupling selectivity of oligophenol derivatives have been previously studied and reported in the literatures.[22] Crosslinking in polymer structures is expected in those cases where the ortho and para positions (C—C coupling) and oxyphenylene (C—O—C coupling) in the corresponding monomer structures if they are unsubstituted. At the ^{1}H NMR spectra of the polymers, the integration areas of —OH protons were used to determine the rate of the C—O—C coupling to C—C coupling. According to these values the polymerization of the 2-HBA and 4-HBA largely maintained with C—O—C coupling whereas at the polymerization of the 3,4-HBA and HMBA C—O—C coupling is less than C—C coupling. Additionally, it is seen in the ^{13}C NMR spectra of P-2-HBA, P-4-HBA, P-3,4-HBA, and PHMBA that the C—C coupling between any two adjacent phenyl rings are largely at ortho and para positions of the —OH groups. However, this type of linkage may strain the polymer backbone in such a manner that the phenyl rings are out of plane with respect to the adjacent rings. The peak values for C3 and C5 were observed in 123.60 and 117.93 ppm for 2-HBA and 133.45 (showing as C14) and 123.23 ppm (new peaks) for P-2-HBA, respectively. The peaks observed at 115.98 and 114.58 ppm at the ^{13}C NMR spectra of 3,4-HBA for C2 and C5 shifted at 122.67 and 121.13 ppm at the ^{13}C NMR spectra of P-3,4-HBA, respectively. Also, the peak at 115.82 ppm of the ^{13}C NMR spectra of HMBA for C2 shifted at 124.78 ppm at the spectra of PHMBA. These changes indicate that the polymerization progress includes the C—C coupling system. The reaction mechanism on the coupling selectivity has been studied by Ayyagari coworkers and Kaya and coworkers and three possible reaction mechanisms for the C—C

TABLE IV
UV–vis, FTIR, and NMR Spectral Characterization Results of the Synthesized Compounds

Compound	Spectral data
2-HBA	UV–vis: λ/nm: 273, 352 IR: ν/cm^{-1}: 3210 (OH), 3054 (C—H, Phenyl), 1614 (C=N), 1569, 1489, 1456 (C=C phenyl), 1260 (C—O—C), 1281 (C—OH) ^{1}H-NMR (DMSO): δ ppm: 13.05 (s, 2H, —OH), 8.97 (s, 2H, —C*H*=N—), 7.65 (d, 2H, -Ha), 7.51 (d, 4H, -He, -He′), 7.42 (t, 2H, -Hc), 7.15 (d, 4H, -Hf, -Hf′), 6.97 (m, 4H, -Hb, -Hd) ^{13}C-NMR (DMSO): ppm: 163.23 (C7-H), 160.66 (C6-ipso), 155.04 (C11-ipso), 143.05 (C8-ipso), 133.65 (C4-H), 132.96 (C2-H), 123.60 (C3-H), 120.01 (C9-H), 119.64 (C1-ipso), 117.93 (C5-H), 117.05 (C10-H)
P-2-HBA	UV–vis: λ/nm: 262, 323, 346, 470 IR: ν/cm^{-1}: 3350 (OH), 3044 (C—H, Phenyl), 1618 (C=N), 1569, 1488 (C=C phenyl), 1263, 1227 (C—O—C), 1282 (C—OH) ^{1}H-NMR (DMSO): δ ppm: 13.15 (s, —OH), 8.98 (s, 2H, —C*H*=N—), 7.65 (s, 1H, -Hf), 7.51 (d, 1H, -Ha), 7.41 (d, 4H, -Hd), 7.15 (d, 4H, -He), 6.98 (d, 1H, -Hg), 6.79 (d, 1H, -Hc), 6.62 (t, 1H, -Hb), 6.51 (d, 1H, -Hi) ^{13}C-NMR (DMSO): ppm: 163.15 (C7-H), 162.32 (C6-ipso), 160.60 (C11-ipso), 158.48 (C17-ipso), 148.91 (C8-ipso), 145.91 (C15-H), 142.30 (C4-H), 133.45 (C14-ipso), 132.85 (C2, C13-H), 123.23 (C5-ipso), 121.41 (C3-H), 119.50 (C9-H), 117.62 (C1-ipso), 116.99 (C12-ipso), 115.39 (C10, C16-H)
4-HBA	UV–vis: λ/nm: 252, 289, 336 IR: ν/cm^{-1}: 3426 (OH), 3061 (C—H, Phenyl), 1623 (C=N), 1588, 1512, 1496 (C=C phenyl), 1245 (C—O—C), 1281 (C—OH) ^{1}H-NMR (DMSO): δ ppm: 10.15 (s, 2H, —OH), 8.48 (s, 2H, —C*H*=N—), 7.78 (d, 4H, -Hb, -Hb′), 7.27 (d, 4H, -Hc, -Hc′), 7.04 (d, 4H, -Hd, -Hd′), 6.90 (d, 4H, -Ha, -Ha′) ^{13}C-NMR (DMSO): ppm: 161.02 (C5-H), 159.76 (C1-ipso), 155.19 (C9-ipso), 147.81 (C6-ipso), 131.06 (C3-H), 128.04 (C4-ipso), 122.75 (C7-H), 119.65 (C8-H), 116.13 (C2-H)
P-4-HBA	UV–vis: λ/nm: 286, 332 IR: ν/cm^{-1}: 3345 (OH), 3036 (C—H, Phenyl), 1621 (C=N), 1582, 1491 (C=C phenyl), 1226 (C—O—C), 1280 (C—OH) ^{1}H-NMR (DMSO): δ ppm: 9.79 (s, —OH), 8.48 (s, 2H, —C*H*=N—), 5.65–7.30 (m, aromatic) ^{13}C-NMR (DMSO): ppm: 160.3 (C5-H), 159.0 (C1-ipso), 154.5 (C9-ipso), 144.0 (C6-ipso), 130.1 (C3-H), 124.6 (C4-ipso), 121.8 (C2-ipso), 117.1 (C7-H), 115.3 (C8-H)
3,4-HBA	UV–vis: λ/nm: 256, 288, 344, 435 IR: ν/cm^{-1}: 3288 (OH), 3034 (C—H, Phenyl), 1597 (C=N), 1586, 1518, 1493 (C=C phenyl), 1241 (C—O—C), 1279 (C—OH) ^{1}H-NMR (DMSO): δ ppm: 9.53 (s, 4H, —OH), 8.41 (s, 2H, —C*H*=N—), 7.45 (d, 2H, -Hb), 7.27 (d, 4H, -Hd, -Hd′), 7.21 (s, 2H, -Hc), 7.05 (d, 4H, -He, He′), 6.88 (d, 2H, -Ha) ^{13}C-NMR (DMSO): ppm: 159.96 (C7-H), 155.16 (C11-ipso), 149.64 (C1-ipso), 147.77 (C6-ipso), 146.14 (C8-ipso), 128.55 (C4-ipso), 125.08 (C3-H), 122.92 (C9-H), 119.66 (C10-H), 115.98 (C2-H), 114.58 (C5-H)

TABLE IV *Continued*

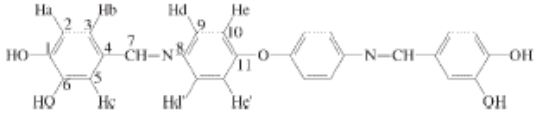
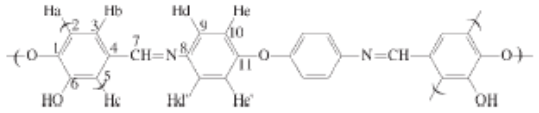
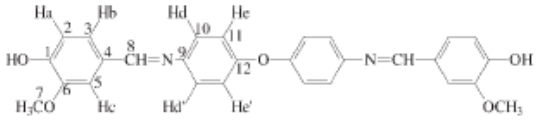
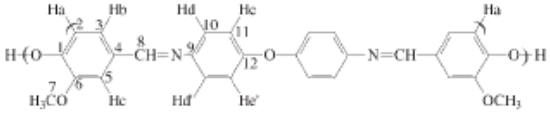
Compound	Spectral data
	
P-3,4-HBA	UV–vis: λ/nm: 259, 341, 444 IR: ν/cm^{-1}: 3378 (OH), 3071 (C−H, Phenyl), 1587 (C=N), 1492, 1449 (C=C phenyl), 1229, 1212 (C−O−C), 1289 (C−OH) ^{1}H-NMR (DMSO): δ ppm: 9.29 (s, −OH), 8.41 (s, 2H, −*CH*=N−), 7.39 (d, 2H, -Hb), 7.20 (d, 4H, -Hd, -Hd′), 7.06 (s, -Hc-terminal), 6.88 (d, 4H, -He, -He′), 6.69 (d, -Ha-terminal) ^{13}C-NMR (DMSO): ppm: 159.32 (C7-H), 157.20 (C11-ipso), 152.61 (C1-ipso), 149.66 (C6-ipso), 146.09 (C8-ipso), 129.32 (C4-ipso), 124.97 (C3-H), 122.67 (C2-ipso), 121.13 (C5-ipso), 119.45 (C9-H), 117.70 (C10-H)
	
HMBA	UV–vis: λ/nm: 232, 285, 339, 437 IR: ν/cm^{-1}: 3509 (OH), 3036 (C−H, Phenyl), 2984 (C−H, aliphatic), 1621 (C=N), 1601, 1509, 1493 (C=C phenyl), 1234 (C−O−C), 1273 (C−OH) ^{1}H-NMR (DMSO): δ ppm: 9.78 (s, 2H, −OH), 8.48 (s, 2H, −*CH*=N−), 7.54 (s, 2H, -Hc), 7.34 (d, 2H, -Hb), 7.28 (d, 4H, -Hd, -Hd′), 7.05 (d, 4H, -He, -He′), 6.91 (d, 2H, -Ha), 3.87 (s, 6H, −O*CH*$_3$) ^{13}C-NMR (DMSO): ppm: 159.98 (C8-H), 155.19 (C12-ipso), 150.49 (C1-ipso), 148.54 (C6-ipso), 147.76 (C9-ipso), 128.46 (C4-ipso), 124.47 (C3-H), 122.80 (C10-H), 119.67 (C11-H), 115.82 (C2-H), 110.70 (C5-H), 55.97 (C7-ipso)
	
PHMBA	UV–vis: λ/nm: 258, 270, 362 IR: ν/cm^{-1}: 3222 (OH), 3070 (C−H, Phenyl), 2932 (C−H, aliphatic), 1578 (C=N), 1563, 1495 (C=C phenyl), 1223 (C−O−C), 1280 (C−OH) ^{1}H-NMR (DMSO): δ ppm: 9.29 (s, −OH), 7.83 (s, 2H, −*CH*=N−), 7.31 (s, 2H, -Hc), 7.01 (s, 2H, -Hb), 6.93 (d, 4H, -Hd, -Hd′), 6.84 (d, 4H, -He, -He′), 6.69 (d, -Ha-terminal), 3.74 (s, 6H, −O*CH*$_3$) ^{13}C-NMR (DMSO): ppm: 158.51 (C8-H), 156.85 (C12-ipso), 155.10 (C1-ipso), 147.31 (C6-ipso), 145.48 (C9-ipso), 126.00 (C4-ipso), 124.78 (C2-ipso), 122.84 (C3-H), 121.24 (C10-H), 117.73 (C11-H), 116.20 (C5-H), 56.51 (C7-ipso)
	
2-HBA-Cu	UV–vis: λ/nm: 228, 295, 392 IR: ν/cm^{-1}: 3349 (OH), 3056 (C−H, Phenyl), 1606 (C=N), 1587, 1532, 1492 (C=C, phenyl), 1236 (C−O−C), 1296 (C−OH), 594 (Cu−O), 689 (Cu−N)
2-HBA-Co	UV–vis: λ/nm: 299, 378 IR: ν/cm^{-1}: 3337 (OH), 3053 (C−H, Phenyl), 1615 (C=N), 1568, 1502,1490 (C=C, phenyl), 1238 (C−O−C), 1282 (C−OH), 587 (Cu−O), 652 (Cu−N)
P-2-HBA-Cu	UV–vis: λ/nm: 299, 402 IR: ν/cm^{-1}: 3403 (OH), 3056 (C−H, Phenyl), 1606 (C=N), 1587, 1532, 1492 (C=C phenyl), 1236 (C−O−C), 1298 (C−OH), 594 (Co−O), 616 (Co−N)
P-2-HBA-Co	UV–vis: λ/nm: 258, 298, 387 IR: ν/cm^{-1}: 3346 (OH), 3010 (C−H, Phenyl), 1607 (C=N), 1575, 1533, 1492 (C=C phenyl), 1238 (C−O−C), 1290 (C−OH), 595 (Co−O), 664 (Co−N)

TABLE V
Thermal Degradation Values of the Synthesized Monomer, Polymer, and Monomer/Polymer-Metal Complex Compounds

Compounds	T_{on}[a]	T_{max}[b]	20% weight losses	50% weight losses	% Carbine residue at 1000°C	DTA	
						Exo	Endo
2-HBA	333	369	340	364	14.71	–	209
P-2-HBA	177, 420	260, 497	423	847	39.23	–	–
2-HBA-Cu	159, 310	219, 341, 494	264	888	46.48	–	–
2-HBA-Co	154, 379	171, 409	382	895	44.69	–	174
P-2-HBA-Cu	159, 313	198, 348, 511	336	548	40.03	–	–
P-2-HBA-Co	307	340, 506	486	653	29.71	–	–
4-HBA	251	269, 434	441	–	60.43	–	247
P-4-HBA	140, 310	172, 342, 530	433	925	43.92	–	–
3,4-HBA	218	232, 302, 447	382	–	53.70	228	218
P-3,4-HBA	257	354, 453	417	954	49.00	–	–
HMBA	269	301	315	–	51.30	–	162
PHMBA	145	184, 486	424	981	49.72	–	–

[a] The onset temperature.
[b] Maximum weight temperature.

and oxyphenylene C—O—C coupling systems have been proposed in the literature.[23–25]

Thermal analysis

According to TGA, DTG, and DTA curves the calculated thermal degradation data were given in Table V. As seen in the Table V, the initial degradation temperature (°C) and the carbine residue (%) at 1000°C are 333 and 14.71 for 2-HBA, 177, 420, and 39.23 for P-2-HBA, 159, 310, and 46.48 for 2-HBA-Cu, 154, 379, and 44.69 for 2-HBA-Co, 159, 313, and 40.03 for P-2-HBA-Cu, and 307 and 29.71 for P-2-HBA-Co, respectively. According to these values P-2-HBA is more stable than 2-HBA through to temperature and thermal decomposition. Because of long conjugated bond systems, the polymer demonstrated higher resistance against high temperature than the monomer. In addition, the metal complexes have higher carbine residue at 1000°C than the monomer and polymer (except for P-2-HBA-Co). According to thermal analysis results, copper complexes were demonstrated higher thermal stability than the cobalt complexes and these results agree with the previous studies in which Schiff base derivatives of oligosalicylaldehyde were used.[18,19]

Thermal degradation data of 4-HBA, 3,4-HBA, HMBA, and their polymers were also given in Table V. Looking at these values, the initial degradation temperature (°C) and the carbine residue (%) at 1000°C are 251 and 60.43 for 4-HBA, 140, 310, and 43.92 for P-4-HBA, 218 and 53.70 for 3,4-HBA, 257 and 49.00 for P-3,4-HBA, 269 and 51.30 for HMBA, and 145 and 49.72 for PHMBA, respectively. According to these values, the oxidative polycondensation products of 4-HBA, 3,4-HBA, and HMBA are less stable than their monomers through to temperature and thermal decomposition. Although the initial degradation temperature of P-3,4-HBA is higher than 3,4-HBA, its total weight loses at 1000°C is higher. Additionally, although the weight loses of 3,4-HBA and HMBA at 1000°C are close near their polymers, the difference between the weight loses of 4-HBA and P-4-HBA is high.

As seen in the thermal decomposition ratios of the synthesized polymers at 1000°C P-2-HBA and P-4-HBA have lower thermal stabilities than P-3,4-HBA and PHMBA. This is owing to the more C—O—C coupling of P-2-HBA and P-4-HBA, as mentioned earlier. This etheric bond makes the structure unstable. Also, due to this weak bond, P-4-HBA has lower thermal stability than its monomer.

According to thermal degradation values, the synthesized polymers and their copper and cobalt complexes are also more stable than the previously presented oligophenol derivatives and metal complex compounds.[16–19]

Electrical conductivities

Electrical conductivities of the synthesized polymers and the metal complexes and the changes of these values related to doping time with iodine were determined and shown in Table VI. The changes of the electrical conductivities are also given schematically in Figure 1(a) (for polymers) and Figure 1(b) (for the metal complexes). As seen in Table VI, the initial conductivities of the synthesized polymers and the metal complex compounds are quite near at about 10^{-11}–10^{-10} S cm^{-1}. When doped with iodine for 168 h, the conductivities of P-2-HBA, P-4-HBA, and P-3,4-HBA could be increased by about three orders of magnitude (up to 10^{-7} S cm^{-1}, see Fig. 1). But the conductivity of PHMBA could be increased

TABLE VI
Electrical Conductivity of I_2-Doped Synthesized Monomer, Polymer, and Monomer/Polymer-Metal Complex Compounds vs. Doping Time at 25°C

Doping time (h)	Conductivity (S cm^{-1}) × 10^{-10}							
	P-2-HBA	P-4-HBA	P-3,4-HBA	PHMBA	2-HBA-Cu	2-HBA-Co	P-2-HBA-Cu	P-2-HBA-Co
0	1.4142	1.2584	1.2643	1.3207	1.5056	1.3999	1.4517	1.4710
24	16.109	35.138	236.46	5.3728	81.179	2778.2	54.753	650.17
48	53.091	345.90	1211.6	28.718	6323.7	33361	854.96	3360.1
72	141.96	806.15	2278.3	44.926	26108	105018	5118.9	119018
96	435.48	1351.6	2910.2	47.201	33002	124043	26425	142261
120	1197.3	2090.9	3058.1	51.744	38694	130673	38911	163934
144	3114.3	3126.9	3141.4	54.318	44097	133021	52083	172005
168	5788.2	4159.8	3198.2	55.520	48782	134941	61225	182301

only up to about 10^{-9} S cm^{-1}. This is due to the steric barrier of $-OCH_3$ group, to prevent the complexation of iodine ions with imine nitrogen and so doping procedure does not occur adequately. The conductivities of the metal complex compounds also increased by about five orders of magnitude [up to 10^{-5} S cm^{-1}, see Fig. 1(b)] with doping time. According to these results, the synthesized polymers have higher initial and maximal conductivities than the previous studies.[26] In the doping of the polymers and the metal complexes with iodine, it was found that the conductivities firstly increase greatly with doping time, but then tend to level-off. For P-2-HBA only the changes of the conductivity is nearly linear [see Fig. 1(a)]. The increasing conductivity could indicate that a charge-transfer complex between the polymers (or metal complexes) and dopant iodine is continuously formed. Consequently, Figure 1 not only shows the conductivity and doping time relationship but also indicate how quickly the doping reaction takes place. The experimental results showed that a longer doping time is needed to obtain the maximal conductivity. As a result, the conductivity/doping time curves vary with doping conditions. To exclude the influence of doping conditions, the conductivities of the doped polymers and complexes have been related with doping extent (shown in Fig. 1). Nitrogen is a very electronegative element and it is capable of coordinating with iodine ions. On the nitrogen atom, coordination of iodine ions with Schiff base polymers and pyridine solutions had been suggested in the literatures.[27–30]

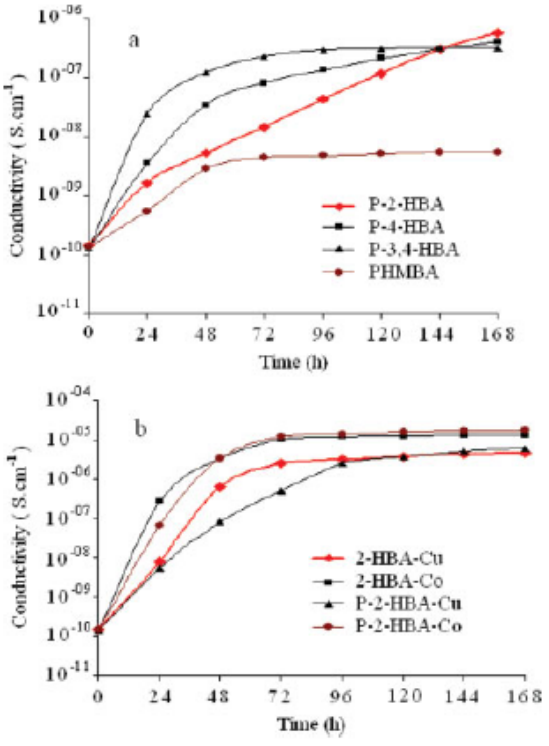


Figure 1 Electrical conductivity of I_2-doped a = [P-2-HBA, P-4-HBA, P-3,4-HBA, and PHMBA] and b = [2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co] versus doping time at 25°C. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Optical properties

The absorption spectra of 2-HBA, 4-HBA, P-2-HBA, and P-4-HBA recorded by using methanol and DMSO for the monomers and polymers, respectively, were shown in Figure 2(a). λ_{max} and the optical band gaps values were calculated as in the literature[31] and shown in Table VII. As seen in Table VII, λ_{max} (nm) and the optical band gaps (E_g, eV) are 352 and 3.15 for 2-HBA, 470 and 2.06 for P-2-HBA, 336 and 3.23 for 4-HBA, and 332 and 3.02 for P-4-HBA, respectively. The absorption spectra of 3,4-HBA, P-3,4-HBA, HMBA, and PHMBA were also recorded and shown in Figure 2(b). The calculated λ_{max} and the optical band gaps were given in Table VII. According to these values, λ_{max} (nm) and the optical band gaps values (E_g/eV) of 3,4-HBA, P-3,4-HBA, HMBA, and PHMBA are 435 and 2.61, 44, and

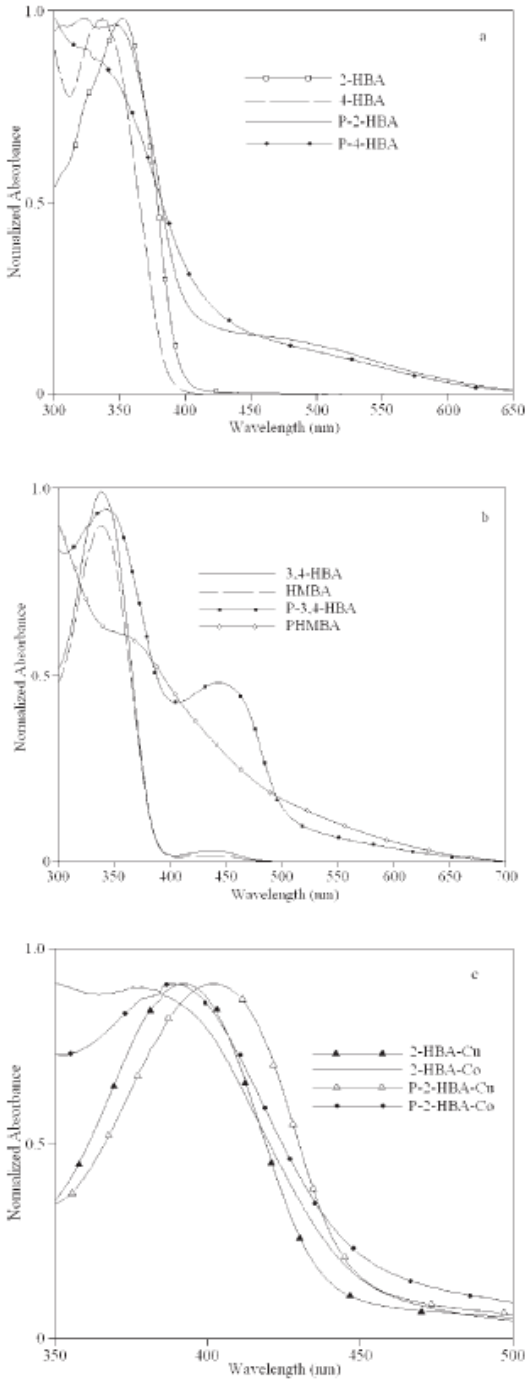


Figure 2 Absorption spectra of a = [2-HBA, 4-HBA, P-2-HBA, and P-4-HBA], b = [3,4-HBA, HMBA, P-3,4-HBA, and PHMBA], and c = [2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co].

TABLE VII
λ_{max} and Optical Band Gap (E_g) Values of Synthesized Compounds Calculated from Absorption Spectra

Compounds	λ_{max} (nm)	E_g (eV)
2-HBA	352	3.15
P-2-HBA	470	2.06
2-HBA-Cu	392	2.83
2-HBA-Co	378	2.77
P-2-HBA-Cu	402	2.78
P-2-HBA-Co	387	2.78
4-HBA	336	3.23
P-4-HBA	332	3.02
3,4-HBA	435	2.61
P-3,4-HBA	444	2.47
HMBA	437	2.64
PHMBA	362	2.42

2.47, 437, and 2.64 and 362 and 2.42, respectively. The oxidative polycondensation products of 2-HBA, 4-HBA, 3,4-HBA, and HMBA have lower band gaps than their monomers due to their polyconjugated structures. The absorption spectra of 2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co were recorded by using DMSO and shown in Figure 2(c). The calculated λ_{max} and the optical band gaps from Figure 2(c) were also given in Table VII. According to these values, λ_{max} (nm) and the optical band gaps values (E_g/eV) of 2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co are 392 and 2.83, 378 and 2.77, 402 and 2.78, and 387 and 2.78, respectively.

CONCLUSIONS

Novel Schiff base monomers abbreviated as 2-HBA, 4-HBA, 3,4-HBA, and HMBA were synthesized and converted to their polycondensation products shown as P-2-HBA, P-4-HBA, P-3,4-HBA, and PHMBA, respectively, via oxidative polycondensation reaction. The integration areas of the —OH protons in the ^{1}H NMR spectra demonstrated that the 2-HBA and 4-HBA mainly polymerized with C—O—C coupling, whereas 3,4-HBA and HMBA mainly polymerized with C—C coupling. This suggestion is also the reason of thermal stability values of the polymers. Highly C—C coupling makes P-3,4-HBA and PHMBA more thermally stable than the others. These polymers were found to have carbine residue of 49–50% at 1000°C. Solubility tests showed that the synthesized polymers are completely soluble in DMF, DMSO, and H_2SO_4. Also, according to SEC analysis, P-3,4-HBA and PHMBA have quite higher molecular weights than the others. Electrical conductivities of the synthesized polymers versus doping time with iodine ions were also measured, and these results showed that the synthesized polymers have higher initial and maximal conductivities than the previous oligophenol derivatives (except PHMBA,

because of barrier effect of methoxy groups). 2-HBA and P-2-HBA metal complexes shown as 2-HBA-Cu, 2-HBA-Co, P-2-HBA-Cu, and P-2-HBA-Co were also synthesized and with doping with iodine their conductivities were found to reach up to 10^{-5} S cm^{-1} in cobalt complexes and up to 10^{-6} S cm^{-1} in copper complexes. Consequently, the electrical conductivity measurements showed that the synthesized polymers and the metal complexes are semiconductors and their conductivities would be increased considerably via doping with iodine. The optical band gap values of the polymers were found to be higher than their monomers. This is because of the polyconjugated structures of the polymers. The observed band gaps are sufficiently low to make these polymers and metal complexes highly promising for electronic and optoelectronic applications.

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Synthesis, characterization, thermal stability, conductivity and band gaps of monomer and oligo-4-[(thien-2-yl-methylene)amino] phenol

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Abstract: In this study, the oxidative polycondensation reaction conditions of 4-[(thien-2-yl-methylene) amino] phenol (4-TMAP) by using oxidants such as air O_2, H_2O_2 and NaOCl were studied in an aqueous alkaline medium between 313 and 363 °K. The structures of the synthesized monomer and oligomer were confirmed by FT-IR, UV-vis, NMR and elemental analysis. The characterization was made by TG-DTA, size exclusion chromatography (SEC) and solubility tests. At the optimum reaction conditions, the yield of oligo-4-[(thien-2-yl-methylene) amino] phenol (O-4-TMAP) was found to be 36% for air O_2 oxidant, 40% for H_2O_2 oxidant and 47% for NaOCl oxidant. According to TG analysis, the weight losses of 4-TMAP and O-4-TMAP were found to be 58.11% and 51.38% at 1273°K, respectively. O-4-TMAP was shown higher stability against thermal decomposition. Also, electrical conductivity of the O-4-TMAP was measured, showing that the polymer is a typical semiconductor. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and electrochemical energy gaps ($E_g^{'}$) of 4-TMAP and O-4-TMAP were found to be -6.13, -6.02; -2.72, -2.69; 3.41 and 3.33 eV, respectively.

Key words: Oxidative polycondensation, oligo-4-[(thien-2-yl-methylene) amino] phenol, thermal analysis, conductivity and band gap.

Introduction

The polyazomethine polymers attracted attention in the early 1960 [1] as new semi-conducting materials. The polyazomethine which included azomethine (-CH=N) and active hydroxyl (-OH) groups have been used in various fields. They have useful properties such as paramagnetism, electrochemical cell and resistance to high energy. Because of these properties, they were used to prepare the composites with resistance to high temperature and graphite materials, epoxy oligomer and block copolymers adhesives, photoresists and antistatic materials [2-8]. Research interest in poly-Schiff bases (polyazomethines) continues owing to their different characteristics such as chelating properties [9], thermal stability [10], liquid crystal properties [11], as well as intrinsic conductivity [12], etc. Recently, it was reported that the electrical conductivity of conjugated poly-Schiff bases may be increased by about eight orders of magnitude (up to the level of semiconductors) when they are doped by iodine and such doped materials has good stability, electro activity and electro conductivity [13-15].

However, it was also found that they are neither soluble (inorganic solvents) nor meltable due to their rigid polymer chains and strong intermolecular forces, which greatly obstruct the characterization and processing of the polymers. The halogen and sulphur derivatives of oligophenols were used to prepare the composite materials enduring to flame of the specific detergents such as lead storing battery cathodes [16]. These compounds yielded new properties by adding other functional groups to their structures. Because of azomethine (–C=N) and hydroxyl (–OH) groups, these type oligomers may be used as an anti-microbial agent [17]. Also, due to these groups, azomethine polymers have the capability of coordination with different metal ions and they can be used for cleaning of poisonous heavy metals in industrial waste waters. Therefore, the synthesis of oligomer-metal complexes is very important for analytic and environmental chemistry. It seemed advantageous to attempt to design and prepare a polymer-bound chelating ligand, which would be able to form complexes with a variety of transition metals and therefore have a large range of applications [18].

In this paper, we have investigated the effects of different parameters such as temperature, reaction time and initial concentration of NaOCl and H_2O_2 for the oligo-4-[(thien-2-yl-methylene)amino] phenol (O-4-TMAP) synthesis. We have characterized 4-TMAP and O-4-TMAP by using FT-IR, UV-vis, ^{1}H-^{13}C-NMR, elemental analysis, TG-DTA and SEC techniques. The electrical conductivity of the polymer was measured by four-point probe technique after doping with I_2 at room temperature and atmospheric pressure. Also, HOMO, LUMO energy levels and electrochemical band gaps of the monomer and oligomer were measured with cyclic voltammetry.

Results and Discussion

The Investigation of synthesis conditions of O-4-TMAP

4-[(Thien-2-yl-methylene) amino] phenol was oxidized in an aqueous alkaline medium by air O_2, H_2O_2 (30% aqueous solution), and NaOCl (30% aqueous solution). In the aqueous alkaline medium, when 4-TMAP interacted with oxidants such as air O_2, H_2O_2 and NaOCl, it immediately precipitated phenoxy radicals in brown. The conditions of oxidative polycondensation reaction of 4-TMAP with 30% NaOCl solution in an aqueous alkaline medium are given in Table 1. The yield of O-4-TMAP was 24% at the NaOCl medium for 10 h at 313 °K. As seen from Table 1, the yield of products increased by increasing of temperature (except for 363 °K). The yield of O-4-TMAP was 47% at the reaction conditions such as $[NaOCl]_0$=0.261 and $[4\text{-TMAP}]_0 = [KOH]_0$ =0.0714 mol/L at 353 °K for 20 h. At the same conditions, when molar amount of alkaline increased, total yield of O-4-TMAP changed from 35% to 40% (see Table 1, Sample No 2 and 4).

The oxidative polycondensation reaction conditions of 4-TMAP with 30% H_2O_2 solution in an aqueous alkaline medium are given in Table 1. The yield of O-4-TMAP was 40% at optimum conditions such as $[4\text{-TMAP}]_0 = [KOH]_0$ =0.0714 and $[H_2O_2]_0$= 0.07 mol/L, at 353 °K for 3 h. At the same conditions, when molar amount of alkaline increased, total yield of O-4-TMAP changed from 40% to 34%. The yield of O-4-TMAP was 15% at the reaction conditions such as $[4\text{-TMAP}]_0 = [KOH]_0$= 0.0714 and $[H_2O_2]_0$=0.14 mol/L at 353 °K for 3 h. According to these values, yield of O-4-TMAP increased with increase in reaction temperatures (except for 363 °K). At the oxidative

polycondensation reaction of 4-TMAP, when air O_2 passed into 8.5 L/h rate at the reaction medium at 333 °K, the yield of product was 24%.

Tab. 1. The oxidative polycondensation reaction parameters of 4-[(thien-2-yl-methylene)amino] phenol[a] with NaOCl (sample number: 1–10) and H_2O_2 (sample number: 11–20) in aqueous KOH.

Sample No	Temp., (°K)	Times (h)	$[KOH]_0$ (mol L^{-1})	$[NaOCl]_o$ /$[H_2O_2]_o$ (mol L^{-1})	%, yield of O-4-TMAP
1	363	3	0.0714	0.261	22
2	353	3	0.0714	0.261	35
3	353	3	0.1428	0.261	24
4	353	3	0.0714	0.522	40
5	353	10	0.0714	0.261	37
6	353	20	0.0714	0.261	47
7	343	3	0.0714	0.261	34
8	333	3	0.0714	0.261	32
9	323	3	0.0714	0.261	25
10	313	3	0.0714	0.261	24
11	363	3	0.0714	0.07	26
12	353	3	0.0714	0.07	40
13	353	3	0.1428	0.07	34
14	353	3	0.0714	0.14	15
15	353	10	0.0714	0.07	28
16	353	20	0.0714	0.07	27
17	343	3	0.0714	0.07	16
18	333	3	0.0714	0.07	13
19	323	3	0.0714	0.07	16
20	313	3	0.0714	0.07	13

a= The initial concentration of 4-TMAP was used as 0.0714 mol L^{-1}.

The yield of O-4-TMAP was 36% at optimum conditions such as $[4\text{-TMAP}]_0$= $[KOH]_0$ = 0.0714 mol/L at 343 °K for 10 h. The various conditions for O-4-TMAP are given in Table 2. As is seen from Table 1 and 2, in these reactions the yield of the oligomer was dependent upon temperature, times and initial concentrations of alkaline and oxidants. At the same conditions, the yield of O-4-TMAP was about the same for all oxidants.

Structure of O-4-TMAP

According to SEC chromatograms, the values of number-average molecular weight (M_n) and weight-average molecular weight (M_w) of O-4-TMAP were calculated according to a Polystyrene standard calibration curve and are given in Table 3. According to the SEC analysis, the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of O-4-TMAP were found to be 3680, 7450 g mol^{-1} and 2.024, using H_2O_2, and 2400, 6900 g mol^{-1} and 2.875, using air O_2 and 3700, 4260 g mol^{-1} and 1.151, using NaOCl, respectively.

Tab. 2. The oxidative polycondensation reaction parameters of 4-[(thien-2-yl-methylene)amino] phenol[a] with air O_2 (sample number: 1–9) and non oxidant (sample number: 10–21) in aqueous KOH.

Sample No	Temp., (^oK)	Times (h)	$[KOH]_0$ (mol L^{-1})	Air O_2 (L h^{-1})	%, yield of O-4-TMAP
1	363	3	0.0714	8.5	27
2	353	3	0.0714	8.5	29
3	343	3	0.0714	8.5	35
4	343	3	0.1428	8.5	29
5	343	10	0.0714	8.5	36
6	343	20	0.0714	8.5	32
7	333	3	0.0714	8.5	24
8	323	3	0.0714	8.5	11
9	313	3	0.0714	8.5	24
10	313	3	0.0714	-	56
11	313	3	0.0714	-	46
12	333	3	0.1428	-	26
13	343	3	0.0714	-	37
14	353	3	0.0714	-	29
15	363	3	0.0714	-	27
16	313	1	0.0714	-	67
17	313	1	0.134	-	30
18	313	5	0.0714	-	52
19	313	10	0.0714	-	20
20	313	15	0.0714	-	26
21	313	20	0.0714	-	29

a= The initial concentration of 4-TMAP was used as 0.0714 mol L^{-1}.

Tab. 3. The number average molecular weight (M_n), mass average molecular weight (M_w), polydispersity index (PDI) and % values of oxidative polycondensation products of O-4-TMAP.

	Molecular weight distribution parameters														
	Total			Fraction I				Fraction II				Fraction III			
Compounds	M_n	M_w	PDI	M_n	M_w	PDI	%	M_n	M_w	PDI	%	M_n	M_w	PDI	%
O-4-TMAP[1]	2400	6900	2.875	2030	2470	1.217	80	2320	2830	1.220	5	36150	8400	2.324	15
O-4-TMAP[2]	3700	4260	1.151	1920	2280	1.154	70	2120	2865	1.351	5	38500	44200	1.148	25
O-4-TMAP[3]	3680	7450	2.024	1980	2440	1.175	65	2150	2850	1.326	5	32150	68730	2.138	30

1= Air O_2 oxidant; 2= NaOCl oxidant 3= H_2O_2 oxidant

The UV-vis spectra of 4-TMAP and O-4-TMAP were similar to one together. However, at the spectra of 4-TMAP, K bands of phenol and C_6H_5-N= were observed in 235 nm and 269 nm, respectively. Benzene band of 4-TMAP and strength R band

of -CH=N- groups were observed in 292 and 345 nm, respectively. λ_{max} values of O-4-TMAP were observed in 205, 232, 280 and 360. UV-vis spectra of O-4-TMAP, K and R bands were observed in 280 nm and 360 nm, respectively. The shifting of the -CH=N- group band from 345 nm to 360 nm has been demonstrated for the formation of the oligomeric conjugate π electron system. The FT-IR spectra of oxidative polycondensation product of 4-[(thien-2-yl-methylene)amino] phenol are only different by reduction of band strength and peak numbers from the FT-IR spectra of 4-TMAP. In the FT-IR spectra of 4-TMAP and O-4-TMAP, bands of –OH and –CH=N groups were observed in 3135 and 1610 cm^{-1}; 3288 and 1606 cm^{-1}, respectively. In order to identify the structures of monomer and oligomer, the ^{1}H-NMR spectra were recorded in DMSO-d_6. ^{1}H-NMR and ^{13}C-NMR spectra of the 4-TMAP are given in Figures 1 and 2, respectively. At the ^{1}H-NMR spectra of 4-TMAP and O-4-TMAP, the signals of –OH and –CH=N groups were observed in 9.52 and 8.75 ppm and 9.64 and 9.16 ppm, respectively. Because of C-C coupling system, a new peak was observed in 5.57 ppm at the ^{1}H-NMR spectra of oligomer. According to ^{1}H-NMR spectra results, the shifting to down field of signals of –OH and –CH=N groups is demonstration of formation of conjugate π-bond systems. The ^{1}H- ^{13}C-NMR spectra results of the O-4-TMAP (Figures 3 and 4) confirm the formation of oligomer units.

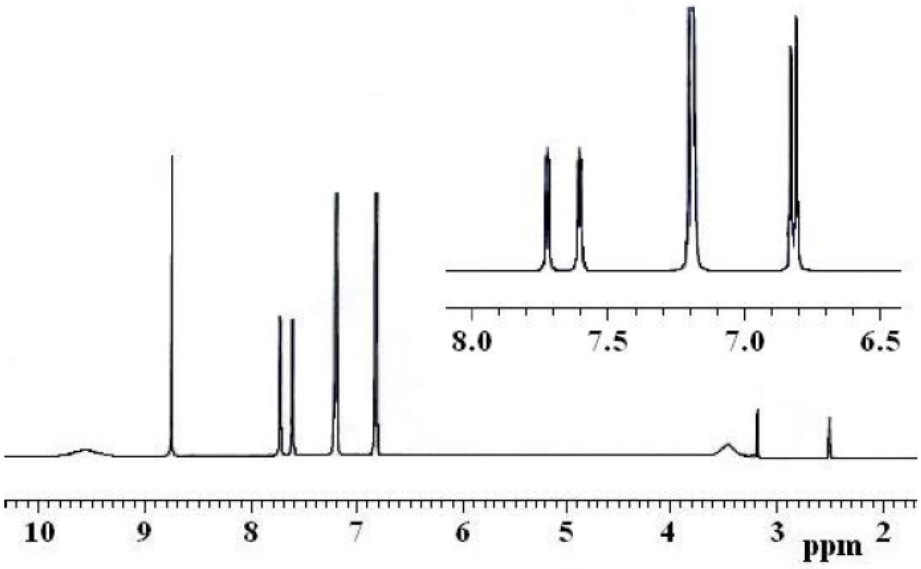


Fig. 1. ^{1}H-NMR spectrum of 4-[(thien-2-yl-methylene)amino] phenol.

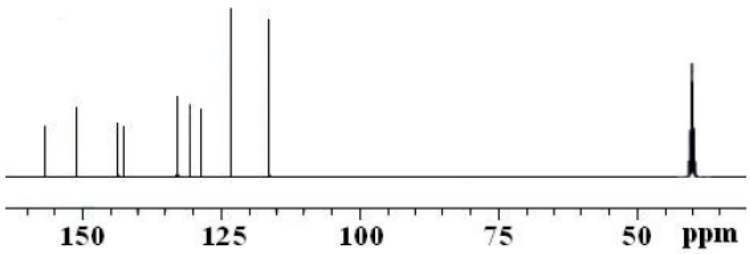


Fig. 2. ^{13}C-NMR spectrum of 4-[(thien-2-yl-methylene)amino] phenol.

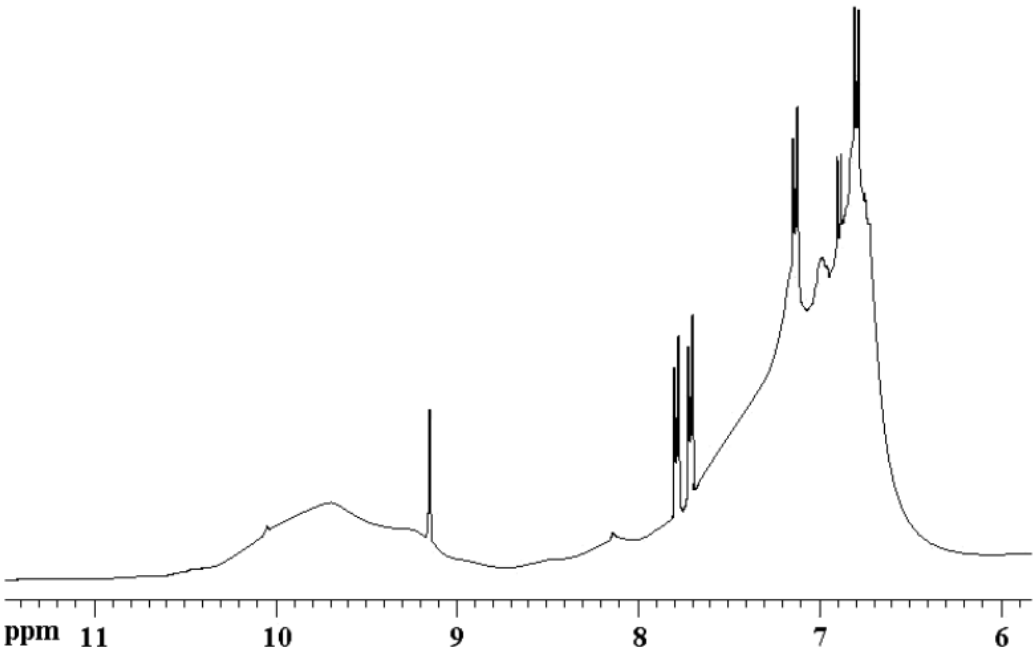


Fig. 3. ^{1}H-NMR spectrum of oligo-4-[(thien-2-yl-methylene) amino] phenol.

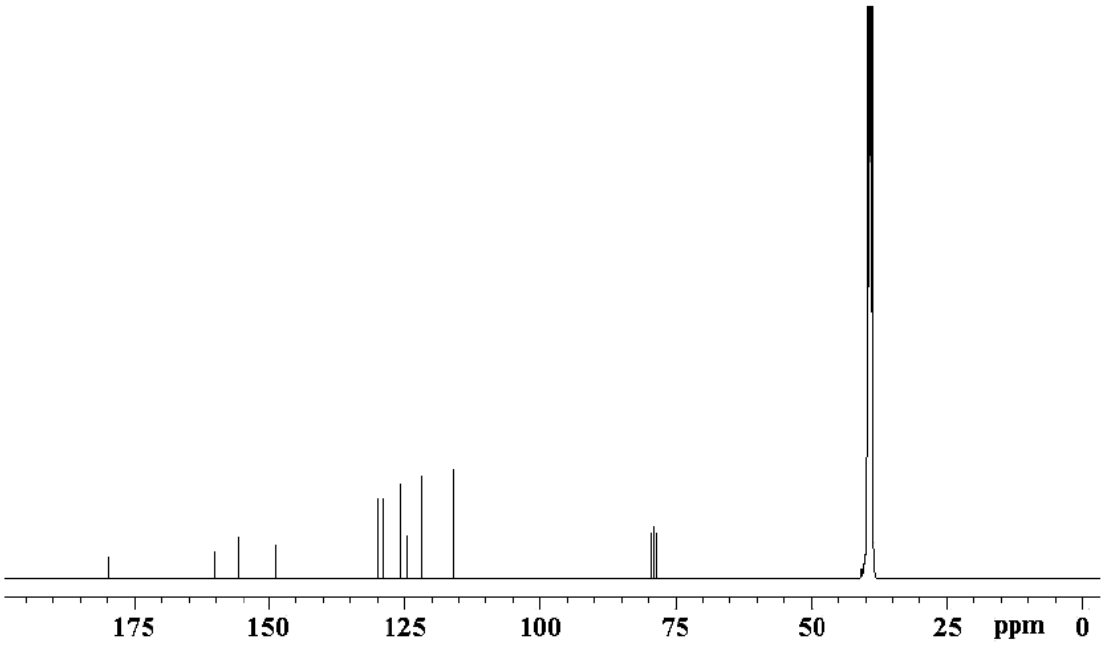
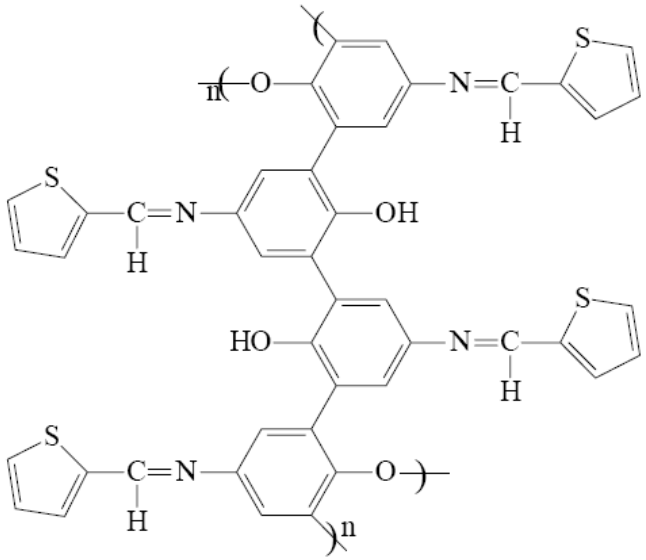


Fig. 4. ^{13}C-NMR spectrum of oligo-4-[(thien-2-yl-methylene) amino] phenol.

Other phenol derivatives were also polymerized, and the results have been reported in the literature [20]. Cross-linking in oligomer structure is expected in those cases where the *ortho* positions in the corresponding monomer structure are unsubstituted. ^{13}C-NMR studies on O-4-TMAP indicate that the linkage between any two adjacent phenyl rings is largely at *ortho* positions. However, this type of linkage may strain the oligomer backbone in such a manner that the phenyl rings are out of plane with

respect to the adjacent rings. The peak values for C2,6 were observed in 116.24 ppm in the monomer and 124.64 ppm in the oligomer, respectively.



Scheme 1. Structure of O-4-TMAP.

The oxyphenylene are involved in the formation of free radicals leading to oligomer formation and they appear to be involved in bond formation. Thus the phenyl rings in the oligomer appears to be linked primarily at *ortho* positions of oxyphenylene. The ^{1}H-NMR and ^{13}C-NMR results showed that the polymerization of 4-TMAP proceeded by C-C and C-O-C coupling from *ortho* positions according to –OH group and oxyphenylene, respectively [21]. According to spectral analyses, a segment of O-4-TMAP chain can be formulated as follows (Scheme 1).

Thermal analyses of 4-TMAP and O-4-TMAP

TG-DTG-DTA curves of monomer and oligomer are given in Fig. 5 and 6. The initial degradation temperature, 50% and 58.11% weight loss of 4-TMAP was found to be 492, 871 and 1273 °K, respectively. According to DTA analysis, endothermic and exothermic peaks were observed in 475 and 529°K, respectively. According to DTG curve, T_{max} value of 4-TMAP was 516 °K. The initial degradation temperature, 50% and 51.38% weight loss of O-4-TMAP was found to be 465, 980 and 1273 °K, respectively. According to TGA curve, thermal degradation of O-4-TMAP occurred in one step and it weight loss was found as 51.38% between 423-1273 °K. Because of C-O-C coupling formation, initial degradation temperature of oligomer was lower than monomer from TGA measurements. This result C-O-C bond has degraded at lower temperature than C-C bond. Because of long conjugated band systems, oligomer demonstrated higher resistance against high temperature than monomer. According to DTG and DTA curves, exothermic peak and T_{max} value of O-4-TMAP was 703 and 817 °K, respectively. According to TG analysis, although initial degradation temperature of O-4-TMAP was lower than monomer, it was more stable than monomer to temperature and thermal decomposition because carbines residue was formed at high amounts such as 48.62% at 1273 °K. The presence of water can be seen in TGA curve of oligomer (Fig. 6), showing between 7.75% wt losses in the

323-423 °K and 323-463 °K range, respectively, and corresponding to the loss of water of crystallization (323-423 °K) and coordination water (323-473 °K) [22].

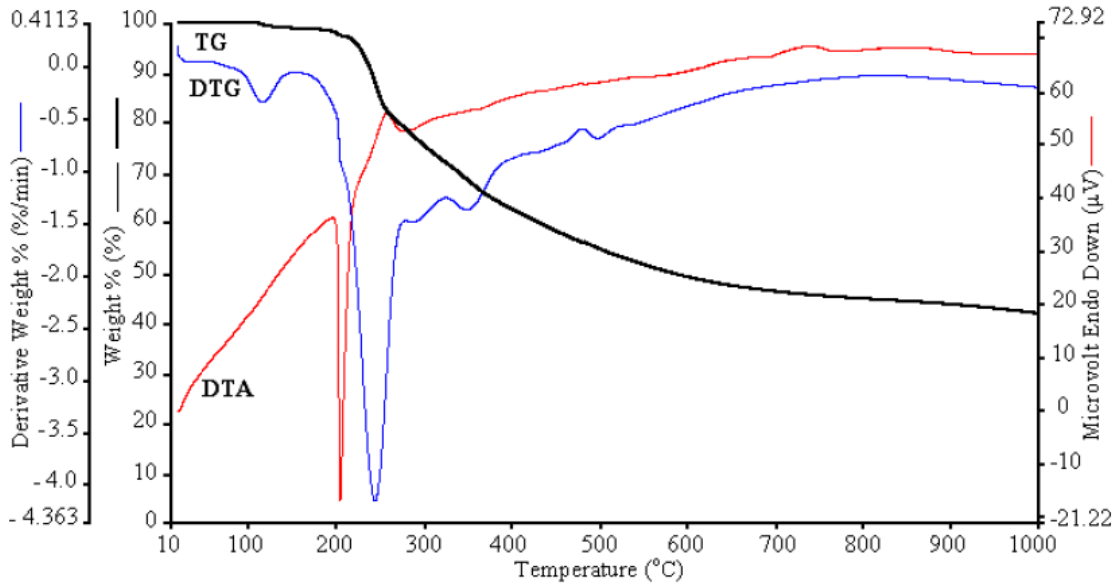


Fig. 5. TG-DTG-DTA curves of 4-[(thien-2-yl-methylene) amino] phenol.

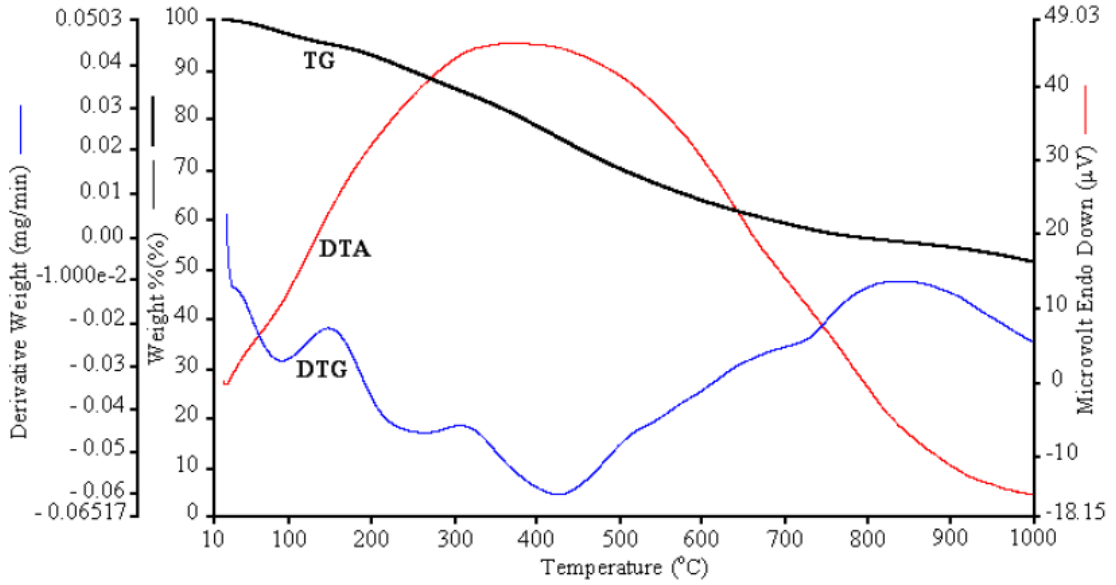


Fig. 6. TG-DTG-DTA curves of oligo-4-[(thien-2-yl-methylene) amino] phenol.

Electrochemical Properties of 4-TMAP and O-4-TMAP

The voltammetric measurements of 4-TMAP and O-4-TMAP were carried out in acetonitrile and DMSO, respectively. The HOMO, LUMO energy levels and electrochemical energy gaps ($E_g^{'}$) were calculated from oxidation and reduction onset values [21] and are shown in Figure 7. The HOMO, LUMO energy levels and

electrochemical band gaps ($E_g^{'}$) of 4-TMAP and O-4-TMAP were found to be -6.13, -6.02; -2.72, -2.69; 3.41 and 3.33 eV, respectively.

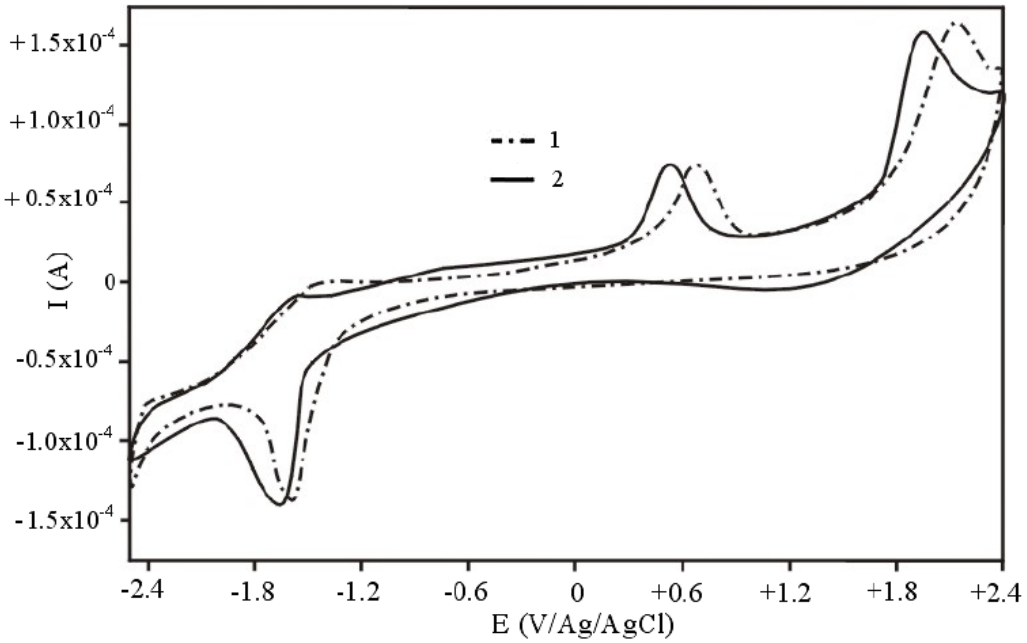


Fig. 7. Cyclic voltammograms of 4-TMAP (1) and O-4-TMAP (2).

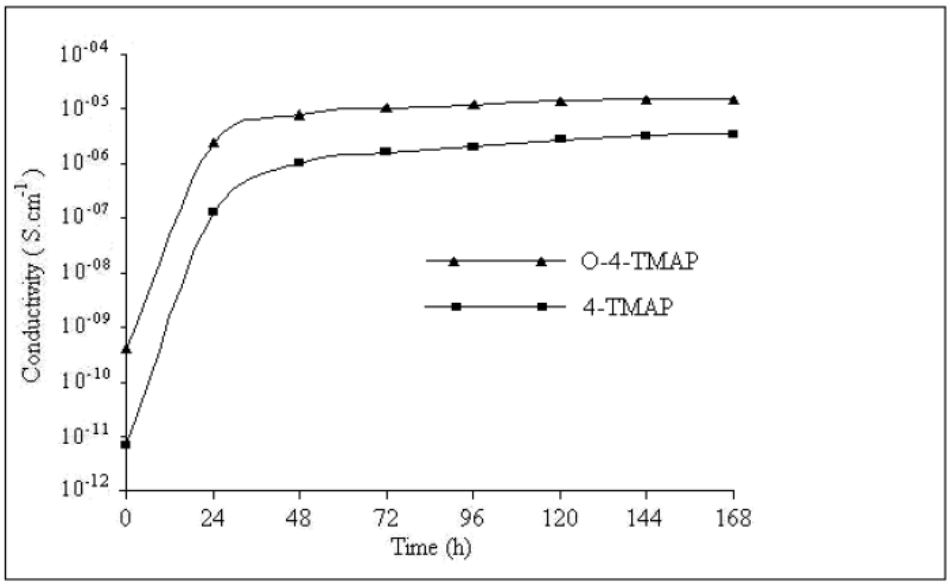
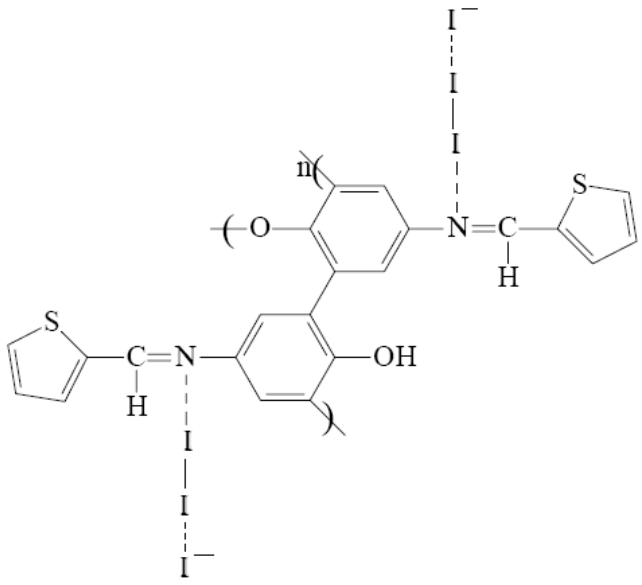


Fig. 8. Electrical conductivity of I_2-doped 4-TMAP and O-4-TMAP vs. doping time at 25°C.

The initial conductivity values (undoping with I_2) of 4-TMAP and O-4-TMAP was between 10^{-12}-10^{-11} and 10^{-10}-10^{-9} S/cm, respectively. When doped with iodine, their conductivities were increased by about four orders of magnitude (up to 10^{-4} S/cm).

Figure 8 show results of 4-TMAP and O-4-TMAP doped with iodine at various times at 25 °C. In the doping of 4-TMAP and O-4-TMAP with iodine, it was found that the conductivity of 4-TMAP and O-4-TMAP first increases greatly with doping time, but then tends to level-off. The maximum (or saturated) conductivity was 3.30 x 10^{-6} and 1.55 x 10^{-5} S/cm. The increasing conductivity could indicate that a charge-transfer complex between 4-TMAP and O-4-TMAP and dopant iodine is continuously formed. Consequently, Figures 8 not only shows the conductivity/doping time relationship but also indicates how quickly the doping reaction takes place. The experimental studies showed that a longer doping time is needed to obtain the maximum conductivity. As a result, the conductivity/doping time curve varies with doping conditions. In order to exclude the influence of doping conditions, the conductivity of doped 4-TMAP and O-4-TMAP has been related with doping extent. According to Figure 8, oligomer demonstrated higher conductivity than monomer. Nitrogen is a very electronegative element and it is capable of coordinating an iodine ions. Coordination of iodine during 4-TMAP and O-4-TMAP doping is as indicated in Scheme 2. The coordination of iodine with Schiff base polymers on the nitrogen atom and pyridine solutions has been suggested in the literature [7, 23-26].



Scheme 2. Coordination of iodine during product doping.

Conclusions

O-4-TMAP was synthesized by oxidants such as air O_2, H_2O_2 and NaOCl in an aqueous alkaline medium. The yield of O-4-TMAP was found to be 36, 40 and 47% for air O_2, H_2O_2 and NaOCl oxidants, respectively. At the oxidative polycondensation reaction of 4-TMAP, NaOCl demonstrated higher activity than H_2O_2 and air O_2. Thermal analysis results demonstrated resistance of synthesized oligomer against thermal degradation to be enough. Properties of monomer and oligomer with potential low-band gap characteristics were determined. The band gap value of monomer was higher than oligomer. This is a result of the azomethine group that is an electron-donor. This increases the HOMO more than the LUMO and therefore

lowers the band gap. The observed band gaps are sufficiently low to make these monomer and oligomer highly promising for photovoltaic applications.

Experimental

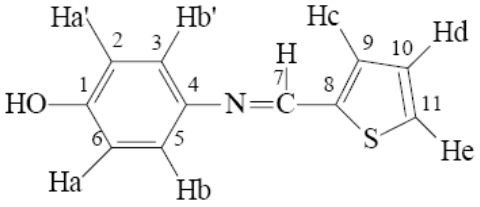
Materials

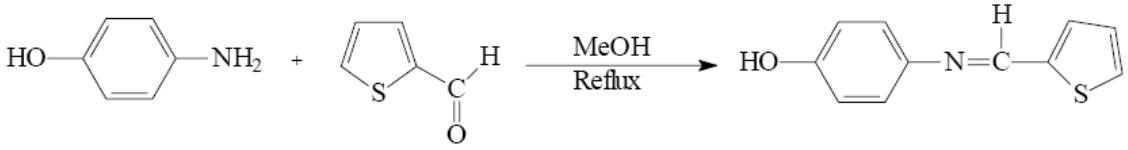
Thiophene-2-carboxyaldehyde, 4-amino phenol, dioxane, methanol, ethanol, 1-butanol, 2-propanol, acetonitrile, benzene, toluene, ethyl acetate, heptane, hexane, CCl_4, $CHCl_3$, tetrahydrofurane, THF, dimethylformamide, DMF, dimethylsulfoxide, DMSO, H_2SO_4 (98%), NaOH, H_2O_2 (30% aqueous solution), KOH and HCl (37%) were supplied from Merck Chemical Co. and they were used as received. Sodium hypo chloride (NaOCl), (30% aqueous solution) was supplied from Paksoy Chemical Co. (Turkey).

Preparation of 4-[(thien-2-yl-methylene) amino] phenol (4-TMAP)

4-TMAP was prepared by the condensation of thiophene-2-carboxyaldehyde (1.12 g, 0.01 mol) with 4-amino phenol (1.09 g, 0.01 mol) in methanol (25 ml) achieved by boiling the mixture under reflux for 3 h at 343°K (Scheme 3). The precipitated 4-[(thien-2-yl-methylene) amino] phenol was filtered, recrystallized from methanol and dried in a vacuum desiccators (yield 95%).

Calcd. for 4-TMAP: C, 70.59; H, 4.81; N, 7.49; S, 17.11. Found: C, 70.40; H, 4.65; N, 7.36; S, 16.89. FT-IR (cm^{-1}): ν (O-H) 3135 s, ν (C-H Phenyl) 3050 m, ν (C=N) 1610 s, ν (C=C phenyl) 1582, 1500, 1421 s, ν (C-O) 1226 s, ν (C-S) 708 s. ^{1}H-NMR (DMSO): δ ppm, 9.52 (s, 1H, –OH), 8.75 (s, 1H, –CH=N–), 6.82 (d, 1H, Ar-Haa'), 7.18 (d, 1H, Ar-Hbb'), 7.20 (d, 1H, -C=CHc), 7.60 (t, 1H, -C=C-Hd), 7.72 (d, 1H, -C=C-He). ^{13}C-NMR (DMSO): ppm, 156.78 (C1-ipso-OH), 116.24 (C2, 6-H), 128.56 (C3, 5-H), 143.54 (C4-ipso), 150.93 (C7-H), 142.50 (C8-ipso), 132.82 (C9-H), 122.95 (C10-H), 130.54 (C11-H).





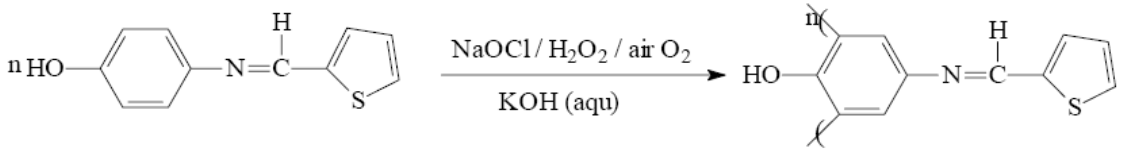
Scheme 3. Synthesis of 4-[(thien-2-yl-methylene) amino] phenol.

Synthesis of oligo-4-[(thien-2-yl-methylene) amino] phenol with NaOCl, H_2O_2, air O_2 and not oxidant in an aqueous alkaline medium

O-4-TMAP was synthesized through oxidative polycondensation of 4-[(thien-2-yl-methylene) amino] phenol with aqueous solutions of NaOCl (30%), H_2O_2 (30%) and

air O_2, respectively, [17]. The 4-TMAP (0.203 g 0.001 mol) was dissolved in an aqueous solution of KOH (10%, 0.001 mol) and placed into a 50-ml three-necked round-bottom flask (Scheme 2). It was fitted with a condenser, thermometer, stirrer and an addition funnel containing NaOCl or H_2O_2. After heating to room temperature, NaOCl and H_2O_2 were added drop by drop over about 20 min. The reaction mixtures were stirred at various temperatures and durations (Table 1 and 2). Air was passed into an aqueous solution of KOH (20%) before being sent through the reaction tube to prevent water loss in the reaction mixture and to neutralize CO_2 in the air (Scheme 4). The reaction mixtures were cooled to room temperature, and then 0.001 mol HCl (37%) was added. For the separation of mineral salts and unreacted monomer, the mixture was filtered and washed with hot water (3 x 25 ml) and then dried in a vacuum oven at 333°K.

Calcd. for O-4-TMAP: C, 71.35; H, 3.78; N, 7.57; S, 17.30. Found: C, 71.03; H, 3.90; N, 7.20; S, 17.00. FT-IR (cm^{-1}): ν (O-H) 3288 s, ν (C-H Phenyl) 3070 m, ν (C=N) 1606 s, ν (C=C phenyl) 1565, 1508, 1493s, ν (C-O) 1275 s, ν (C-S) 713 s. ^{1}H-NMR (DMSO): δ ppm, 9.64 (s, 1H,–OH), 9.16 (s, 1H, –CH=N–), 6.87 (terminal protons, d, 2H, Ar-Haa'), 7.15 (d, 2H, Ar-Hbb'), 6.93 (d, 1H, -C=CHc), 7.64 (t, 1H, -C=C-Hd), 7.72 (d, 1H, -C=C-He). ^{13}C-NMR (DMSO): ppm, 179.50 (C1-ipso-OH), 115.69 (C2, 6-H, terminal), 124.64 (C2, 6-ipso), 125.72 (C3, 5-H), 156.00 (C4-ipso), 160.25 (C7-H), 148.25 (C8-ipso), 130.22 (C9-H), 121.70 (C10-H), 129.36 (C11-H).



Scheme 4. Synthesis of oligo-4-[(thien-2-yl-methylene) amino] phenol.

Electrical Properties

Conductivity was measured on a Keithley 2400 Electrometer. The pellets were pressed on hydraulic press developing up to 1687.2 kg/cm^2. Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in desiccators [7].

Electrochemical Properties

Cyclic voltammetry (CV) measurements were carried out with a CH instruments 660C Electrochemical Analyzer at a potential scan rate of 20 mV/s. All the experiments were performed in dry box under Ar atmosphere at room temperature. The electrochemical potential of Ag was calibrated with respect to the ferrocene/ferrocenium (Fc/Fc^+) couple. The half-wave potential ($E^{1/2}$) of (Fc/Fc^+) measured in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) acetonitrile solution is 0.39 V vs. Ag wire or 0.38 V vs. supported calomel electrode (SCE). The voltammetric measurements were carried out for 4-TMAP and O-4-TMAP in acetonitrile and DMSO, respectively [19]. The HOMO, LUMO energy levels and electrochemical energy gaps ($E_g^{'}$) were calculated from oxidation and reduction onset values.

Solubility and Characterization Techniques

O-4-TMAP was dark brown at powder forms and it was completely soluble in organic solvents such as methanol, DMF, DMSO, aqueous alkaline and conc. H_2SO_4. O-4-TMAP was insoluble in ethanol, 1-butanol, 2-propanol, heptane, hexane, benzene, toluene, ethyl methyl ketone, ethyl acetate, acetonitrile, $CHCl_3$, CCl_4 and dioxane. The solubility tests were done by using 1 mg sample and 1 ml solvent at 298 °K.

Ultraviolet-visible (UV-vis) and the infrared spectra were measured by Perkin Elmer FT-IR Spectrum One and Perkin Elmer Lambda 25, respectively. The FT-IR spectra were recorded using universal ATR sampling accessory (4000-550 cm^{-1}). UV-vis spectra of 4-TMAP and O-4-TMAP were determined by using methanol and DMSO. Elemental analysis was carried out with a Carlo Erba 1106. 4-TMAP and O-4-TMAP were characterized by using ^{1}H and ^{13}C-NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) and recorded at 298 °K by using deuterated DMSO as solvent. Tetramethylsilane was used as internal standard. Thermal data were obtained by using Perkin Elmer Diamond Thermal Analysis. The TG-DTA measurements were made between 293-1273°K (in N_2, rate 10°C/min). The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were determined by size exclusion chromatography (SEC) techniques of Shimadzu Co. For SEC investigations a SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. x 300 mm columns; eluent: DMF (0.4 ml/min), polystyrene standards were used. A refractive index detector was used to analyze the oligomers at 298 °K.

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PAT

Schiff base substitute polyphenol and its metal complexes derived from *o*-vanillin with 2,3-diaminopyridine: synthesis, characterization, thermal, and conductivity properties†

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Poly-2,3-bis[(2-hydroxy-3-methoxyphenyl)methylene]diamino pyridine (PHMPMDAP) that a new Schiff base polymer has been synthesized and characterized by spectroscopy, elemental, and thermal analyses techniques. This azomethine polymer was found to form complexes readily with Cu(II), Zn(II), Co(II), Pb(II), and Fe(II). From IR and UV-Vis studies, the phenolic oxygen and imine nitrogen of the ligand were found to be the coordination sites. Thermogravimetric analysis (TGA) data indicate the polymer to be more stable than the monomer. The structure of the polymer obtained was confirmed by FT-IR, UV-Vis, ^{13}C-NMR, and ^{1}H-NMR. Characterization was undertaken by TGA, size exclusion chromatography (SEC), and solubility tests. Also, electrical conductivities of PHMPMDAP and polymer–metal complexes are measured by four probe technique. Copyright © 2008 John Wiley & Sons, Ltd.

KEYWORDS: polymeric Schiff base; oxidative polycondensation; polymer-metal complexes; thermal degradation; electrical conductivity; coupling process

INTRODUCTION

Schiff base polymers, known as polyimines and polyazomethine or also named polyazines (when hydrazine is used as diamine compound) or polyketanils (when diketones are used as dicarbonyl compounds), were first reported by Adams *et al*. in 1923.[1] Soluble conjugated poly(Schiff base)s provide the opportunity of correlating chemical structure with their electronic, optical, and optoelectronic properties such as band gap, refractive index, nonlinear optical properties, luminescence characteristics, charge carrier mobility. It has been shown that the electronic properties of conjugated Schiff base polymers could be varied through different backbone rings, electron donating/accepting side group substitution, intramolecular hydrogen bonding, or complexation.[2] Schiff base polymers are generally synthesized by polycondensation reactions, a method that has some disadvantages; among them the necessity is to ensure special reaction conditions (such as high temperature) and the use, in some cases, of special catalysts.[3] Recently, a new method of synthesizing Schiff base polymers reported were oxidative polycondensation of monomers containing azomethine links.[4,5] There are some significant advantages of this method because of using of oxidants such as NaOCl, H_2O_2, and air O_2. For example, these type of oxidants are cheap and easily provided. They are simple structured oxidants. Also, they can be easily separated from reaction mixture. Phenols and Schiff base substitute phenols were polymerized by using this oxidants.[6–10] In addition, synthesized compounds have good solubility properties. With a view to searching for potential materials for electric, magnetic, and optical application, our group has been working at the synthesis of Schiff base substitute oligophenol and their metal complexes in recent years.

This article reports the synthesis, characterization, conductivity, and thermal properties of a new Schiff base polymer and its some transition metals.

MATERIALS AND METHODS

Materials

2,3-Diaminopyridine, *o*-vanillin, methanol, ethanol, benzene, toluene, ethyl acetate, CH_2Cl_2, $CHCl_3$, CCl_4, acetone, hexane, THF, DMF, DMSO, H_2SO_4 (98%), KOH, hydrochloric acid (HCl, 37%), H_2O_2 (30% aqueous solution), Co $(AcO)_2 4H_2O$, Cu $(AcO)_2 4H_2O$, $FeSO_4 7H_2O$, $Zn(AcO)_2 4H_2O$, $Pb(AcO)_2 3H_2O$were supplied from Merck Chem. Co. (Germany) and they were

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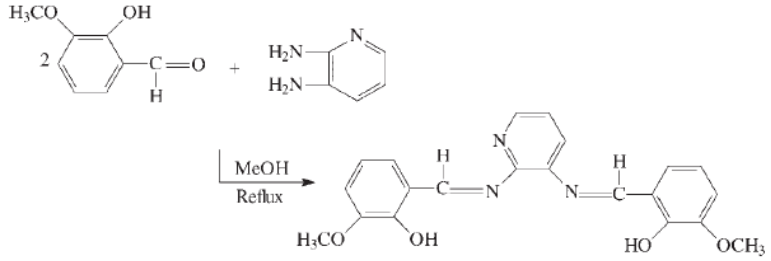
†Errors were discovered subsequent to publication on 28 January 2008 that have been incorporated here. This notice is included in the online and print versions to indicate that both have been corrected [3 July 2008].



Scheme 1. Synthesis of 2,3-bis[(2-hydroxy-3-methoxyphenyl)methylene]diamino pyridine.

used as received. Sodium hypo chloride (NaOCl), (30% aqueous solution) was supplied from Paksoy Chem. Co. (Turkey).

Preparation of HMPMDAP

2,3-bis[(2-hydroxy-3-methoxyphenyl)methylene]diamino pyridine was prepared by the condensation of *o*-vanillin (1.36 g, 0.01 mol) and 2,3-diaminopyridine (0.545 g, 0.005 mol) in the 15 ml methanol achieved by boiling the mixture under reflux for 3 hr (Scheme 1). The precipitated 2,3-bis[(2-hydroxy-3-methoxyphenyl)methylene]diamino pyridine was filtered and recrystallized from the methanol and dried in a vacuum desiccator.

^{1}H-NMR (DMSO): δ ppm, 8.98 (s, 1H, –C<u>H</u>=N–), 9.54 (s, 1H, –C<u>H</u>=N–), 12.62 (s, 1H, –OH), 13.24 (s, 1H, –OH), 6.94 (d, 2H, Ar–Ha and Ar–Hj), 7.18 (t, 2H, Ar–Hb and Ar–Hi), 7.38 (d, 1H, Ar–Hc), 8.46(d, 1H, Ar–Hd), 7.29 (t, 1H, Ar–He), 7.93 (d, 1H, Ar–Hf), 7.50 (d, 1H, Ar–Hg), 3.79(s, 3H, –OC<u>H</u>$_3$), 3.84 (s, 3H, –OC<u>H</u>$_3$). ^{13}C–NMR (DMSO): ppm, 148.50 (C1–OH–ipso), 150.94 (C2, C18–OCH$_3$–ipso), 119.49 (C3–H), 116.18 (C4–H), 124.46 (C5–H), 119.17 (C6–ipso), 166.40 (C7–H), 148.40 (C8–ipso), 147.13 (C9–H), 124.02 (C10–H), 129.60 (C11–H), 139.38 (C12–ipso), 164.79 (C13–H), 119.28 (C14–ipso), 124.88 (C15–H), 116.38 (C16–H), 119.95 (C17–H), 152.24 (C19–ipso), 56.20 (C20–H$_3$), 56.09 (C21–H$_3$).

Synthesis of PHMPMDAP with NaOCl, H_2O_2 and air O_2 oxidants in the alkaline medium

PHMPMDAP was synthesized from the oxidative polycondensation reaction of HMPMDAP with water solution of NaOCl (30%), H_2O_2 (30%), and air O_2, respectively, at the various temperatures and times in the alkaline medium as follows (Scheme 2).[11]

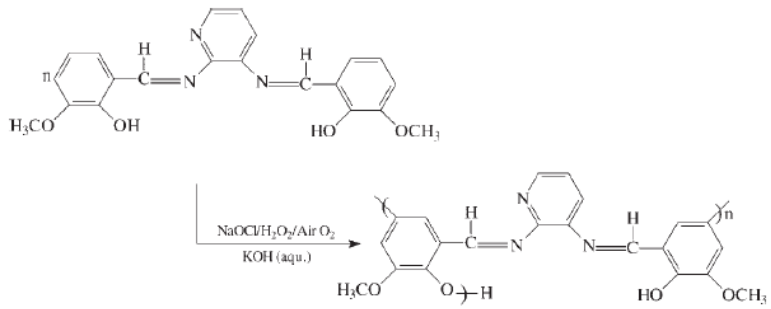
^{1}H–NMR (DMSO): δ ppm, 8.87 (s, 1H, –C<u>H</u>=N–), 9.55 (s, 1H, –C<u>H</u>=N–), 10.28 (s, 1H, –OH), 13.20 (s, 1H, –OH), 6.50–750 (m, 2H, Ar–Ha and Ar–Hj, 2H, Ar–Hb–terminal and Ar–Hi–terminal and 1H, Ar–He), 7.70 (d, 1H, Ar–Hc), 8.38(d, 1H, Ar–Hd), 8.07 (d, 1H, Ar–Hf), 7.90 (d, 1H, Ar–Hg), 3.82 (s, 3H, –OC<u>H</u>$_3$), 3.84 (s,3H–OC<u>H</u>$_3$). ^{13}C–NMR (DMSO): ppm, 149.97 (C1–OH–ipso), 152.92 (C2–OCH$_3$–ipso), 119.27 (C3–H), 117.85 (C4–H), 123.48 (C5–H), 118.96 (C6–ipso), 166.40 (C7–H), 149.05 (C8–ipso), 149.26 (C9–H), 123.00 (C10–H), 132.03 (C11–H), 144.69 (C12–ipso), 164.76 (C13–H), 119.21 (C14–ipso), 127.60 (C15–H), 118.52 (C16–H), 120.52 (C17–H), 152.34 (C18–OCH$_3$–ipso), 154.33 (C19–OH–ipso), 56.80 (C20–H$_3$), 56.05 (C21–H$_3$), 148.62, 145.23 (new peaks of C–C and C–O–C coupling systems).

Electrical properties

Electrical properties of doped and undoped polymer and polymer–metal complex compounds were determined by four-point probe technique at room temperature and atmospheric pressure using Keithley 2400 conductivity instrument (Keithley, Ohio, USA). The pellets were pressed on hydraulic press developing up to 1687.2 kg/cm^2. Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in a desiccator.[12]

Synthesis of PHMPMDAP–metal complexes

A solution of Co $(AcO)_2$ $4H_2O$, Cu $(AcO)_2$ $4H_2O$, $FeSO_4$ $7H_2O$, $Zn(AcO)_2$ $4H_2O$, $Pb(AcO)_2$ $3H_2O$ (1 mmol) in methanol (10 ml) was added to a solution of PHMPMDAP



Scheme 2. Synthesis of poly-2,3-bis[(2-hydroxy-3-methoxyphenyl)methylene]diamino pyridine.

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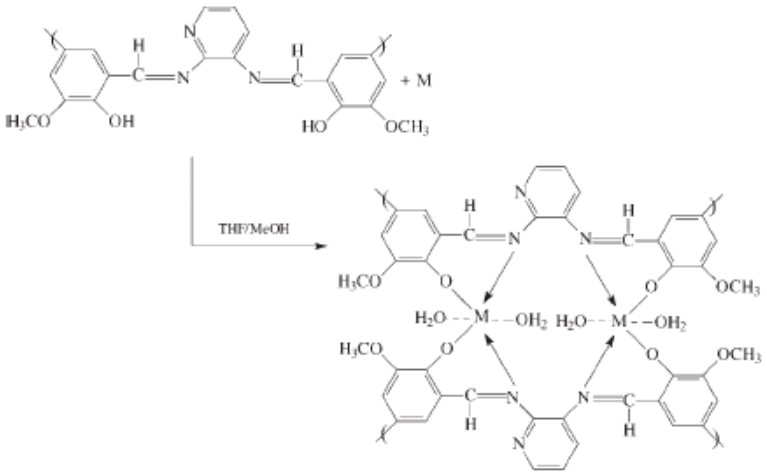

Scheme 3. Synthesis of poly-2,3-bis[(2-hydroxy-3-methoxyphenyl)methylene]diamino pyridine–metal complex compounds.

(2 mmol/unit) in THF (20 ml). The mixture was stirred and refluxed at 70°C for 3 hr (Scheme 3). The precipitated complex was filtered, washed with cold MeOH/THF (1:1), and then dried in a vacuum oven.

Characterization techniques

The infrared spectra were measured by Perkin Elmer Spectrum One FT-IR system. The FT-IR spectra were recorded using ATR attachment (4000–550 cm^{-1}). Elemental analysis was carried out with a LECO CHNS 932. UV-Vis spectra of HMPMDAP and PHMPMDAP were determined by using DMSO. HMPMDAP and PHMPMDAP were characterized by using ^{1}H-NMR and ^{13}C-NMR spectra (Bruker Avance DPX-400 and 100.6 MHz, respectively) recorded at 25°C by using deuterated DMSO as a solvent. Tetramethylsilane was used as an internal standard. Thermal data were obtained by using Perkin Elmer Diamond Thermal Analysis. The TGA-DTA measurements were made between 15°C and 1000°C (in N_2, rate 10°C/min). SEC analyses were performed at 30°C using DMF/MeOH (v/v, 4/1) as an eluent at a flow rate of 0.4 ml/min. A refractive index detector was used as a detector. The instrument (Shimadzu 10AVp series HPLC-SEC system) was calibrated with a mixture of polystyrene standards (Polymer Laboratories; the peak molecular weights, M_p, between 162 and 500,000) using GPC software for the determination of the molecular weight (M_n), weight-average molecular weight (M_w), and polydispersity index (PDI) of the polymer samples. For SEC investigations a Macherey-Nagel GmbH & Co. (100 Å and 7.7 nm diameter loading material) 3.3 mm i.d. × 300 mm columns were used. Metal analyses were carried out by AAS Shimadzu 6200 in a solution prepared by the decomposition of the complex compounds with HNO_3 followed by the dilution with deionized water.

RESULTS AND DISCUSSION

Synthesis of PHMPMDAP

Poly-2,3-bis[(2-hydroxy-3-methoxyphenyl)methylene]diamino pyridine was oxidized by air O_2, H_2O_2, and NaOCl oxidants in an aqueous alkaline medium and reaction conditions and yields of products are given in Table 1. The yield of PHMPMDAP was 70.0% at optimum reaction conditions such as $[HMPMDAP]_0 = 0.014$ mol/l and $[KOH]_0 = [NaOCl]_0 = 0.028$ mol/l at 50°C for 1 hr. The yield of PHMPMDAP was 68% at the reaction conditions such as $[HMPMDAP]_0 = [KOH]_0 = [NaOCl]_0 = 0.014$ mol/l at 50°C for 1 hr. The yield of PHMPMDAP was 40% at the reaction conditions such as $[HMPMDAP]_0 = [KOH]_0 = 0.014$ mol/l and $[NaOCl]_0 = 0.028$ mol/l at 50°C for 1 hr. According to these values, increasing the oxidant amount decreased the polymer yield. Under the same conditions, increasing the reaction times decreased the yield of the polymer. When reaction times changed from 1 hr to 5 hr, the yield of PHMPMDAP changed from 70% to 62% at the same conditions (such as $[HMPMDAP]_0 = [KOH]_0 = [NaOCl]_0 = 0.014$ mol/l at 50°C) for NaOCl oxidant. At the oxidative polycondensation reaction of HMPMDAP, when air O_2 passed into at the rate of 8.5 l/hr in the reaction medium at 50°C for 1 hr, the yield of the product was 27%. The yield of PHMPMDAP was 38% at the reaction conditions such as $[HMPMDAP]_0 = [KOH]_0 = 0.014$ mol/l at 60°C for 1 hr. According to these values, increasing the reaction temperatures decreased the polymer yield. The yield of PHMPMDAP was 44% at the reaction conditions such as $[HMPMDAP]_0 = [KOH]_0 = 0.014$ mol/l at 60°C for 3 hr. At the same conditions, increasing the reaction times decreased the yield of the polymer. When reaction times was changed from 3 hr to 25 hr, the yield of PHMPMDAP changed from 44% to 8% at the same conditions (such as $[HMPMDAP]_0 = [KOH]_0 = 0.014$ mol/l at 60°C) for air O_2 oxidant.

Solubility

PHMPMDAP was dark brown in powder form and it was completely soluble in the organic solvents such as DMF, THF, and DMSO. PHMPMDAP was insoluble in hexane, benzene, toluene, ethyl acetate, CH_2Cl_2, $CHCl_3$, CCl_4, and acetone. Polymer–metal complex compounds were insoluble in hexane, benzene, toluene, ethyl acetate, CH_2Cl_2, $CHCl_3$,

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Table 1. The oxidative polycondensation reaction parameters of 2,3-bis[(2-hydroxy-3-methoxyphenyl)methylene]diamino pyridine[a] with NaOCl (sample numbers: 1–9), air O_2 (sample numbers: 10–19), and H_2O_2 (sample numbers: 20–21) in aqueous KOH

Sample number	$[KOH]_o$ ($mol\,l^{-1}$)	$[NaOCl]_o$ ($mol\,l^{-1}$)/air O_2 (l/hr)/$[H_2O_2]_o$, ($mol\,l^{-1}$)	Temperature (°C)	Time (hr)	Yield of PHMPMDAP (%)
1	0.014	0.014	50	1	68
2	0.014	0.014	60	1	67
3	0.014	0.014	70	1	67
4	0.014	0.014	80	1	66
5	0.014	0.014	90	1	65
6	0.028	0.028	50	1	70
7	0.014	0.028	50	1	40
8	0.028	0.028	50	3	65
9	0.028	0.028	50	5	62
10	0.014	8.5	50	1	27
11	0.014	8.5	60	1	38
12	0.014	8.5	70	1	34
13	0.014	8.5	80	1	30
14	0.014	8.5	90	1	23
15	0.014	8.5	60	3	44
16	0.014	8.5	60	5	26
17	0.014	8.5	60	10	21
18	0.014	8.5	60	15	17
19	0.014	8.5	60	25	8
20	0.014	0.014	50	1	20
21	0.014	0.014	70	3	25

[a]The initial concentration of HMPMDAP was used as $0.014\,mol\,l^{-1}$.

CCl_4, and acetone. These polymer–metal complex compounds were partly soluble in DMSO and DMF.

Structure of PHMPMDAP

According to SEC chromatograms, the values of number-average molecular weight (M_n) and weight-average molecular weight (M_w) of PHMPMDAP were calculated according to a polystyrene (PS) standard calibration curve and are given in Table 2. For NaOCl oxidant, SEC chromatogram of polymer is given in Fig. 1. The M_n, M_w, and PDI values of PHMPMDAP were found to be 6200, 6900 g mol^{-1}, and 1.113, respectively, using NaOCl; and 4100, 16,200 g mol^{-1}, and 3.951 using air O_2, respectively. When reaction temperatures and reaction times increased, molecular weight distribution (MWD) of PHMPMDAP increased, but the yield of PHMPMDAP decreased. The increasing of polymerization time, temperatures, and oxidant concentrations increased the molecular weight and MWD of PHMPMDAP. Because of the increasing the molecular weight, together with the broadening of the polydispersity, NMR analyses fail to give valuable information for the characterization of these compounds. However, GPC analysis shows that the new polymer was formed and the traces being shifted to higher molecular weights. In the same time, the molecular weights measured by GPC based on PS standards should be taken as the minimum estimation because of the highly branched or comb-like structure of the obtained Schiff base polymer.

The UV-Vis spectroscopic studies carried out with DMSO solutions of the HMPMDAP and PHMPMDAP. At the spectra of HMPMDAP, K bands of phenol and –C=N– were observed in 223 nm and 282 nm, respectively. Benzene band of HMPMDAP and strength R band of –C=N–groups were observed in 206 nm and 335 nm, respectively. λ_{max} values of PHMPMDAP were observed in 227, 271, 295, 308, and 332 nm. UV-Vis spectra of PHMPMDAP, K and R bands were observed in 227 nm and 271 nm, respectively. The band of –C=N– group was observed in 332 nm. The UV-Vis spectra

Table 2. The number average molecular weight (M_n), weight average molecular weight (M_w), polydispersity index (PDI) and % values of oxidative polycondensation (OP) products of HMPMDAP

	Total			Molecular weight distribution parameters											
				Fraction I				Fraction II				Fraction III			
Compounds	M_n	M_w	PDI	M_n	M_w	PDI	(%)	M_n	M_w	PDI	(%)	M_n	M_w	PDI	(%)
PHMPMDAP[a]	6,200	6,900	1.113	7,500	9,000	1.200	60	9,300	11,500	1.237	25	62,000	64,800	1.045	15
PHMPMDAP[b]	4,100	16,200	3.951	600	900	1.500	60	19,800	79,800	4.030	40	—	—	—	—
PHMPMDAP[c]	5,400	7,700	1.426	750	1,000	1.333	45	8,000	12,900	1.613	45	123,500	169,800	1.375	10

[a]NaOCl oxidant.
[b]Air O_2 oxidant.
[c]H_2O_2 oxidant.

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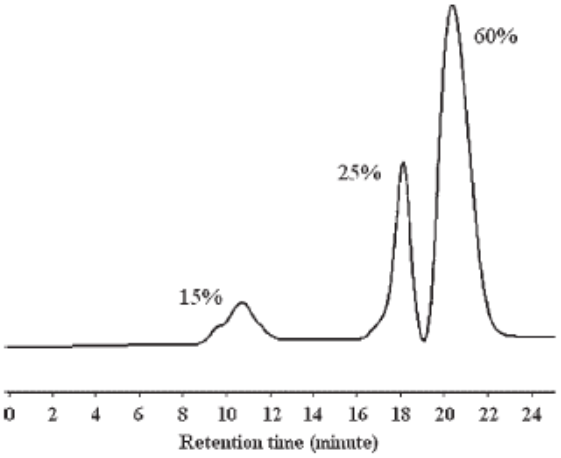

Figure 1. The chromatographic curve of the OP product of HMPMDAP for NaOCl oxidant.

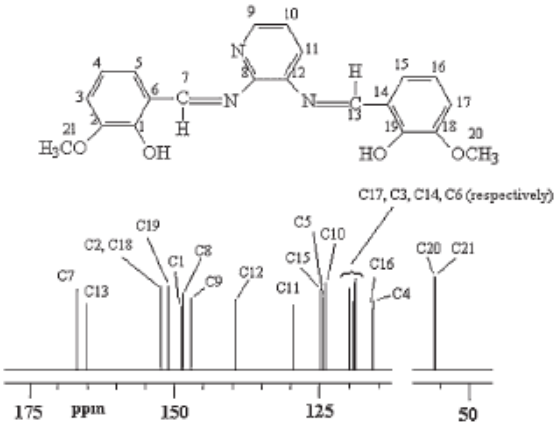

Figure 3. ^{13}C-NMR spectrum of 2,3-bis[(2-hydroxy-3-methoxyphenyl)methylene]diamino pyridine (Table 1, sample number 8, NaOCl oxidant).

shows specific bands for λ_{max} assigned to aromatic and azomethinic π–π^* transitions at about 280 nm and 350 nm, respectively.[13]

The FT-IR spectral data of monomer, polymer, and polymer–metal complexes are given Table 4. At the FT-IR spectra of HMPMDAP and PHMPMDAP, bands of –OH and –CH=N groups were observed in 3378 and 1603 cm^{-1}; 3400 and 1620 cm^{-1}, respectively. At the FT-IR spectra of polymer–metal complex compounds, most of the band shifts observed at the wave number region 1200–900 cm^{-1} are in agreement with the structural changes observed in the molecular carbon skeleton after complexation, which cause some important changes in (C–C) bond lengths. New peaks of sharp, small, or broad intensities are observed in the wave number range 563–594 cm^{-1} is assigned to the M–O vibration. The ν(M–N) band for the ligand complexes are appeared in the wave number range of 632–664 cm^{-1}. In order to identify the structures of monomer and polymer, the ^{1}H-NMR spectra were recorded in DMSO-d_6. ^{1}H-NMR and ^{13}C-NMR spectra of the monomer and polymer are given in Figs 2–5, respectively. According to the ^{1}H-NMR spectra results, the signals of phenyl –OH and –CH=N groups were observed in 12.62, 13.24 ppm and 8.98, 9.54 ppm for monomer; 10.28, 13.20 ppm and 8.87, 9.55 ppm for polymer, respectively. The FT-IR spectral data and the results of the ^{1}H-^{13}C-NMR spectra of the PHMPMDAP have confirmed together. Other phenol derivatives were also polymerized and the results were reported in the literatures.[14] Elemental

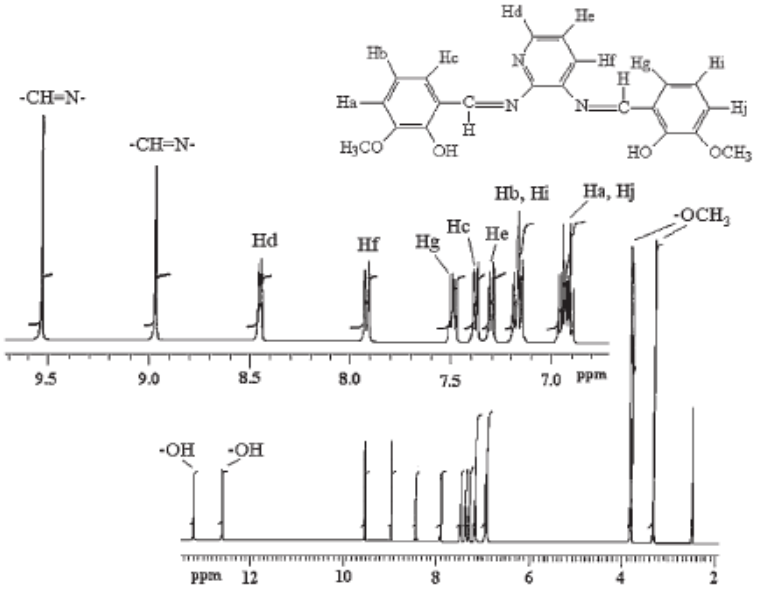

Figure 2. ^{1}H-NMR spectrum of 2,3-bis[(2-hydroxy-3-methoxyphenyl)methylene] diamino pyridine (Table 1, sample number 8, NaOCl oxidant).

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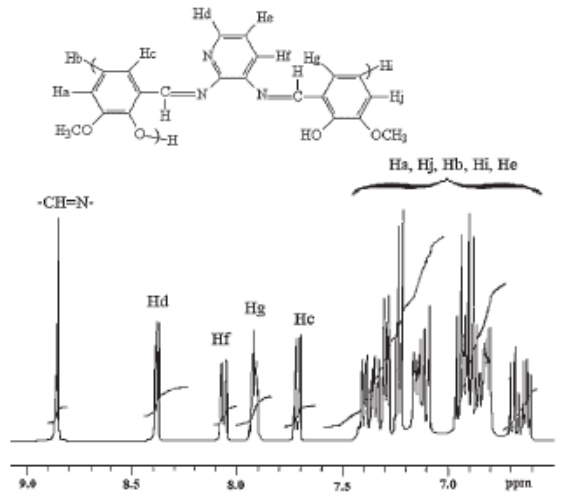

Figure 4. ^{1}H-NMR spectrum of poly-2,3-bis[(2-hydroxy-3-methoxyphenyl)methylene]diamino pyridine (Table 1, sample number 8, NaOCl oxidant).

analyses and FT-IR data of monomer, polymer, and polymer–metal complex compounds are given in Tables 3 and 4, respectively. The elemental analyses were satisfactory and show that the complexes have a ligand-to-metal ratio of 2:1.

According to ^{13}C-NMR, the peak values for C1, C4, C16, and C19 are observed in 148.50, 116.18, 116.38, and 152.24 ppm in the monomer and 149.97, 117.85, 118.52, and 154.33 ppm in the polymer, respectively. These values are in agreement with the theoretically calculated peak position for *para* linkages on the ring. The oxyphenylene are involved in the formation of free radicals leading to polymer formation and they appeared to be involved in the bond formation. According to ^{1}H-NMR, total proton integral values of hydroxyl groups were found to be 1.496. Thus, the phenyl rings in the polymer appears to be linked primarily at *para* and oxyphenylene positions. On the other hand, the new peaks are observed in 148.62 ppm and 145.23 ppm at the ^{13}C-NMR spectra of the polymer. These peaks are not present in the case of monomer. These new peaks are assigned to C–C and C–O–C coupling systems (Scheme 2). Metal ion values of PHMPMDAP-Cu, PHMPMDAP-Fe, PHMPMDAP-Pb, PHMPMDAP-Zn, and PHMPMDAP-Co complex compounds are calculated by AAS. The elemental analyses results of metal ions of these complex compounds were found to be less than the expected values. This case can be explained by the C–O–C coupling system.

Thermal studies

The thermal degradations of HMPMDAP, PHMPMDAP, PHMPMDAP-Co, PHMPMDAP-Cu, PHMPMDAP-Fe, PHMPMDAP-Pb, and PHMPMDAP-Zn were studied by TGA–DTG–DTA analyses at N_2 medium and thermal analyses results and the curves of these analyses are given in Table 5 and Figs 6–8, respectively. The initial degradation temperature of PHMPMDAP was higher than HMPMDAP. This polymer formed a residue at high amount such as 42.27% at 1000°C. Because of the long conjugated band systems, polymer demonstrated higher resistance against high temperature according to the monomer. The high thermal stability of PHMPMDAP demonstrated to be formed of C–C coupling system. PHMPMDAP–Cu compound demonstrated higher thermal stability according to other polymer–metal complex compounds. The initial degradation temperature and 58.06% weight loss of PHMPMDAP–Fe compound was found to be 304°C and 1000°C, respectively. According to TGA curves, high of thermal stability of polymer–metal complex compounds may indicate the formation of metal–oxygen valance and metal–nitrogen coordination bond between polymer–metal ions. The presence of water can be seen in TGA and DTG curves of polymer–metal complex compounds (Figs 6, 7) showing between 6 and 17 wt% losses in the 100–225°C range and corresponds to the loss of water of crystallization (50–150°C)

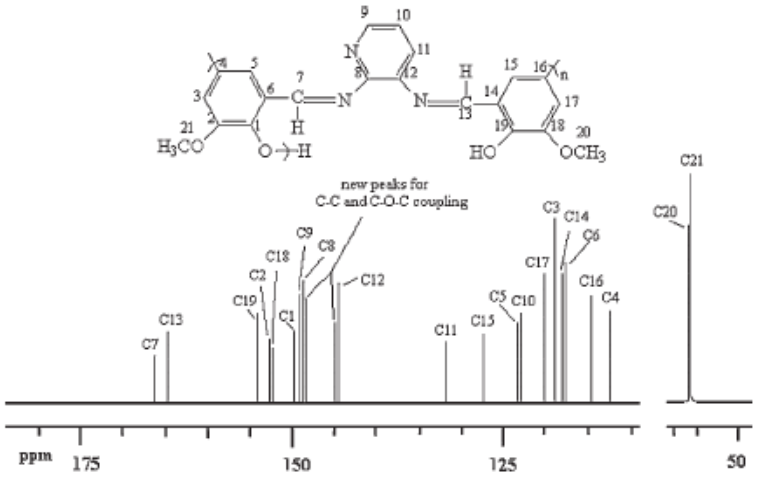

Figure 5. ^{13}C-NMR spectrum poly-2,3-bis[(2-hydroxy-3-methoxyphenyl)methylene] diamino pyridine (Table 1, sample number 8, NaOCl oxidant).

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Table 3. Elemental analyses data and yields of HMPMDAP, PHMPMDAP, and polymer–metal complexes

	Calculated (%, found)				
Compounds	C	H	N	Metal	Yield (%)
HMPMDAP	66.83 (66.74)	5.07 (4.92)	11.13 (11.02)	—	—
PHMPMDAP	67.19 (67.00)	4.57 (4.42)	11.19 (11.00)	—	70
PHMPMDAP-Cu	62.26 (62.05)	3.73 (3.61)	10.37 (10.21)	7.84 (7.65)	38
PHMPMDAP-Co	62.61 (62.44)	3.75 (3.63)	10.43 (10.32)	7.31 (7.19)	18
PHMPMDAP-Pb	52.88 (52.72)	3.17 (3.05)	8.81 (8.69)	21.72 (21.58)	12
PHMPMDAP-Fe	62.85 (62.73)	3.77 (3.66)	10.47 (10.33)	6.96 (5.42)	41
PHMPMDAP-Zn	62.11 (62.00)	3.72 (3.61)	10.35 (10.23)	8.05 (7.92)	14

Table 4. FT-IR spectral data of HMPMDAP, PHMPMDAP, and polymer–metal complexes

	Wave number (cm^{-1})						
Compounds	–OH	–CH=N	–C=C	–C–O	$–CH_3$	Metal–O	Metal–N
HMPMDAP	3378	1603	1460, 1440, 1423	1244	2936	—	—
PHMPMDAP	3400	1620	1606, 1560, 1463	1245	2932	—	—
PHMPMDAP-Cu	3361	1603	1540, 1473, 1440	1240	2933	573	652
PHMPMDAP-Co	3339	1604	1560, 1542, 1420	1242	2923	575	664
PHMPMDAP-Fe	3198	1603	1541, 1475, 1423	1247	2930	594	645
PHMPMDAP-Pb	3235	1532	1465, 1432, 1404	1235	2923	563	656
PHMPMDAP-Zn	3297	1604	1565, 1538, 1469	1239	2928	560	632

Table 5. Thermal decomposition values of HMPMDAP, PHMPMDAP, and polymer–metal complex compounds

	TGA					DTA	
Compounds	T_{on}[a]	$W_{max}.T$[b]	20% Weight loss	50% Weight loss	% Residue at 1000°C	Exo	Endo
HMPMDAP	296	345	323	375	29.74	206	141
PHMPMDAP	303	340	345	506	42.27	300	—
PHMPMDAP-Cu	304	342	374	—	58.06	—	—
PHMPMDAP-Zn	282	329, 690, 863	458	880	40.90	—	—
PHMPMDAP-Fe	332	407, 621, 841	538	—	56.87	—	—
PHMPMDAP-Pb	193	267, 592	466	968	41.57	—	—
PHMPMDAP-Co	290	332, 581	457	737	32.19	—	—

[a]The onset temperature.
[b]Maximum weight temperature.

and coordination water (150–200°C). This can also explain the differences appeared between the found and calculated elemental analysis values. PHMPMDAP–Co demonstrated lower thermal stability against thermal degradation than other polymer–metal complex compounds. According to TG analyses weight loses of polymer metal complex compounds changed at 1000°C as follows: PHMPMDAP–Cu > PHMPMDAP–Fe > PHMPMDAP–Pb > PHMPMDAP–Zn > PHMPMDAP–Co.

Electrical properties

HMPMDAP and PHMPMDAP have conductivities of 7.90×10^{-11} and 4.77×10^{-11} S/cm, respectively. When doped with iodine, their conductivities could be increased by about two orders of magnitude (up to 10^{-2} S/cm). Figure 9 shows the doping results for PHMPMDAP and polymer–metal complex compounds with iodine for the various times at 25°C. In the doping of HMPMDAP and PHMPMDAP with iodine, it was found that the conductivities of HMPMDAP and PHMPMDAP first increase greatly with doping time, but then tend to level-off. The maximal (or saturated) conductivity was 2.28×10^{-9} and 4.84×10^{-7} S/cm, respectively (shown in Fig. 9). The increasing conductivity could indicate that a charge-transfer complex between compounds and dopant iodine is continuously formed. In order to exclude the influence of doping conditions, the conductivity of doped polymer–metal complex compounds have been related with the doping extent. The maximal or saturated conductivity values of PHMPMDAP–Cu, PHMPMDAP–Co, PHMPMDAP–Zn, PHMPMDAP–Pb, and PHMPMDAP–Fe were found to be 7.51×10^{-8}, 9.55×10^{-8}, 1.94×10^{-8}, 1.25×10^{-7} and 1.08×10^{-7} S/cm, respectively. According to the values, the highest conductivity was observed in PHMPMDAP–Fe

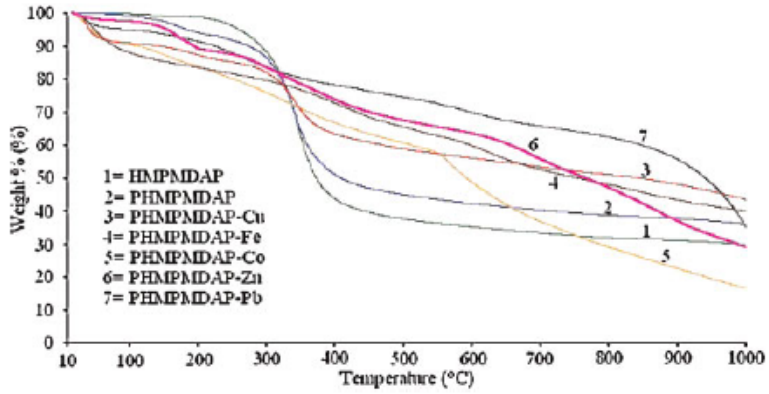

Figure 6. TGA curves of monomer, polymer, and polymer–metal complex compounds. This figure is available in color online at www.interscience.wiley.com/journal/pat

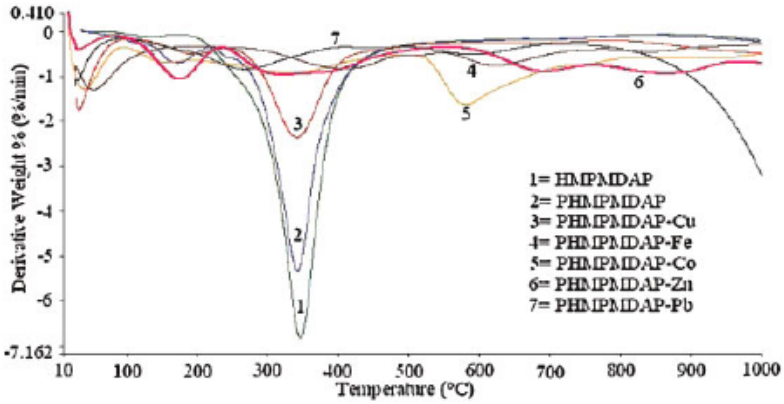

Figure 7. DTG curves of monomer, polymer, and polymer–metal complex compounds. This figure is available in color online at www.interscience.wiley.com/journal/pat

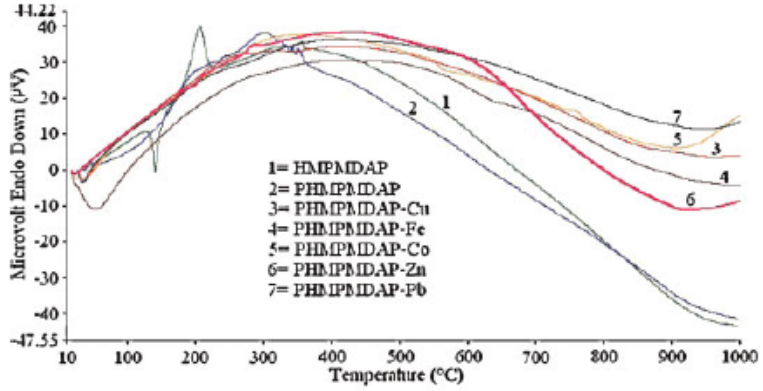

Figure 8. DTA curves of monomer, polymer, and polymer–metal complex compounds. This figure is available in color online at www.interscience.wiley.com/journal/pat

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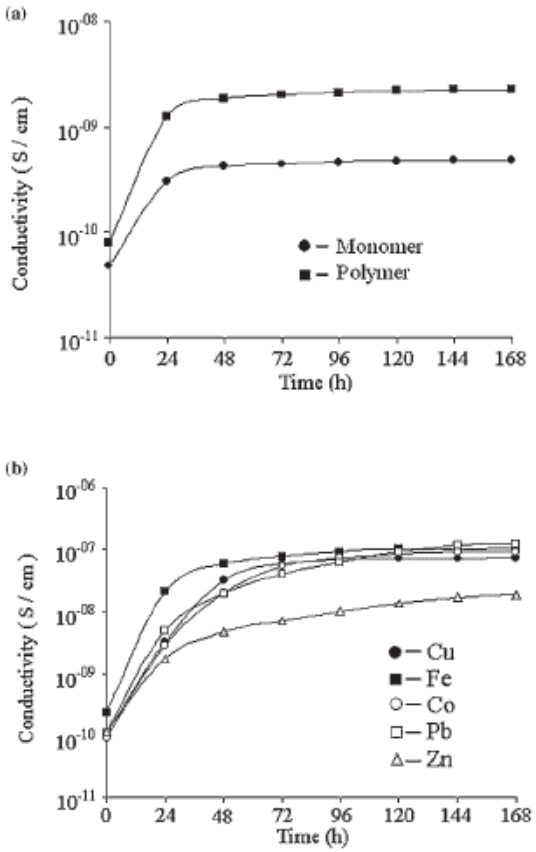
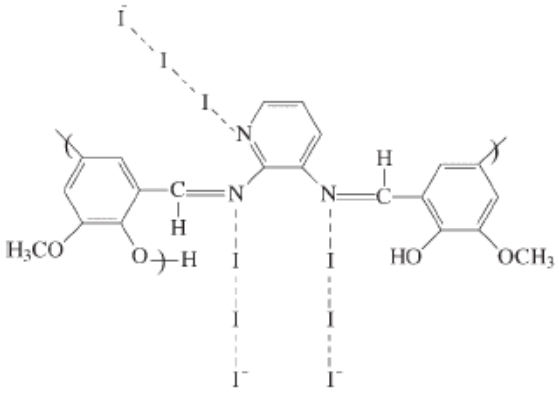


Figure 9. Electrical conductivities changes of I_2-doped (a) monomer and polymer; (b) polymer–metal complexes (Cu, Co, Pb, Zn, and Fe) versus doping time at 25°C.

compound. Diaz *et al.*[12] had suggested the conductivity mechanisms of Schiff base polymers for doping with iodine. Nitrogen is a very electronegative element and it is capable of coordinating an iodine molecule. Coordination of iodine during PHMPMDAP doping is as follows: (Scheme 4). On the nitrogen atom coordination of iodine with Schiff base polymers and pyridine solutions had been suggested in the literatures below.[15]



Scheme 4. Coordination of iodine during PHMPMDAP doping.

Table 6. The optical band gaps (E_g), λ_{max} (nm), and λ_{onset} (nm) values of monomer, polymer, and polymer–metal complex compounds

Products	λ_{max} (nm)	E_g (eV)	λ_{onset} (nm)
HMPMDAP	206, 223, 282, 335	2.94	422.45
PHMPMDAP	227, 271, 295, 308, 332	2.80	443.57
PHMPMDAP–Cu	262, 312, 358, 437	2.36	526.27
PHMPMDAP–Co	268, 306, 418	2.05	605.85
PHMPMDAP–Zn	258, 307, 332, 429	2.40	517.50
PHMPMDAP–Pb	261, 309, 330, 347	2.45	506.94

As seen from these results, the conductivity of the polymer is higher than the monomer. This may be ascribed to the conjugation length in the complexes arising from delocalization of π-electrons in the chelate ring. The increasing conjugation length in the complexes may lead to higher conductivity.[16,17] In the case of the doped polymer–metal complexes, if one is to ignore the little details, the behaviors of the five polymer–metal complexes are clearly similar. The curves are mostly indistinguishable. It can be noticed that the introduction of the metal ions into organic polymer increased its electrical conductivity.

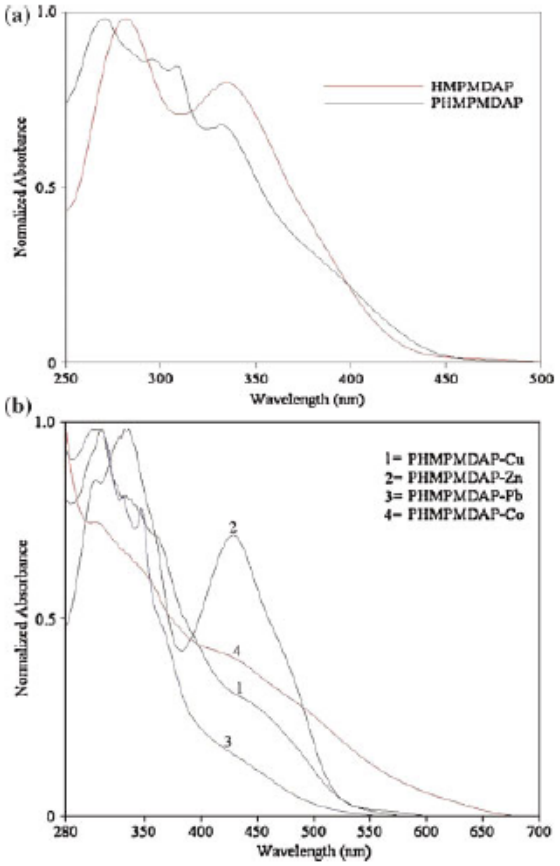


Figure 10. UV-Vis spectra of (a) monomer and polymer, (b) polymer–metal complex compounds with Cu^{+2}, Zn^{+2}, Pb^{+2}, and Co^{+2}. This figure is available in color online at www.interscience.wiley.com/journal/pat

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The absorption spectra of monomer, polymer, and polymer–metal complex compounds were recorded by using methanol and DMSO, respectively, at 25°C and are given in Table 6 and Fig. 10. The optical band gap (E_g) values of HMPMDAP, PHMPMDAP, PHMPMDAP–Cu, PHMPMDAP–Co, PHMPMDAP–Zn, and PHMPMDAP–Pb were found to be 2.94, 2.80, 2.36, 2.05, 2.40, and 2.45, respectively. According to these results, E_g value of PHMPMDAP-Co was lower than other monomer, polymer, and polymer–metal complex compounds.

CONCLUSION

Oxidative polymerization experiments of HMPMDAP were performed at varying temperatures and times using different oxidant agents such as air O_2, NaOCl, and H_2O_2. The major feature of the synthesized Schiff base polymer is their good solubility in aprotic organic solvents such as DMSO and DMF unlike most aromatic poly-Schiff bases which are insoluble. This opens up the opportunities for various applications such as electroactive and photoactive materials. Also, these conjugated polymers exhibited fairly good thermal stability on the basis of thermogravimetric analysis. The existence of dentate *O*- and *N*-donor sites for binding metal ions indicates that these compounds would have potential uses in making organic functional materials.

Acknowledgments

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Synthesis, characterization and electrochemical properties of poly-4-[1-(4-hydroxyphenyl)ethylidenamino]phenol

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Abstract

The polymer of 4-[1-(4-hydroxyphenyl)ethylidenamino]phenol (4-HPEAP) with Schiff base substitute was formed by oxidants such as air O_2, H_2O_2 and NaOCl in an aqueous alkaline medium. The yield of polymer was found to be 95, 51 and 96% for air O_2, H_2O_2 and NaOCl oxidants, respectively. During these polymerization reactions of 4-HPEAP, H_2O_2 demonstrated to less activity than NaOCl and air O_2. The spectral analyses results such as ^{1}H-NMR and ^{13}C-NMR showed that the presence of phenol units was connected at the *ortho* positions by forming of C-C coupling system. The polymer was found to possess relatively high thermal stability. This polymer lost half of the weights at 230°C. The highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and electrochemical energy gaps ($E_g^{'}$) of 4-HPEAP and P-4-HPEAP were found to be -6.30, -6.15; -2.41, -2.57; 3.89 and 3.58 eV, respectively. According to UV-vis measurements, optical band gaps (E_g) of 4-HPEAP and P-4-HPEAP were found to be 3.56 and 3.47 eV, respectively.

Key words: Oxidative polycondensation, poly-4-[1-(4-hydroxyphenyl)ethylidenamino] phenol, thermal analysis, conductivity and optic and electrochemical band gaps.

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1. Introduction

The oligophenols and their derivatives which included azomethine (-CH=N) and active hydroxyl (-OH) groups are an attractive class of polymers that exhibit interesting properties which are associated mainly with their conjugated backbone and the presence of imine sites.

Thus, they present good thermal stability, the ability to form metal chelates , electrical and optical properties. Because of these properties, oligophenols are used to prepare composites with resistance to high temperature and graphite materials, epoxy polymer and block copolymers adhesives, and antistatic materials [1-12]. These compounds can gain new properties when other functional groups are added to their structures[13]. Also, these type polymers can be used as anti-microbial agents [14, 15]. Most of these compounds exhibit an unusual adsorptive behavior with different solvents, very similar to those of molecular sieves[16-19]. They have the capability of coordination with different metal ions[20, 21] and they can be used for cleaning of poisonous heavy metals in the industrial waste waters. Therefore, the synthesis of polymer-metal complexes is very important for analytic and environmental chemistry [22, 23]. It seemed advantageous to attempt to design and prepare a polymer-bound chelating ligand, which would be able to form complexes with a variety of transition metals. There are some typical synthetic methods for oligophenols. The first oxidative polymerization represents nucleofilic substitution of halogenated aromatic compounds by metal phenolates and other catalytic oxidative polymerization of phenols[24]. The other one method is the oxidative polycondensation of Schiff base monomers including phenol. Phenols and Schiff base substitute phenols were easily polymerized using these oxidants. This method has significant advantages such as moderate reaction temperatures, and water as by-product. Used oxidants are cheap and simple structured oxidants. The oxidative polymerization, therefore, is to be regarded as a clean and low-loading process for synthesis of phenolic polymers.

In this paper, we have investigated the effects of different parameters such as temperature, reaction time, various oxidants and initial concentration of NaOCl for the formation of P-4-HPEAP. We have characterized 4-HPEAP and P-4-HPEAP by using FT-IR, UV-vis, ^{1}H-NMR, ^{13}C-NMR, elemental analysis, TG-DTA and SEC techniques. The electrical conductivity of the polymer was measured after doping with I_2. Also, electrochemical (E_g') and optical (E_g) band gaps of the monomer and polymer were determined from cyclic voltammetry and UV-vis measurements.

2. Materials and Methods

2.1. Materials

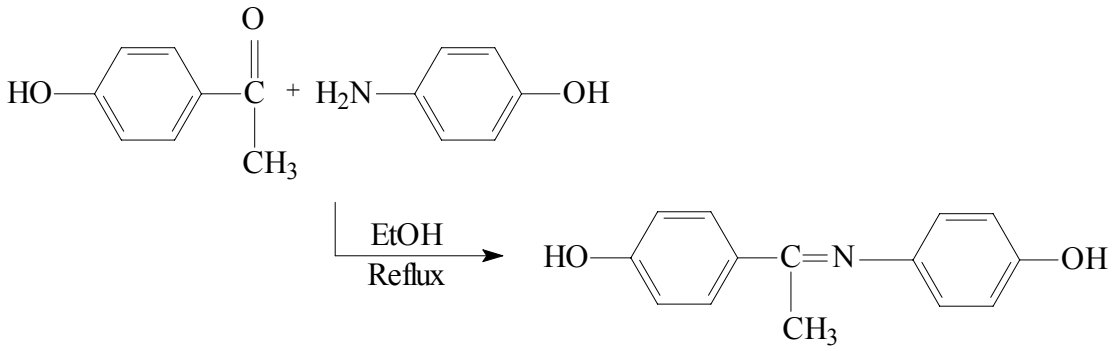
4-Hydroxyacetophenon, 4-aminophenol, dioxane, methanol, ethanol, 1-butanol, acetonitrile, benzene, toluene, acetone, ethyl acetate, heptane, CCl_4, $CHCl_3$, tetrahydrofurane, THF, dimethylformamide, DMF, dimethylsulfoxide, DMSO, H_2SO_4 (98%), NaOH, KOH and

hydrochloric acid (37%, HCl) were supplied from Merck Chemical Co. and they were used as received. Sodium hypo chloride (NaOCl), (30% aqueous solution) was supplied from Paksoy Chemical Co. (Turkey). 4-[1-(4-hydroxyphenyl)ethylidenamino]phenol was synthesized from condensation reaction of 4-hydroxyacetophenon with 4-aminophenol and its recrystallized in methanol.

2.2. Preparation of 4-[1-(4-hydroxyphenyl)ethylidenamino]phenol (4-HPEAP)

4-[1-(4-hydroxyphenyl)ethylidenamino]phenol was prepared by the condensation of 4-hydroxyacetophenon (1.36 g, 0.01 mol) with 4-aminophenol (1.09 g, 0.01 mol) in ethanol (50 ml) achieved by boiling the mixture under reflux for 2h at 70°C (Scheme1). The precipitated 4-[1-(4-hydroxyphenyl)ethylidenamino]phenol was filtered, recrystallized from ethanol and dried in vacuum desiccators (yield 88%).

Calcd. for 4-HPEAP: C, 74.01; H, 5.73; N, 6.17**.** Found: C, 73.90; H, 5.59; N, 6.05. UV-vis (λ_{max}): 204, 220, 277 and 335 nm. FT-IR (cm^{-1}): ν (O-H) 3285 s, ν (C-H Phenyl) 3073 m, ν (C-H aliphatic) 2992 s, ν (C=N) 1659 s, ν (C=C phenyl) 1602, 1576, 1509 s, ν (C-O) 1277 s. ^{1}H-NMR (DMSO): δ ppm, 9.15 (s, 2H, -OH); 6.51 (d, 2H, Ar-Haa'), 6.45 (d, 2H, Ar-Hbb'), 7.83 (d, 2H, Ar-Hcc') 6.93 (d, 2H, Ar-Hdd') 2.50 (s, 3H, $-CH_3$). ^{13}C-NMR (DMSO): ppm, 148.81 (C1-ipso-OH), 115.83 (C2,6-H), 129.11 (C3,5-H), 141.01 (C4-ipso), 170.25 (C7-ipso), 137.44 (C8-ipso), 131.17 (C9,13-H), 116.06 (C10,12-H), 162.48 (C11-ipso-OH), 26.65 (C14-H_3).



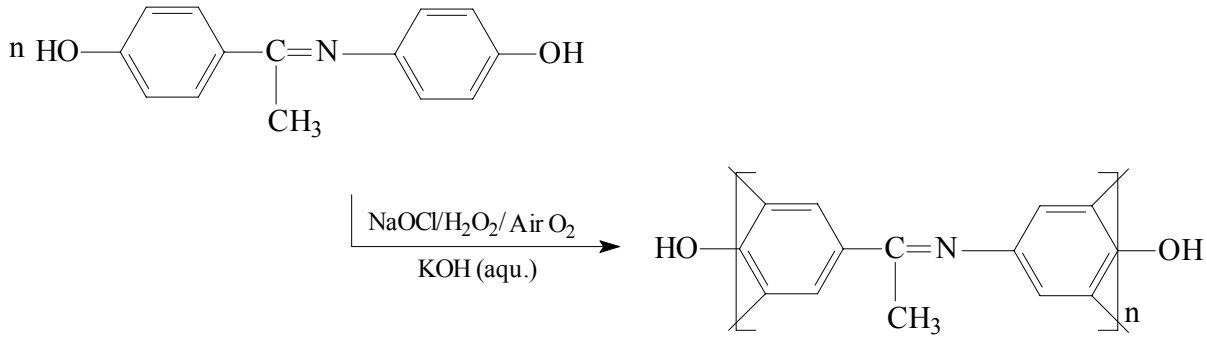
Scheme 1. Synthesis of 4-[1-(4-hydroxyphenyl)ethylidenamino]phenol

2.3. Synthesis of P-4-HPEAP with NaOCl, H_2O_2 and air O_2 in aqueous alkaline medium

P-4-HPEAP was synthesized through oxidative polycondensation of 4-[1-(4-hydroxyphenyl)ethylidenamino]phenol with aqueous solutions of NaOCl (30%), H_2O_2 (30%) and air O_2, respectively, [10]. The 4-HPEAP (0.227 g 0.001 mol) was dissolved in an aqueous solution of KOH (10%, 0.001 mol) and placed into a 50-ml three-necked round-bottom flask

(Scheme 2). It was fitted with a condenser, thermometer, stirrer and an addition funnel containing NaOCl or H_2O_2. After heating to room temperature, NaOCl and H_2O_2 were added drop by drop over about 20 min. The reaction mixtures were stirred at the various temperatures and durations (Table 1 and 2). Air was passed into an aqueous solution of KOH (20%) before being sent through the reaction tube to prevent water loss in the reaction mixture and to neutralize CO_2 in the air (Scheme 2). The reaction mixtures were cooled to room temperature, and then 0.001 mol HCl (37%) was added. For the separation of mineral salts, the mixture was filtered and washed in 25 ml of hot water for three times. Unreacted monomer was separated from the reaction products by washing ethyl acetate and then dried in an oven at 110°C.

Calcd. for P-4-HPEAP: C, 74.67; H, 4.89; N, 6.22**.** Found: C, 74.40; H, 5.20; N, 6.00. UV-vis (λ_{max}): 205, 233, 296 and 381. FT-IR (cm^{-1}): ν (O-H) 3328 s, ν (C-H Phenyl) 3075 m, ν (C-H aliphatic) 2994 s, ν (C=N) 1618 s, ν (C=C phenyl) 1595, 1570, 1498 s, ν (C-O) 1280 s**.** ^{1}H-NMR (DMSO): δ ppm, 8.68 (s, 2H, -OH); 5.50 (s, 2H, Ar-Hbb'); 5.92 (s, 2H, Ar-Hcc'); [terminal protons: 6.48 (d, 2H, Ar-Haa'), 6.41 (d, 2H, Ar-Hbb'), 7.10 (d, 2H, Ar-Hcc') 6.81 (d, 2H, Ar-Hdd')]; 2.51(s, 3H, -CH_3). ^{13}C-NMR (DMSO): ppm, 166.86 (C1, C11-ipso-OH), 116.20 (C2-6-H, terminal), 125.16 (C2-6-ipso), 129.85 (C3-H, C-5), 149.44 (C4-ipso), 175.53 (C7-ipso), 141.32 (C8-ipso), 132.58 (C9-H, C13-H), 116.45 (C10-12-H, terminal), 126.55 (C10-12-ipso), 27.40 (C14-H_3).



Scheme 2. Synthesis of poly-4-[1-(4-hydroxyphenyl)ethylidenamino]phenol

2.4. Electrical Properties

Conductivity was measured on a Keithley 2400 Electrometer. The pellets were pressed on hydraulic press developing up to about $1.70 \cdot 10^3$ kg/cm^2. Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in desiccators [25].

2.5. Electrochemical Properties

Cyclic voltammetry (CV) measurements were carried out with a CH instruments 660C Electrochemical Analyzer at a potential scan rate of 20 mV/s. All the experiments were performed in dry box under Ar atmosphere at room temperature. The electrochemical potential of Ag was calibrated with respect to the ferrocene/ferrocenium (Fc/Fc^+) couple. The half-wave potential ($E^{1/2}$) of (Fc/Fc^+) measured in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) acetonitrile solution is 0.39 V vs. Ag wire or 0.38 V vs. supported calomel electrode (SCE). The voltammetric measurements were carried out for monomer and polymer in acetonitrile and DMSO, respectively. The HOMO and LUMO energy levels of the monomer and polymer were determined from the onset potentials of the n-doping ($\phi_n^{'}$) and p-doping ($\phi_p^{'}$), respectively, as literature[26].

2.6. Optical Properties

The optical band gaps (E_g) of monomer and polymer compounds were calculated from their absorption edges. Ultraviolet-visible (UV-vis) spectra were measured by Perkin Elmer Lambda 25. The absorption spectra of monomer and polymer were recorded by using methanol and DMSO, respectively, at 25°C.

2.7. Solubility and Characterization Techniques

P-4-HPEAP was dark brown at powder forms and it was completely soluble in organic solvents such as DMF, THF, DMSO, aqueous alkaline and conc.H_2SO_4 but it was partly soluble in methanol, ethanol and 1-butanol. P-4-HPEAP was any insoluble in heptane, hexane, benzene, toluene, ethyl acetate, acetonitrile, $CHCl_3$, CCl_4 and dioxane. The solubility tests were done by using 1 mg sample and 1 ml solvent at 25°C.

The infrared spectra was measured by Perkin Elmer FT-IR Spectrum one. The FT-IR spectra were recorded using universal ATR sampling accessory (4000-550 cm^{-1}). Elemental analysis was carried out with a Carlo Erba 1106. UV-vis spectra of 4-HPEAP and P-4-HPEAP were measured by Perkin Elmer Lambda 25. UV-vis spectra of 4-HPEAP and P-4-HPEAP were determined by using methanol and DMSO. 4-HPEAP and P-4-HPEAP were characterized by using ^{1}H-NMR and ^{13}C-NMR spectra (Bruker AC FT-NMR spectrometer operating at 400 and 100.6 MHz, respectively) and recorded by using deuterated DMSO-d_6 as a solvent at 25°C. Tetramethylsilane was used as internal standard. Thermal data were obtained by using Perkin-Elmer Diamond Thermal Analysis. The TG-DTA measurements were made between 20-1000°C (in N_2, rate 10°C/min). The number average molecular weight (M_n), weight average molecular weight (M_w) and polydispersity index (PDI) were determined by size

exclusion chromatography (SEC) techniques of Shimadzu Co. For SEC investigations were used a SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. x 300 mm columns; eluent: DMF (0.4 ml/min), polystyrene standards. A refractive index detector (at 25°C) was used to analyze the product.

3. Results and Discussion

3.1. The Investigation of synthesis conditions of P-4-HPEAP

4-[1-(4-hydroxyphenyl)ethylidenamino]phenol not oxidized at the normal condition at the neutral aqueous and organic medium by air O_2, H_2O_2 (30% aqueous solution), and NaOCl (30% aqueous solution). When 4-HPEAP interacted by oxidants such as air O_2, H_2O_2 and NaOCl, it immediately precipitated phenoxy radicals with brown adding to alkaline solution. The conditions of oxidative polycondensation reaction of 4-HPEAP with 30% NaOCl solution in aqueous alkaline medium are given in Table 1. The yield of P-4-HPEAP was 86% at the NaOCl medium for 3 h at 80°C. As seen from Table 1, the yields increased in increasing of temperature (except for 90°C). The yield of 4-HPEAP was 96% at the reaction conditions such as $[KOH]_0$=0.002 and $[4\text{-HPEAP}]_0$= $[NaOCl]_0$=0.001 mol/L at 60°C for 5h. At the same conditions, when molar amount of alkaline increased in two coating, total yield of P-4-HPEAP changed from 83% to 94%.

The oxidative polycondensation reaction conditions of 4-MPIMP with 30% H_2O_2 solution in an aqueous alkaline medium are given in Table 2. The yield of P-4-HPEAP was 51% at optimum conditions such as $[4\text{-HPEAP}]_0 = [KOH]_0 = [H_2O_2]_0$=0.001 mol/L, at 70°C for 5h. At the same conditions, when molar amount of alkaline increased in two coating, total yield of P-4-HPEAP changed from 51% to 46%. The yield of P-4-HPEAP was 36% at the reaction conditions such as $[4\text{-HPEAP}]_0$= $[KOH]_0$=$[H_2O_2]_0$=0.001 mol/L at 70°C for 15h. According to these values, yield of P-4-HPEAP decreased increasing of reaction time. At the oxidative polycondensation reaction of 4-HPEAP, when air oxygen passed into 8.5 L/h rate at the reaction medium at 30°C, the yield of product was 82%. The yield of P-4-HPEAP was 95% at optimum conditions such as $[4\text{-HPEAP}]_0 = [KOH]_0$ = 0.01 mol/L at 50°C for 10 h. The various conditions for P-4-HPEAP are given in Table 2. As is seen from Table 1 and 2, in these reactions the yield of the polymer was dependent upon temperature, times and initial concentrations of alkaline. At the same conditions, the yield of P-4-HPEAP with NaOCl and air O_2 was higher than H_2O_2.

Table 1. The oxidative polycondensation reaction parameters of 4-[1-(4-hydroxyphenyl)ethylidenamino]phenol[a] with NaOCl in aqueous KOH

Sample No	$[KOH]_0$ (mol L^{-1})	$[NaOCl]_0$ (mol L^{-1})	Temp., (^oC)	Times (h)	The yield of P-4-HPEAP,%
1	0.001	0.001	50	3	76
2	0.001	0.001	60	3	83
3	0.001	0.001	70	3	85
4	0.001	0.001	80	3	86
5	0.001	0.001	90	3	79
6	0.001	0.001	80	5	91
7	0.001	0.001	80	10	88
8	0.001	0.001	80	15	81
9	0.001	0.001	80	25	80
10	0.002	0.001	50	3	91
11	0.002	0.001	60	3	94
12	0.002	0.001	70	3	90
13	0.002	0.001	80	3	86
14	0.002	0.001	90	3	79
15	0.002	0.001	60	5	96
16	0.002	0.001	60	10	93
17	0.002	0.001	60	15	88
18	0.002	0.001	60	25	85
19	0.001	0.002	50	3	86
20	0.001	0.002	60	3	90
21	0.001	0.002	70	3	84
22	0.001	0.002	80	3	80
23	0.001	0.002	90	3	80
24	0.001	0.002	60	5	90
25	0.001	0.002	60	10	93
26	0.001	0.002	60	15	90
27	0.001	0.002	60	25	90

a= The initial concentration of 4-HPEAP was used as 0.001 mol L^{-1}.

Table 2. The oxidative polycondensation reaction parameters of 4-[1-(4-hydroxyphenyl)ethylidenamino]phenol with H_2O_2 (1-18) and air O_2 (19-27) in aqueous KOH

Sample No	$[KOH]_0$ (mol L^{-1})	$[H_2O_2]_0$ (mol L^{-1}) or Air O_2 (L/h)	Temp., (^oC)	Times (h)	The yield of P-4-HPEAP, %
1	0.001	0.001	50	3	38
2	0.001	0.001	60	3	43
3	0.001	0.001	70	3	47
4	0.001	0.001	80	3	40
5	0.001	0.001	90	3	38
6	0.001	0.001	70	5	51
7	0.001	0.001	70	10	44
8	0.001	0.001	70	15	36
9	0.002	0.001	50	3	24
10	0.002	0.001	60	3	31
11	0.002	0.001	70	3	38
12	0.002	0.001	80	3	30
13	0.002	0.001	90	3	29
14	0.002	0.001	70	5	46
15	0.002	0.001	70	10	42
16	0.002	0.001	70	15	31
17	0.002	0.001	70	25	26
18	0.001	8.5	30	3	82
19	0.001	8.5	40	3	87
20	0.001	8.5	50	3	91
21	0.001	8.5	60	3	90
22	0.001	8.5	70	3	81
23	0.001	8.5	80	3	73
24	0.001	8.5	90	3	68
25	0.001	8.5	50	1	79
26	0.001	8.5	50	5	93
27	0.001	8.5	50	10	95
28	0.001	8.5	50	15	91
29	0.001	8.5	50	25	88

3.2. Structure of P-4-HPEAP

According to SEC chromatograms, the values of number-average molecular weight (M_n) and weight-average molecular weight (M_w) of P-4-HPEAP were calculated according to a Polystyrene standard calibration curve and are given in Table 3. According to the SEC analysis, the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of total of P-4-HPEAP were found to be 3000, 3300 g mol^{-1} and 1.100, using H_2O_2 and 1400, 1550 g mol^{-1} and 1.107, using air O_2 and 5000, 5470 g mol^{-1} and 1.094, using NaOCl, respectively.

Table 3. The number average molecular weight (M_n), weight average molecular weight (M_w), polydispersity index (PDI) and % values of P-4-HPEAP

	Molecular weight distribution parameters															
	Total			Fraction I				Fraction II				Fraction III				
Compounds	M_n	M_w	PDI	M_n	M_w	PDI	%	M_n	M_w	PDI	%	M_n	M_w	PDI	%
P-4-HPEAP[1]	1400	1550	1.107	2000	2200	1.100	60	2700	3200	1.185	30	22500	24000	1.067	10
P-4-HPEAP[2]	5000	5470	1.094	2500	2900	1.160	15	3000	3750	1.250	30	25000	27000	1.080	55
P-4-HPEAP[3]	3000	3300	1.100	2800	3350	1.196	30	2900	3500	1.207	45	27000	29500	1.093	25

1= Air O_2 oxidant; 2= NaOCl oxidant 3= H_2O_2 oxidant

The UV-vis spectra of 4-HPEAP and P-4-HPEAP were similar to one together. However, at the spectra of 4-HPEAP, K bands of phenol and C_6H_5-N= were observed in 220 nm and 277 nm, respectively. Strength R band of -CH=N- group was observed in 335 nm. λ_{max} values of P-4-HPEAP were observed in 205, 233, 296 and 381 nm. UV-vis spectra of P-4-HPEAP, K and R bands were observed in 296 nm and 381 nm, respectively. The UV-vis spectra shows specific bands for λ_{max} assigned to aromatic and azometinic π-π^* transitions at about 280 and 350 nm, respectively, [27]. The shifting of the –CH=N– group band from 296 nm to 381 nm has been demonstrated to the formation of the polymeric conjugate π system.

According to the FT-IR spectra of 4-HPEAP, at the FT-IR spectra of oxidative polycondensation product of 4-[1-(4-hydroxyphenyl)ethylidenamino]phenol are only different by reduction of band strength and peak numbers. At the FT-IR spectra of 4-HPEAP and P-4-HPEAP, bands of –OH and –C=N groups were observed in 3285 and 1659 cm^{-1}; 3328 and 1618 cm^{-1}, respectively. In order to identify the structures of monomer and polymer, the ^{1}H-^{13}C-NMR spectra were recorded in DMSO-d_6. ^{1}H-NMR and ^{13}C-NMR spectra of the 4-HPEAP and P-4-HPEAP are given in Figs.1, 2, 3 and 4, respectively. At the ^{1}H-NMR spectra of 4-HPEAP and P-4-HPEAP, the chemical shift values (ppm) of –OH and aromatic and aliphatic protons were observed in 9.15 (s, 2H, -OH); 6.51 (d, 2H, Ar-Haa'), 6.45 (d, 2H, Ar-Hbb'), 7.83 (d, 2H, Ar-Hcc') 6.93 (d, 2H, Ar-Hdd') 2.50 (s, 3H, -CH_3) and 8.68 (s, 2H, -OH); 5.50 (s, 2H, Ar-Hbb'); 5.92 (s, 2H, Ar-Hcc'); [terminal protons: 6.48 (d, 2H, Ar-Haa'), 6.41 (d, 2H, Ar-Hbb'), 7.10 (d, 2H, Ar-Hcc') 6.81 (d, 2H, Ar-Hdd')]; 2.51(s, 3H, -CH_3), respectively. The peak values for C2, 6 and C10, 12 observed in 115.83 and 116.06 ppm in the monomer and 125.16 and 126.55 ppm in the polymer, respectively. The ^{1}H-NMR and ^{13}C-NMR spectra results of the P-4-HPEAP confirm to form of polymer units. Shifting to below field of the peak values for C2, 6 and C10, 12 have been demonstrated formation of polymer units. The ^{13}C-NMR spectra of P-4-HPEAP have been demonstrated C-C coupling systems. Monomer and dimmer interconversion combinations of radical units are proposed as literature [28]. The hydroxyl groups are involved in the formation of free radicals leading to polymer formation. According to ^{1}H-NMR, integral value of hydroxyl group was found to be 1.000. Thus, the phenyl rings in the polymer appear to be linked primarily both at *ortho* positions according to –OH groups of P-4-HPEAP (Scheme 2).

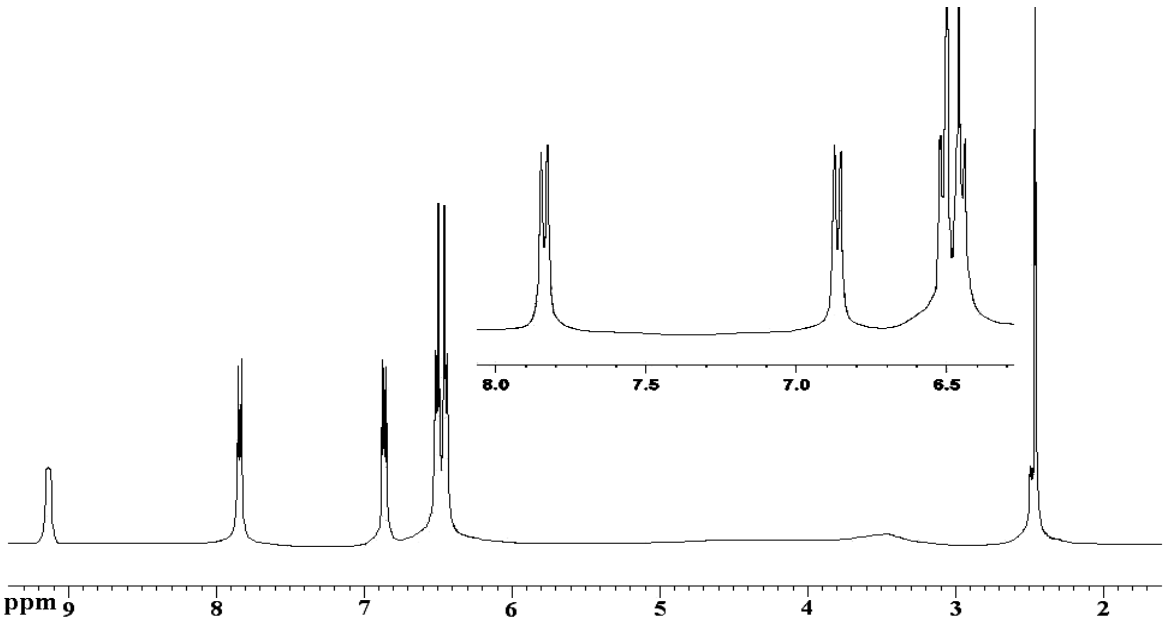
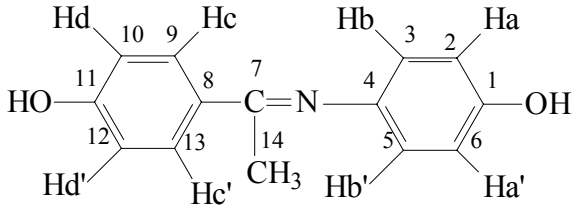


Figure 1. [1]H-NMR spectrum of 4-(1-(4-hydroxyphenyl)ethylidenamino)phenol



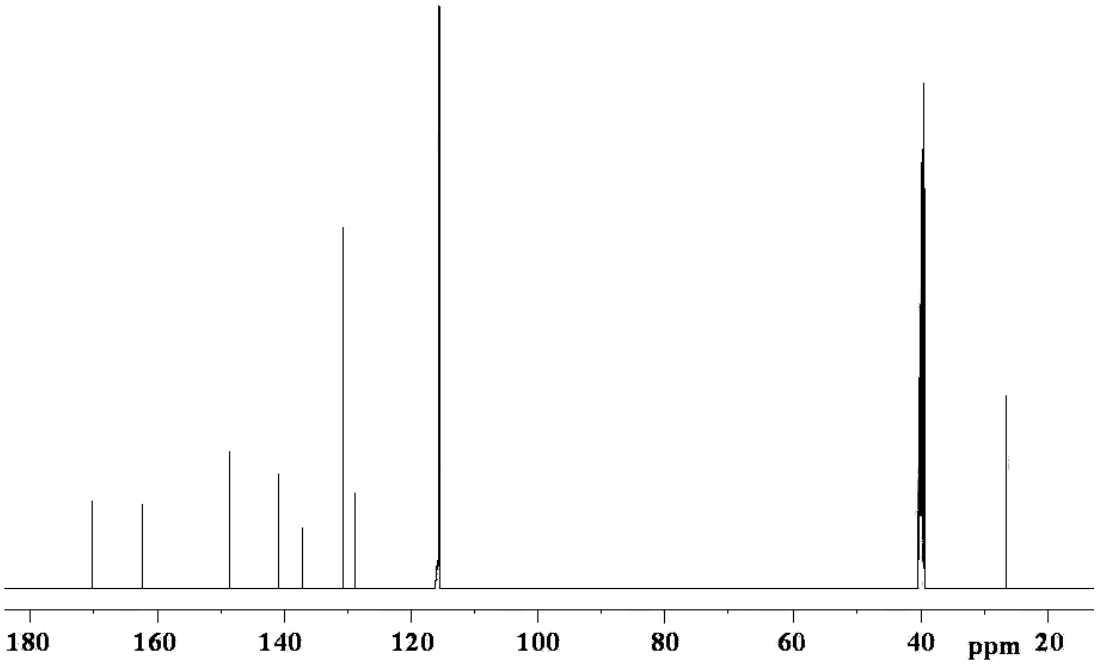


Figure 2. [13]C-NMR spectrum of 4-(1-(4-hydroxyphenyl)ethylidenamino)phenol

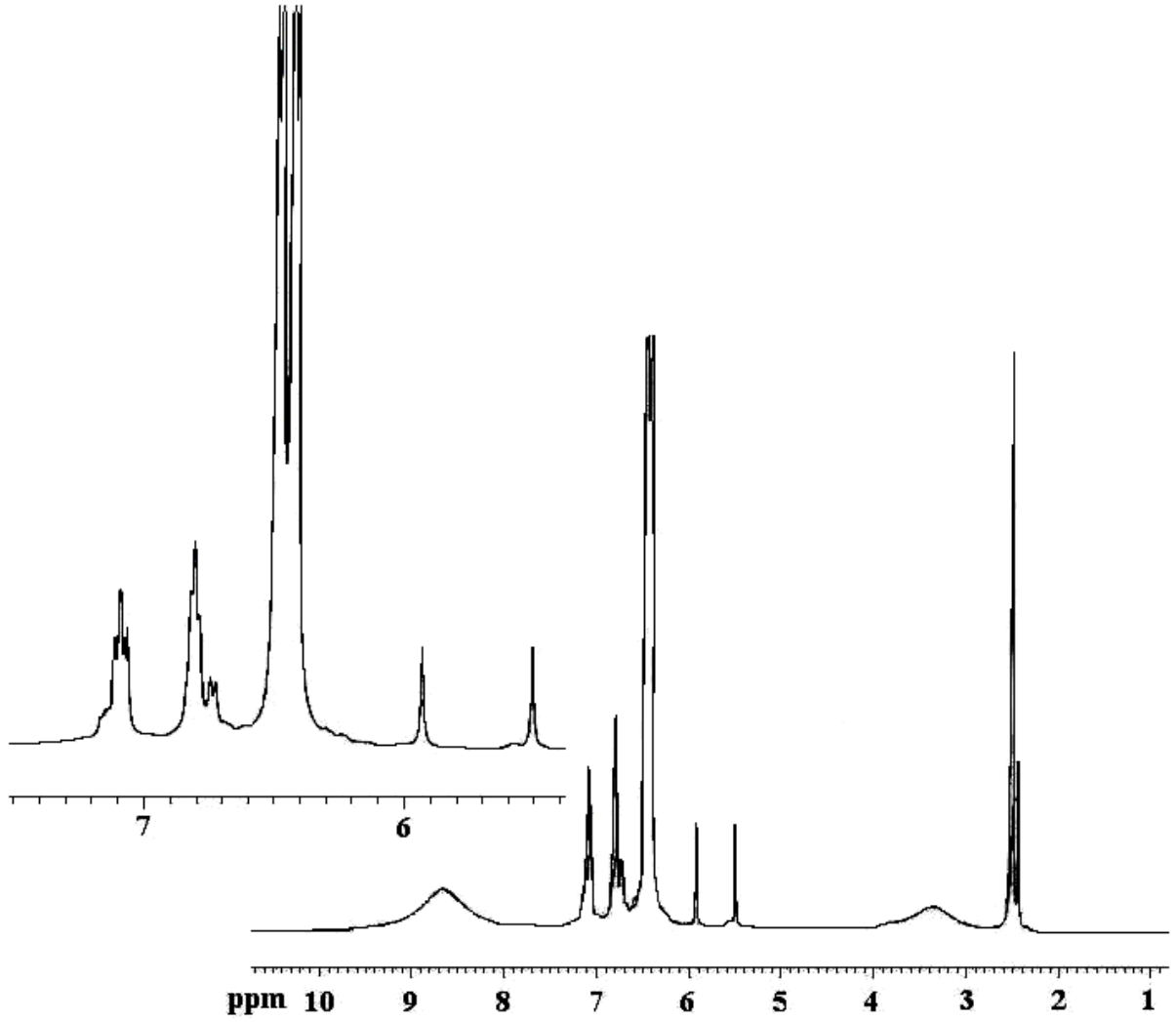


Figure 3. [1]NMR spectrum of poly-4-(1-(4-hydroxyphenyl)ethylidenamino)phenol

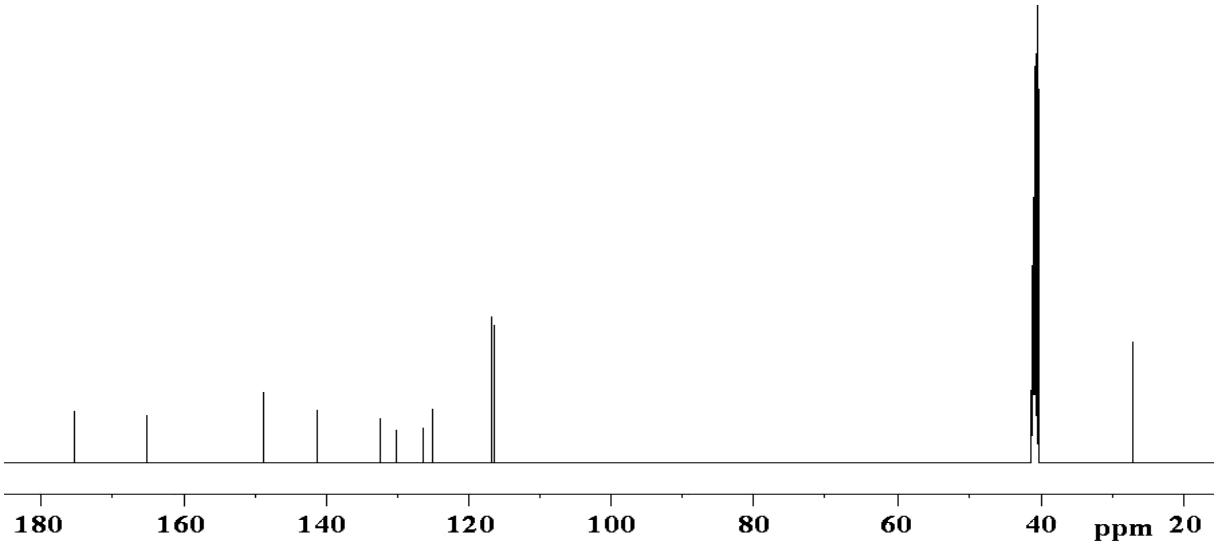


Figure 4. [13]C-NMR spectrum of poly-4-(1-(4-hydroxyphenyl)ethylidenamino)phenol

3.3. Thermal analyses of 4-HPEAP and P-4-HPEAP

TG/DTA curves of monomer and polymer were given in Fig.5 and 6. The initial degradation temperature, 50% and 96.45% weight loss of 4-HPEAP was found to be 115, 242°C and 900°C, respectively. According to DTG curve, thermal degradation of 4-HPEAP was formed at the two steps. The weight loss of the first step was found as 58.44% between 120-295°C. The weight loss of the second step was found as 38.0% between 295-900°C. According to DTA analysis, exothermic peak observed in 101, 150 and 205°C. According to DTG analysis, T_{max} values of monomer were observed in 201 and 387°C. The initial degradation temperature, 50% and 83.48% weight loss of P-4-HPEAP was found to be 151, 230°C and 900°C, respectively. Because of long conjugated band systems, polymer demonstrated higher resist against high temperature than monomer. According to TG analysis, both initial degradation temperature of P-4-HPEAP was higher than monomer and it was more stable than monomer through to temperature and thermal decomposition. Because was formed carbines residue at high amount such as 16.52% at 900°C. According to DTA analysis, the glass transition temperature (T_g) of polymer was observed in 164°C. According to DTG analysis, T_{max} value of polymer was observed in 172°C.

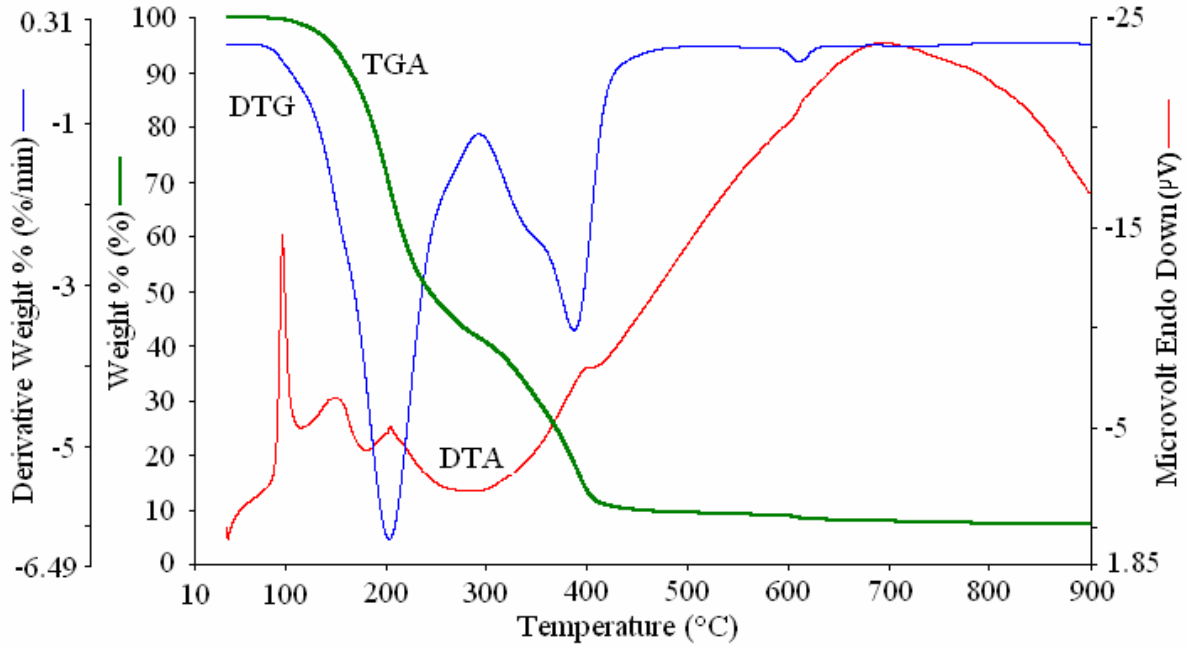


Figure 5. TG-DTG-DTA curves of 4-(1-(4-hydroxyphenyl)ethylidenamino)phenol

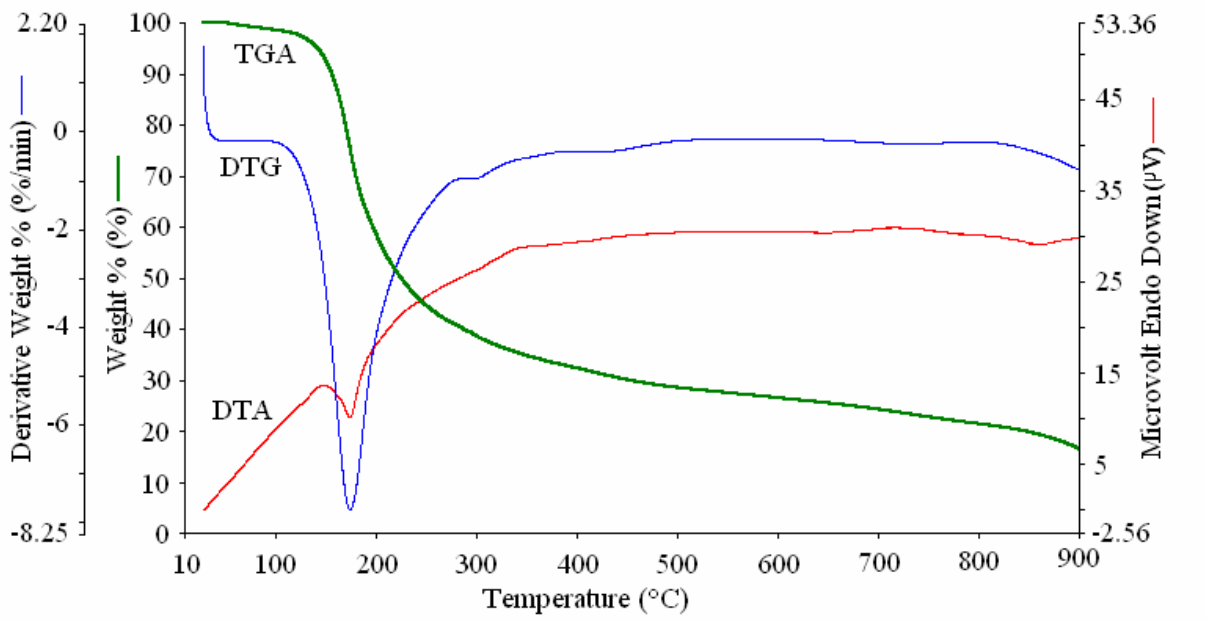


Figure 6. TG-DTG-DTA curves of poly-4-(1-(4-hydroxyphenyl)ethylidenamino)phenol

3.4. Electrochemical Properties of 4-HPEAP and P-4-HPEAP

The voltammetric measurements of 4-HPEAP and P-4-HPEAP were carried out in acetonitrile and DMSO, respectively. The HOMO, LUMO energy levels and electrochemical energy gaps ($E_g^{'}$) were calculated from oxidation and reduction onset values and are shown in Figure 7. The HOMO, LUMO energy levels and electrochemical energy gaps ($E_g^{'}$) of 4-HPEAP and P-4-HPEAP were found to be -6.30, -6.15; -2.41, -2.57; 3.89 and 3.58 eV, respectively. The electrochemical analyses results of 4-HPEAP and P-4-HPEAP showed to be lower band gap values of polymer according to monomer. Band theory is used for explaining conductivity mechanism. According to band theory, the increase in energy level ($E_g^{'}$) between full molecule orbital and empty molecule orbital can be make difficult of passing electrons from full molecule orbital to empty molecule orbital. In addition, electrochemical band gap values of 4-HPEAP and P-4-HPEAP were found as 3.89 and 3.58 eV. This result has demonstrated to be lower of the difference between HOMO and LUMO energy levels of P-4-HPEAP according to 4-HPEAP.

The absorption spectra of 4-HPEAP and P-4-HPEAP were recorded by using methanol and DMSO at 25°C (Fig. 8) and λ_{max} (nm) and E_g (eV) values of 4-HPEAP and P-4-HPEAP were found to be 289, 296 nm and 3.56 and 3.47, respectively. Both electrochemical energy gaps

($E_g^{'}$) and optical band gap values of 4-[(2-hydroxybenzylidene)amino]benzoic acid and poly-4-[(2-hydroxybenzylidene)amino]benzoic acid had been determined by CV technique [28]. The optical band gaps value of 4-HPEAP is higher than P-4-HPEAP. This results combines with electrochemical energy gaps ($E_g^{'}$) value which obtained from calculation from electrochemical oxidation and reduction potentials. The band gap value of polymer was low at the comparison with band gap of monomer.

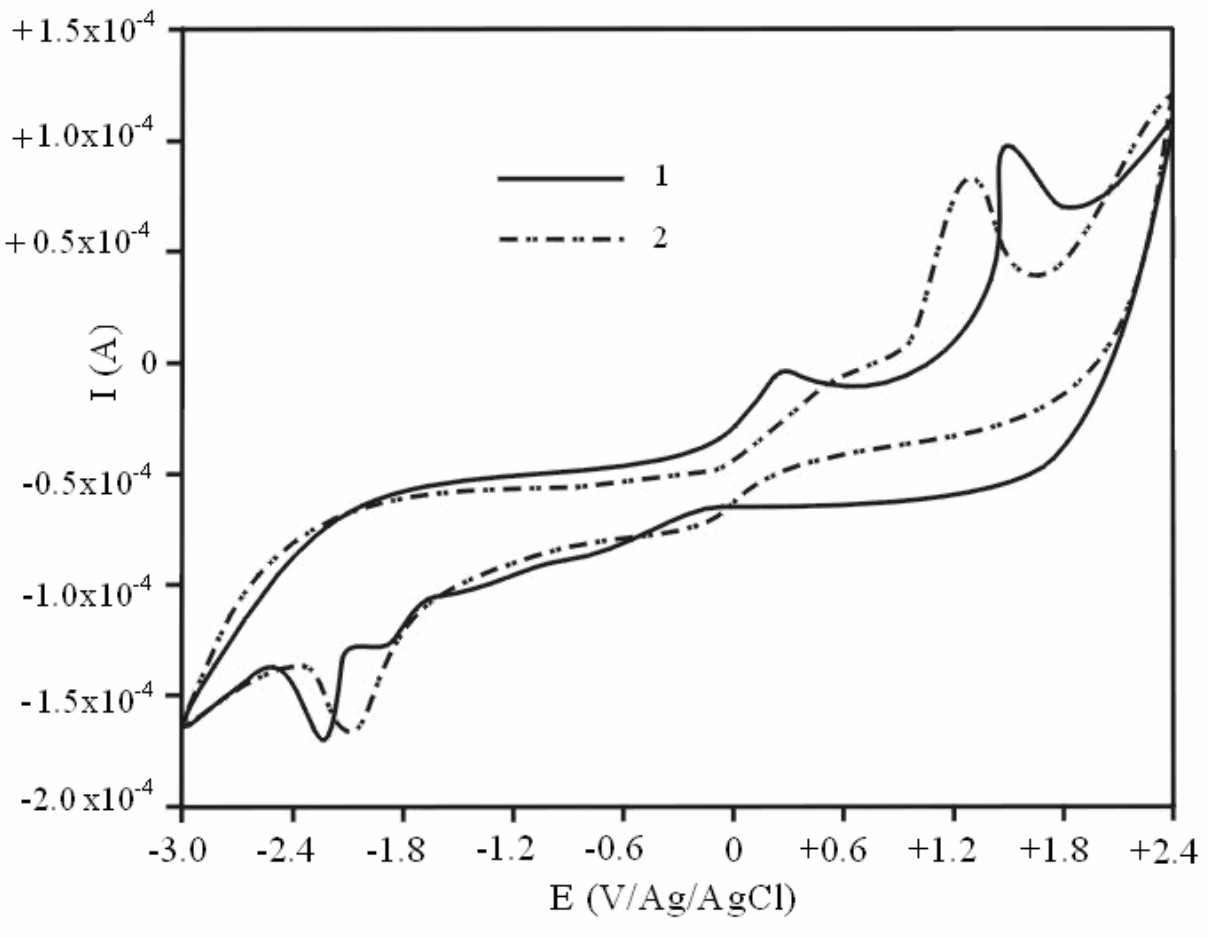


Figure 7. Cyclic voltammograms of 4-HPEAP (1) and P-4-HPEAP (2) (cyclic voltammograms measured *vs*. Ag/AgCl)

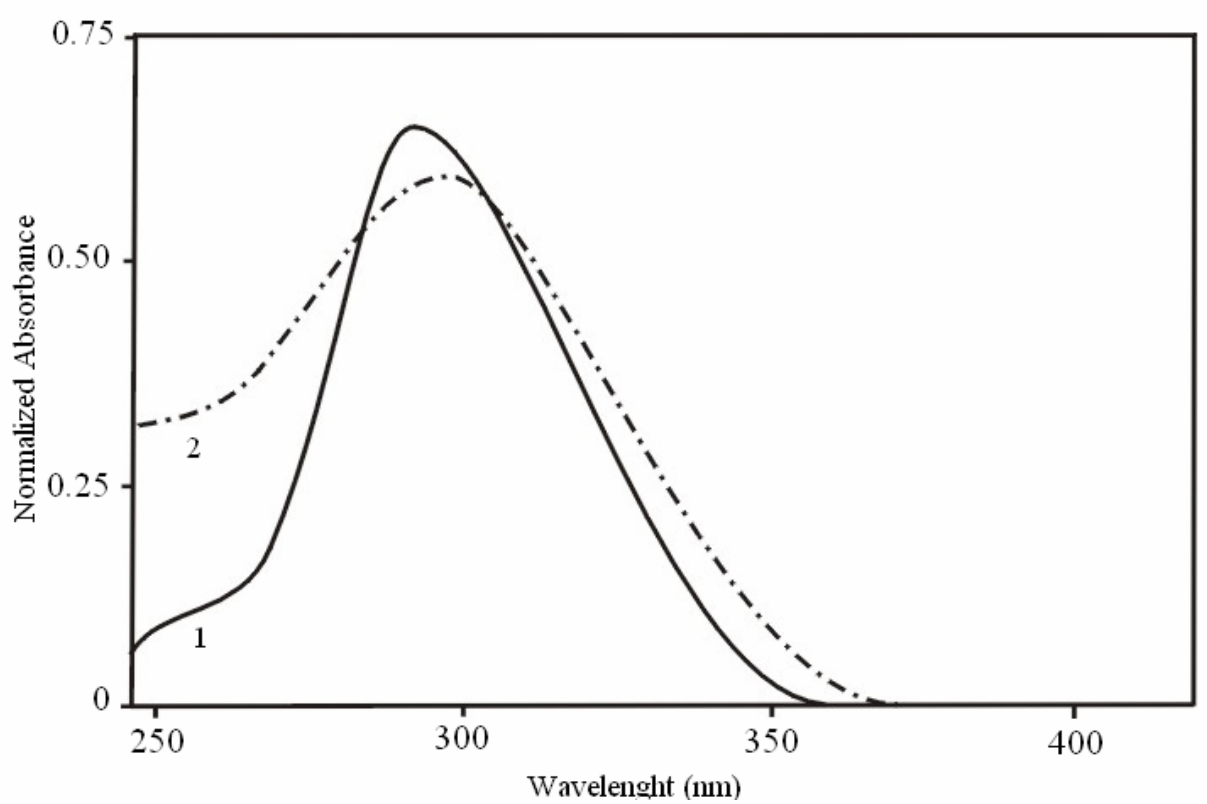
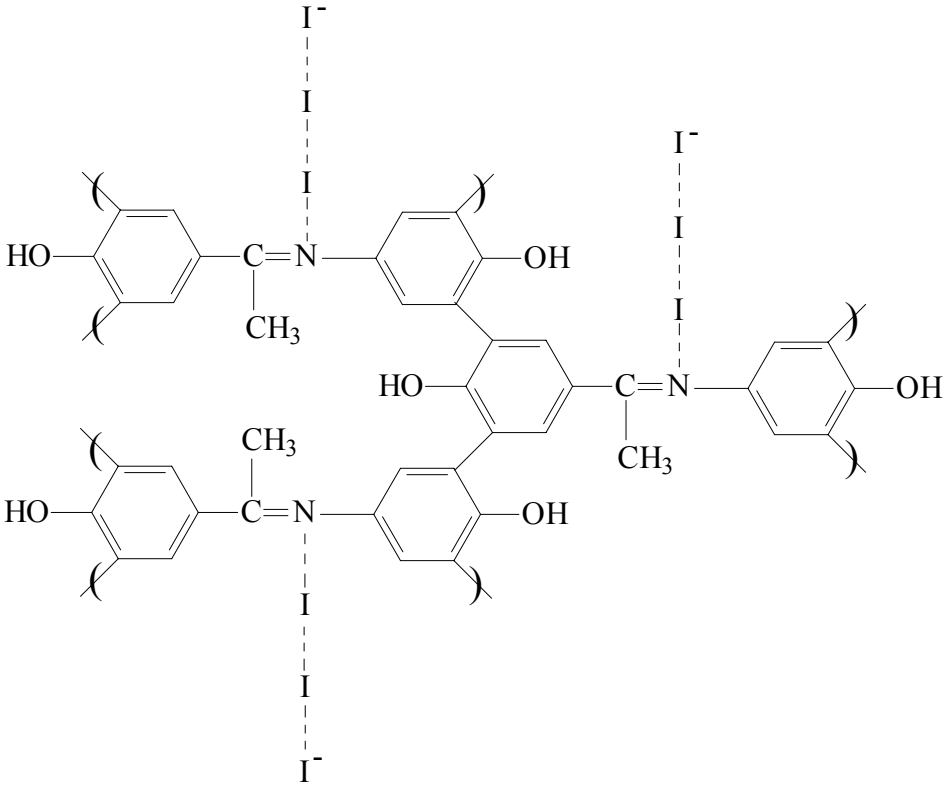


Figure 8. Absorption spectra of 4-HPEAP (1) and P-4-HPEAP (2)

Before conductivity value from doped with iodine of polymer was measured as 10^{-ll}-10^{-10}S/cm. When doped with iodine, their conductivities could be increased by about four orders of magnitude (up to 10^{-4} S/cm). Figure 9 show results of P-4-HPEAP doped with iodine at various times at 25°C. In the doping of P-4-HPEAP with iodine, it was found that the conductivity of P-4-HPEAP first increases greatly with doping time, but then tends to level-off. The maximal conductivity of polymer was 1.55 x 10^{-7} S/cm. The increasing conductivity could indicate that a charge-transfer complex between P-4-HPEAP and dopant iodine is continuously formed. Consequently, Figure 9 not only shows the conductivity/doping time relationship but also indicates how quickly the doping reaction takes place. The experiments showed that a longer doping time is needed to obtain the maximal conductivity. As a result, the conductivity/doping time curve varies with doping conditions. In order to exclude the influence of doping conditions, the conductivity of doped P-4-HPEAP has been related with doping extent. Diaz *et al.* had been suggested the conductivity mechanisms of Schiff base polymers for doping with iodine [25, 29]. Nitrogen is a very electronegative element and it is capable of coordinating an iodine molecule. Coordination of iodine during P-4-HPEAP doping is as follows (Scheme 3): Sakai had been suggested to be on nitrogen atom of

coordination of iodine with Schiff base polymers [30-32]. The conductivity value of P-4-HPEAP before doping with iodine was lower.



Scheme 3. Coordination of iodine during P-4-HPEAP doping

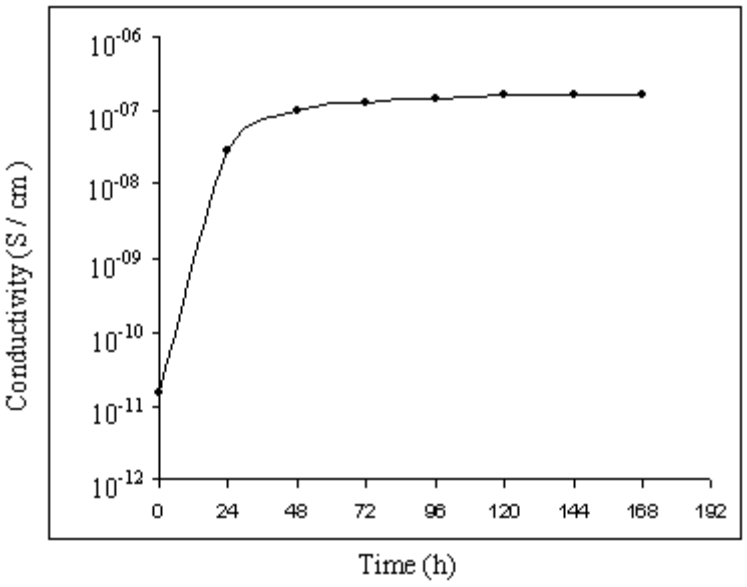


Figure 9. Electrical conductivity of I_2-doped P-4-HPEAP vs. doping time at 25°C

4. Conclusion

The oxidative polycondensation reaction conditions of 4-[1-(4-hydroxyphenyl)ethylidenamino]phenol (4-HPEAP) by using oxidants such as air O_2, H_2O_2 and NaOCl were studied in an aqueous alkaline medium between 30 and 90°C. At the optimum reaction conditions, the yield of poly-4-[1-(4-hydroxyphenyl)ethylidenamino]phenol (P-4-HPEAP) was found to be 95%, 51% and 96% for air O_2, H_2O_2 and NaOCl oxidants, respectively. According to the SEC analysis, the number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of P-4-HPEAP were found to be $3.00 \cdot 10^3$, 3300 g mol^{-1} and 1.100, using H_2O_2 and 1400, 1550 g mol^{-1} and 1.107, using air O_2 and 5000, 5470 g mol^{-1} and 1.094, using NaOCl, respectively. According to TG analyses, the weight losses of 4-HPEAP and P-4-HPEAP were found to be 96.86% and 83.48% at 900°C, respectively. Also, electrical conductivity of the P-4-HPEAP was measured, showing that the polymer is typical semiconductors. The band gap value for the monomer is higher than that for the polymer.

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Synthesis, characterization, thermal degradation and electrical conductivity of oligo-2-[(thien-2-yl-methylene)]aminophenol and oligomer-metal complexes

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ABSTRACT

The optimum reaction conditions of the oxidative polycondensation of 2-[(thien-2-yl-methylene)]aminophenol (2-TMAP) has been accomplished by using air O_2, H_2O_2 and NaOCl oxidants in an aqueous alkaline medium between 20 and 90°C. The structures of the monomer and oligomer were confirmed by FT-IR, UV-vis, ^{1}H-NMR and ^{13}C-NMR and elemental analysis. TGA-DTA, size exclusion chromatography (SEC) techniques and solubility tests were applied for characterization. The ^{1}H-NMR and ^{13}C-NMR data shows that the polymerization proceeded with C-C and C-O-C coupling system from *ortho* and *para* positions and oxyphenylene. The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) values of O-2-TMAP were determined with SEC measurements. Thermal analyses of oligomer-metal complex compounds of O-2-TMAP with Cd^{+2}, Co^{+2}, Cu^{+2}, Zn^{+2}, Fe^{+2}, Zr^{+4}, Ni^{+2} and Pb^{+2} ions were investigated in N_2 atmosphere between 15-1000°C. The highest occupied molecular orbital and the lowest unoccupied molecular orbital of monomer and oligomer were determined from the onset potentials for n-doping and p-doping, respectively. Optical band gaps (E_g) of 2-TMAP and O-2-TMAP and oligomer-metal complex compounds determined according to UV-vis measurements. Also, electrical conductivities of O-2-TMAP and its metal complexes measured with four-point probe technique.

Key words: Air O_2; NaOCl; oligo-2-[(thien-2-yl-methylene)]aminophenol; oxidative polycondensation; thermal analysis; electrical conductivity; oligomer-metal complex compounds.

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INTRODUCTION

Polyimines including conjugated bonding and active hydroxyl group have been studied for more than 60 years and they have been used in various fields. They have useful properties such as paramagnetism, semi conductivity, electrochemical cell and resisting to high energy. Because of these properties, they are used to prepare composites having high resistance at high temperature, thermostabilisatiors, graphite materials, epoxy oligomer and block copolymers, photo resists, materials, which are antistatic and enduring to flame[1–8]. These compounds were profited to new properties to their structures adding to other functional groups. Schiff based derivatives of oligophenols have antimicrobial properties[9, 10]. In addition, oligophenols were used to prepare inhibitors with resistance at high temperature, thermostabilizers[11, 12]. Polymer metal complex compounds have useful properties such as catalytic activity, thermal stability, ion selectivity, conductivity and anti-microbial properties. Catalytic activity of a styrene-allylchloride copolymer supported cobalt (II) Schiff base complex compound was studied by Gupta *et al*.[13]. The thermal and conductivity properties of Zn (II), Ni (II), Th (II), Cd (II), Mg (II) complex compounds of poly(8-acryloxyquinoline) were studied by Kaliyappan *et al*.[14]. The thermal and anti-microbial properties of oligophenols with Schiff base substitute and their oligomer metal complex compounds were investigated by Kaya *et al*.[15]. Anti-microbial activity of oligo-N-2-aminopyridinylsalicylaldimine and some oligomer-metal complexes was studied by Kaya *et al*.[16]. The thermal stability of poly(acryloyl benzoic hydrazide) and its complexes with some transition metals was examined by Gad *et al*.[17]. The thermal decomposition behavior of poly(acrylic acid) and its metal complexes were studied by Sebastian *et al.*[18]. Kaya *et al.* studied thermal degradation of oligo-2-[(4-fluorophenyl) imino methylene] phenol and some of its oligomer-metal complexes[19]. The conducting properties of poly(2-hydroxy-4-acryloxyacetophenone-phenylimine), poly(2-hydroxy-4-acryloyloxyacetophe none-N-phenylimine-co-methacrylate) and their metal complexes were studied by Thamizharasi *et al*.[20]. More functional oligophenols may be used to clean poisonous heavy metals in industrial wastewater. In addition, Schiff base compounds had been used for the determination of transition metals in some natural food samples[21]. Therefore, the synthesis of this type oligomer and oligomer-metal complexes is very important in analytic, environmental and food chemistry.

In this study, we have investigated the effects of different parameters such as temperature, reaction time and initial concentration of NaOCl and alkaline for oligo-2-[(thien-2-yl-

methylene)]aminophenol. The structures of 2-TMAP and O-2-TMAP were characterized by using FT-IR, UV-vis, ^{1}H-NMR, ^{13}C-NMR, elemental analysis, TGA and DTA. Molecular weight distribution of O-2-TMAP was determined by SEC technique. Electrochemical properties of monomer and oligomer were determined by cyclic voltammetry and the HOMO, LUMO energy levels and electrochemical energy gaps ($E_g^{'}$) were calculated from oxidation and reduction onset values. However, the optical band gaps (E_g) of monomer, oligomer and oligomer-metal complexes were calculated from their absorption edges. Electrical properties of doped and undoped oligomer and oligomer-metal complex compounds were determined by four-point probe technique at a room temperature and atmospheric pressure. An important increase of the conductivity was attained when iodine was employed as doping agent.

MATERIALS AND METHODS

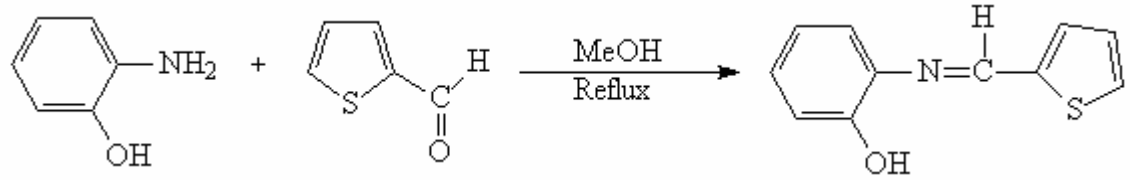
Materials

Thiophene-2-carboxyaldehyde, 2-aminophenol, methanol, ethanol, acetonitrile, toluene, acetone, ethyl acetate, heptane, CCl_4, $CHCl_3$, tetrahydrofurane (THF), dimethylformamide (DMF), dimethylsulfoxide (DMSO), H_2SO_4 (98%), NaOH, KOH, H_2O_2 (30% aqueous solution) and hydrochloric acid (HCl, 37%), Cu $(CH_3COO)_2$ H_2O, Pb $(CH_3COO)_2$ $3H_2O$, Co $(CH_3COO)_2$ $4H_2O$, Zn $(CH_3COO)_2$ $2H_2O$, Cd $(CH_3COO)_2$ $2H_2O$, Ni $(CH_3COO)_2$ $4H_2O$, $FeCl_3$ $6H_2O$ and $ZrCl_4$ were supplied from Merck Chemical Co. and they were used as received. Sodium hypo chloride (NaOCl), (30% aqueous solution) was supplied from Paksoy Chemical Co. (Turkey). 2-[(thien-2-yl-methylene)]aminophenol (2-TMAP) was synthesized to condensation reaction of thiophene-2-carboxyaldehyde with 2-aminophenol and recrystallized from methanol.

Synthesis of 2-[(thien-2-yl-methylene)]aminophenol (2-TMAP)

2-[(thien-2-yl-methylene)]aminophenol was prepared by the condensation of thiophene-2-carboxyaldehyde (1.22 g, 0.01 mol) with 2-aminophenol (1.37 g, 0.01 mol) in methanol (25 ml) achieved by boiling the mixture under reflux for 3h at 70°C (Scheme 1). The precipitated 2-[(thien-2-yl-methylene)]aminophenol was filtered, recrystallized from methanol and dried in vacuum desiccators.

^{1}H-NMR (DMSO-d_6): δ ppm, 9.12 (s, 1H, –OH), 8.84 (s, 1H, –CH=N–), 6.97 (d, 1H, Ar-Ha), 7.08 (t, 1H, Ar-Hb), 6.82 (t, 1H, Ar-Hc), 7.21 (d, 1H, Ar-Hd), 7.13 (d, 1H, -C=C-He), 7.67 (t, 1H, -C=C-Hf), 7.78 (d, 1H, -C=C-Hg). ^{13}C-NMR (DMSO-d_6): ppm, 151.15 (C1-ipso-OH), 116.60 (C2-H), 128.55 (C3-H), 127.53 (C4-H), 120.05 (C5-H), 138.38 (C6-ipso), 153.74 (C7-H), 143.39 (C8-ipso), 133.47 (C9-H), 120.86 (C10-H), 131.38(C11-H).

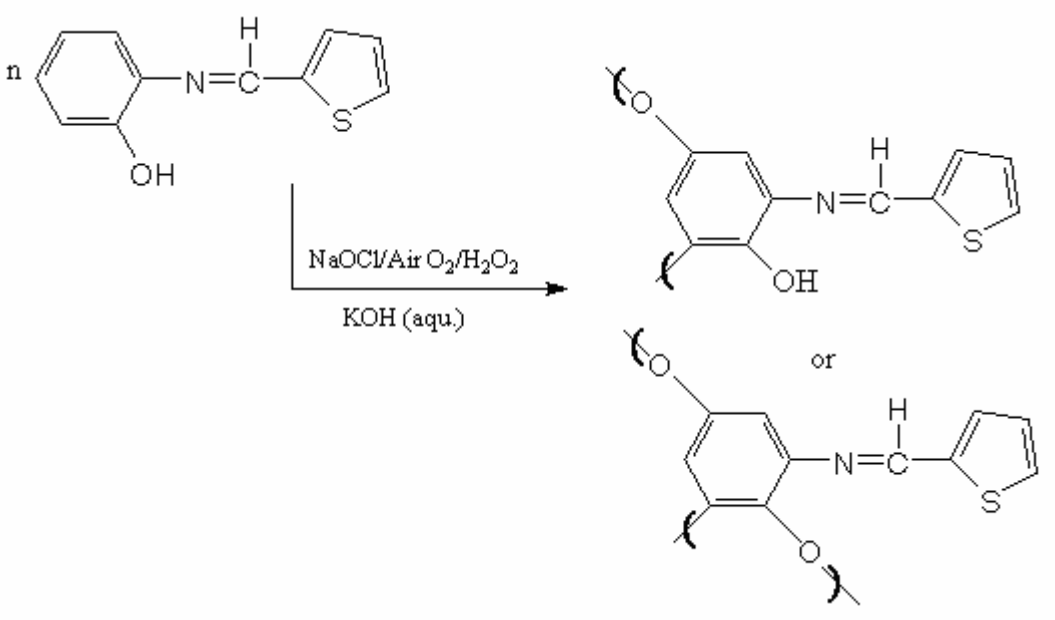


Scheme 1. Synthesis of 2-[(thien-2-yl-methylene)]aminophenol

Synthesis of O-2-TMAP with NaOCl, H_2O_2 and air O_2 oxidants in aqueous alkaline medium

O-2-TMAP was synthesized through oxidative polycondensation of 2-[(thien-2-yl-methylene)]aminophenol with aqueous solutions of NaOCl (30%), H_2O_2 (30%) and air O_2, respectively[11]. The 4-TMAP (0.187 g 0.001 mol) was dissolved in an aqueous solution of KOH (10%, 0.001 mol) and placed into a 50-ml three-necked round-bottom flask (Scheme 2). It was fitted with a condenser, thermometer, stirrer and an addition funnel containing NaOCl or H_2O_2. After heating to 20 °C, NaOCl and H_2O_2 were added drop by drop over about 20 min. The reaction mixtures were stirred at the various temperatures and durations (Table 1 and 2). Air O_2 was passed into an aqueous solution of KOH (20%) before being sent through the reaction tube to prevent water loss in the reaction mixture and to neutralize CO_2 in the air (Scheme 2). The reaction mixtures were cooled to room temperature, and then 0.001 mol HCl (37%) was added. For the separation of mineral salts and unreacted monomers, the mixture was filtered and washed with hot water (3 x 25 ml) and then dried in a vacuum oven at 60°C.

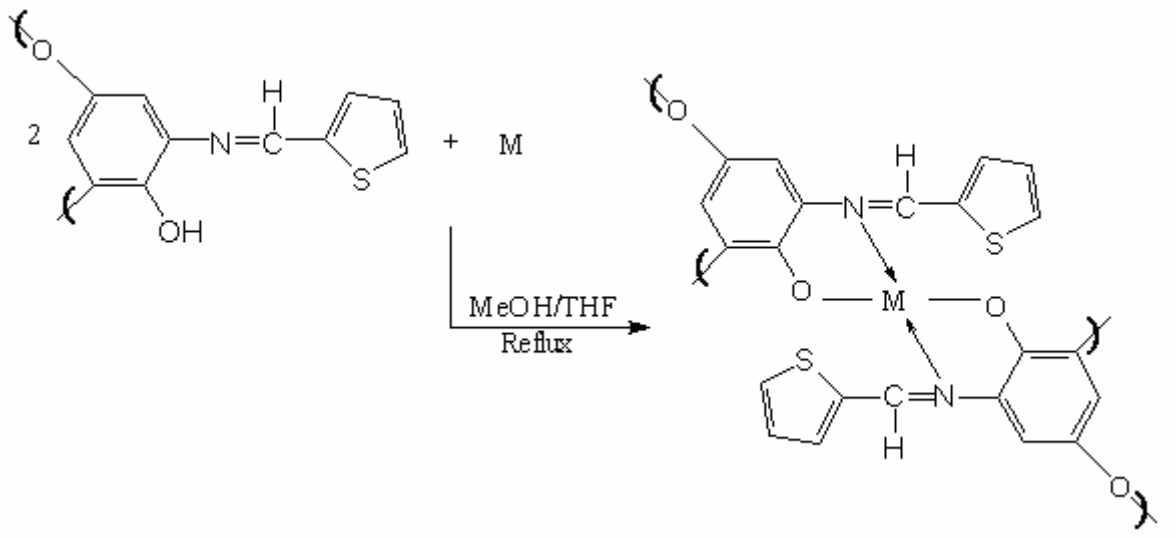
^{1}H-NMR (DMSO-d_6): δ ppm, 10.17 (s, 1H, –OH), 9.55 (s, 1H, –CH=N–), 6.70 (terminal proton, d, 1H, Ar-Ha), 6.91 (d, 1H, Ar-Hb), 6.40 (terminal proton, d, 1H, Ar-Hc), 7.46 (d, 1H, Ar-Hd), 7.30 (d, 1H, -C=C-He), 7.75 (t, 1H, -C=C-Hf), 8.79 (d, 1H, -C=C-Hg). ^{13}C-NMR (DMSO-d_6): ppm, 160.24 (C1-ipso-OH), 126.19 (C2-ipso), 130.95 (C3-H), 129.95 (C4-ipso), 120.00 (C5-H), 144.76 (C6-ipso), 174.76 (C7-H), 149.52 (C8-ipso), 136.43 (C9-H), 121.17 (C10-H), 135.24 (C11-H), 134.29 new peak.



Scheme 2. Synthesis of oligo-2-[(thien-2-yl-methylene)]aminophenol

Syntheses of oligo-2-[(thien-2-yl-methylene)]aminophenol-metal complexes

Solutions of Cu $(AcO)_2$ H_2O, Zn $(AcO)_2.2H_2O$, Cd $(AcO)_2$ $2H_2O$, $Pb(AcO)_2$ $3H_2O$ and Co $(AcO)_2$ $4H_2O$ (1 mmol) in MeOH (10 ml) were added to a solution of O-2-TMAP (2 mmol/unit) in THF (20 ml). The mixture was stirred and heated at 70°C for 5h (Scheme 4). The precipitated complexes were filtered, washed with cold MeOH/THF (1:1) and then dried in a vacuum oven at 60°C.



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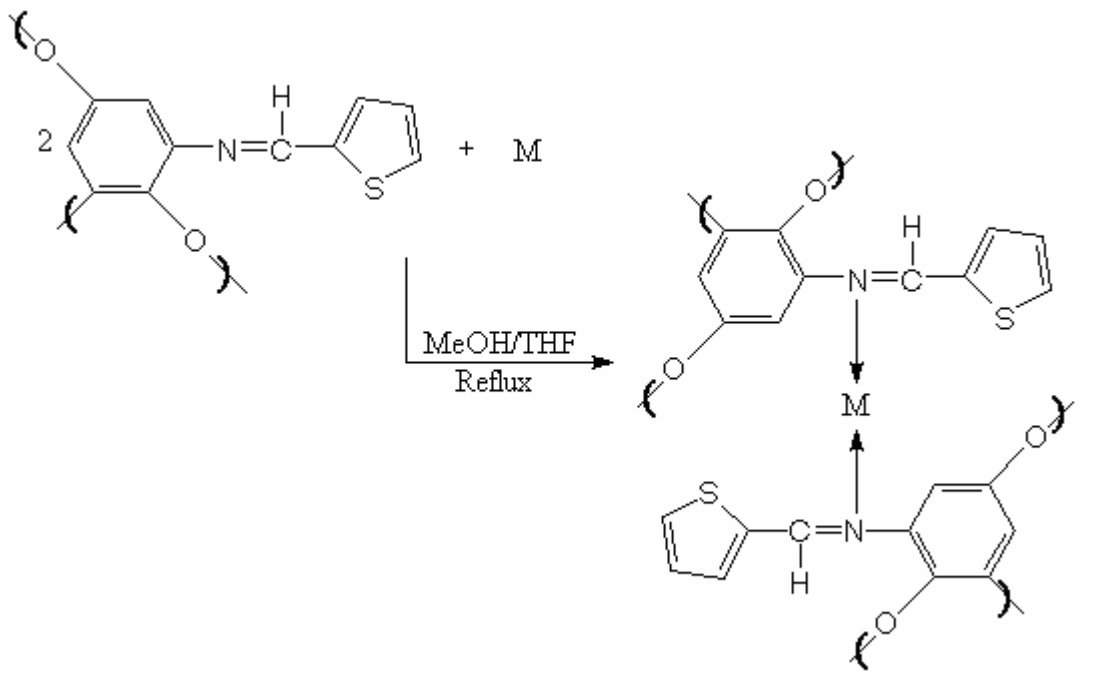


Scheme 3. Syntheses of oligo-2-[(thien-2-yl-methylene)]aminophenol-metal compounds

Electrochemical Properties

Cyclic voltammetry (CV) measurements were carried out with a CH instruments 660C Electrochemical Analyzer at a potential scan rate of 20 mV/s. All the experiments were performed in dry box under Ar atmosphere at room temperature. The electrochemical potential of Ag was calibrated with respect to the ferrocene/ferrocenium (Fc/Fc^+) couple. The half-wave potential ($E^{1/2}$) of (Fc/Fc^+) measured in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) acetonitrile solution is 0.39 V vs. Ag wire or 0.38 V vs. supported calomel electrode (SCE). The voltammetric measurements were carried out for monomer and oligomer in acetonitrile and DMSO, respectively[22]. The HOMO, LUMO energy levels and electrochemical energy gaps *(E_g')* were calculated from oxidation and reduction onset values.

Electrical Properties

Conductivity was measured on a Keithley 2400 Electrometer. The pellets were pressed on hydraulic press developing up to 1687.2 kg/cm^2. Iodine doping was carried out by exposure of the pellets to iodine vapor at atmospheric pressure and room temperature in desiccator[7].

Optical Properties

The optical band gaps (E_g) of monomer and oligomer compounds were calculated from their absorption edges. Ultraviolet-visible (UV-vis) spectra were measured by Perkin Elmer

Lambda 25. The absorption spectra of monomer and oligomer were recorded by using methanol and DMSO, respectively, at 25°C.

Solubility and Characterization Techniques

While 2-TMAP was bright yellow color in crystal form and was completely soluble in organic solvents such as methanol, acetone, acetonitrile, dioxane, THF, ethyl acetate, chloroform, CH_2Cl_2, DMF, and DMSO but it was partly soluble in toluene and ethanol. 2-TMAP was insoluble in heptane and hexane. O-2-TMAP was dark brown in powder form and was completely soluble in organic solvents such as THF, DMF and DMSO. O-2-TMAP was partly soluble in dioxane. O-2-TMAP was insoluble in chloroform, acetone, toluene, acetonitrile, ethyl acetate, heptane and hexane. Oligomer-metal complex compounds were insoluble in benzene, toluene, heptane, hexane, $CHCl_3$, ethyl acetate, dioxane, CH_2Cl_2, THF, DMF, CCl_4 and acetone. These oligomer-metal complex compounds were partly soluble in DMSO.

The infrared spectra were measured by a Perkin Elmer FT-IR Spectrum One. The FT-IR spectra were recorded using universal ATR sampling accessory (4000-550 cm^{-1}). Elemental analysis was carried out with a LECO CHNS 932. UV-vis spectra of 2-TMAP, O-2-TMAP and oligomer-metal complex compounds were recorded by using methanol and DMSO, respectively. 2-TMAP and O-2-TMAP were characterized by using ^{1}H-NMR and ^{13}C-NMR spectra (Bruker Avance DPX-400 and 100.6 MHz, respectively) recorded at 25°C by using deuterated DMSO as a solvent. Tetramethylsilane was used as internal standard. Thermal data were obtained by using Perkin Elmer Diamond Thermal Analysis. The TG-DTA measurements were made between 20-1000°C (in N_2, rate 10°C/min). The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index (PDI) were determined by size exclusion chromatography (SEC) techniques of the Shimadzu Co. For SEC investigations we used an SGX (100 Å and 7 nm diameter loading material) 3.3 mm i.d. x 300 mm column; eluent: DMF/methanol (v/v, 4/1, 0.4 ml/min), polystyrene standards. A refractive index detector (at 25^{o}C) was used to analyze the product. Metal analyses of oligomer-metal complex compounds were carried out by AAS Shimadzu 6200 in a solution prepared by decomposition of the complex compounds with HNO_3 followed by dilution with deionized water.

RESULTS AND DISCUSSION

The investigation of synthesis conditions of O-2-TMAP

Oligo-2-[(thien-2-yl-methylene)]aminophenol synthesized in an aqueous alkaline medium by air O_2, H_2O_2 and NaOCl oxidants. When 2-TMAP interacted with oxidants such as air O_2, H_2O_2 and NaOCl, it immediately precipitated brown phenoxy radicals with adding to the alkaline. Therefore, O-2-TMAP synthesized in an aqueous alkaline medium at using without any oxidant. The oxidative polycondensation reaction conditions of 2-TMAP are given in Table 1, for 30% NaOCl solution. The yield of O-2-TMAP was 53% at optimum conditions such as $[2\text{-TMAP}]_o = [KOH]_o = 0.0714$ and $[NaOCl]_o = 0.261$ mol/L, at 30°C for 1 h. The yield of O-2-TMAP was 25% in the reaction conditions such as $[2\text{-TMAP}]_o = [KOH]_o = 0.0714$ and $[NaOCl]_o = 0.261$ mol/L at 90°C for 1 h. Under the same conditions, when the molar amount of oxidant increased, the total yield of O-2-TMAP was found to be 41% (see Table 1). While the yield of O-2-TMAP was 53% at 30°C for 1h, it was 25% at 90°C for 1h. The reason of this may be depolymerization to monomer of the oligomer at high temperatures. As may be seen from Tables 1 and 2, the yield of the oligomer was dependent upon some factors such as temperature, initial concentrations of oxidant and reaction times.

The oxidative polycondensation reaction conditions of 2-TMAP with 30% H_2O_2 solution in aqueous alkaline medium are given in Table 2. The yield of O-2-TMAP was 28% at optimum conditions such as $[2\text{-TMAP}]_0 = 0.0714$, $[KOH]_0 = 0.1428$ and $[H_2O_2]_0 = 0.07$ mol/L, at 90°C for 3h. Under the same conditions, when molar amount of alkaline increased, total yield of O-2-TMAP changed from 21% to 28%. The yield of O-2-TMAP was 15% at the reaction conditions such as $[2\text{-TMAP}]_0 = [KOH]_0 = 0.0714$ and $[H_2O_2]_0 = 0.07$ mol/L at 30°C for 3h. The yield of O-2-TMAP was 25% using the air O_2 medium for 3h at 30°C. The various oxidative polycondensation reaction conditions of 2-TMAP with air O_2 are given in Table 2. The yield of O-2-TMAP was 34% at optimum conditions such as $[2\text{-TMAP}]_o = [KOH]_o = 0.0714$ mol/L at 50°C for 3h. The yield of O-2-TMAP was 15% in reaction conditions such as $[2\text{-TMAP}]_o = [KOH]_o = 0.0714$ mol/L at 50°C for 5h. H_2O_2 oxidant has demonstrated less activity than NaOCl and air O_2 at the formation of oligomer of 2-TMAP. Under the same conditions, when reaction times increasing decreased the yield of products.

Table 1. The oxidative polycondensation reaction parameters of 2-[(thien-2-yl-methylene)]aminophenol[a] with NaOCl in aqueous KOH

Sample Number	Temp., (^{o}C)	Times (h)	$[KOH]_0$ (mol L^{-1})	$[NaOCl]_0$ (mol L^{-1})	Yield of O-2-TMAP, %
1	20	1	0.0714	0.261	48
2	30	1	0.0714	0.261	53
3	30	1	0.1428	0.261	19
4	30	1	0.0714	0.522	41
5	30	3	0.0714	0.261	34
6	30	5	0.0714	0.261	48
7	30	10	0.0714	0.261	33
8	30	15	0.0714	0.261	31
9	30	20	0.0714	0.261	30
10	40	1	0.0714	0.261	50
11	40	3	0.0714	0.261	41
12	40	5	0.0714	0.261	35
13	40	10	0.0714	0.261	13
14	40	15	0.0714	0.261	41
15	40	20	0.0714	0.261	40
16	50	1	0.0714	0.261	48
17	60	1	0.0714	0.261	43
18	70	1	0.0714	0.261	29
19	80	1	0.0714	0.261	23
20	90	1	0.0714	0.261	25

a= Concentration of $[2\text{-TMAP}]_0$ was used as 0.0714 mol L^{-1}.

Table 2. The oxidative polycondensation reaction parameters of 2-[(thien-2-yl-methylene)]aminophenol[a] with H_2O_2 (sample number: 1–7) and air O_2 oxidants (sample number: 8–18) in aqueous KOH

Sample Number	Temp., (^oC)	Times (h)	$[KOH]_0$ (mol L^{-1})	$[H_2O_2]_0$ (mol L^{-1}) or air O_2 (L h^{-1})	Yield of O-2-TMAP, %
1	90	3	0.0714	0.07	21
2	90	3	0.1428	0.07	28
3	90	3	0.0714	0.14	14
4	80	3	0.0714	0.07	20
5	70	3	0.0714	0.07	18
6	60	3	0.0714	0.07	23
7	30	3	0.0714	0.07	15
8	80	3	0.0714	8.5	8
9	70	3	0.0714	8.5	12
10	60	3	0.0714	8.5	20
11	50	3	0.0714	8.5	34
12	50	5	0.0714	8.5	15
13	50	10	0.0714	8.5	14
14	50	15	0.0714	8.5	11
15	50	20	0.0714	8.5	9
16	50	3	0.1428	8.5	15
17	40	3	0.0714	8.5	32
18	30	3	0.0714	8.5	25

a= Concentration of $[2\text{-TMAP}]_0$ was used as 0.0714 mol L^{-1}.

Structure of O-2-TMAP

SEC analyses of O-2-TMAP were performed at 30°C using DMF/Methanol (v/v, 4/1) as eluent at a flow rate of 0.4 ml/min. According to SEC chromatograms, the values of number-average molecular weight (M_n) and weight-average molecular weight (M_w) of O-2-TMAP were calculated according to a Polystyrene standard calibration curve and are given in Table 3. The M_n, M_w and PDI values of O-2-TMAP were found to be 3100, 5700 g mol^{-1} and 1.839, using NaOCl; 2800, 3100 g mol^{-1} and 1.107, using air O_2 and 3300, 5200 g mol^{-1} and 1.576, using H_2O_2, respectively. When reaction temperatures and reaction times increased, molecular weight distribution (MWD) of O-2-TMAP increased, but the conversion of O-2-TMAP decreased. The increasing of polymerization time, temperatures and oxidant concentrations increased the molecular weight and MWD of O-2-TMAP.

Table 3. The number average molecular weight (M_n), mass average molecular weight (M_w), polydispersity index (PDI) and % values of O-2-TMAP

	Molecular weight distribution parameters															
	Total			Fraction I				Fraction II				Fraction III				
Compounds	M_n	M_w	PDI	M_n	M_w	PDI	%	M_n	M_w	PDI	%	M_n	M_w	PDI	%	
O-2-TMAP[1]	2800	3100	1.107	1970	2340	1.187	70	2300	2640	1.148	10	33900	37100	1.094	20	
O-2-TMAP[2]	3100	5700	1.839	2000	2400	1.200	22	2900	3400	1.172	23	16300	31400	1.926	50	
O-2-TMAP[3]	3300	5200	1.576	1900	2450	1.290	15	2500	3000	1.200	36	18100	28800	1.591	49	

1= Air O_2; 2= NaOCl; 3= H_2O_2

The UV-vis spectroscopic studies were carried out with methanol and DMSO solutions of the 2-TMAP and O-2-TMAP, respectively. In the 2-TMAP spectra, K bands of phenol and C_6H_5-N= were observed, 230 nm and 269 nm, respectively. A benzene band of 2-TMAP and strength R band of -CH=N- groups were observed, 294 and 352 nm, respectively. UV-vis spectra of O-2-TMAP, K and R bands were observed, 242 nm and 313 nm, respectively. The band of -CH=N- group observed 405 nm. The UV-vis spectra shows specific bands for λ_{max}

assigned to aromatic and azomethinic π→π* transitions at about 280 and 350 nm, respectively. The shifting of the -CH=N- group band from 352 nm to 405 nm has been demonstrated for the formation of the oligomeric conjugate π system.

Elemental analyses and FT-IR data of monomer, oligomer and oligomer-metal complex compounds are given in Table 4 and 5, respectively. The FT-IR spectra of 2-TMAP and O-2-TMAP, bands of OH and –CH=N groups were observed 3298 and 1610; 3312 and 1618 cm^{-1}, respectively. For monomer and oligomer, the shifting of -CH=N- and –OH groups bands from 3298 and 1610 to 3312 and 1618 cm^{-1}, respectively, have been demonstrated for the formation of oligomeric structure. -CH=N- bonding stretching of oligomer-metal complex compounds observed in 1602-1590 cm^{-1}.

Table 4. Elemental analyses data and yields of 2-TMAP, O-2-TMAP and oligomer-metal complexes

	Calculated (%, Found)					
Compounds	**C**	**S**	**H**	**N**	**Metal**	**Yield, %**
2-TMAP	65.02 (64.86)	15.76 (15.55)	4.43 (4.35)	6.89 (6.73)	-	85
O-2-TMAP	65.67 (65.51)	15.92 (15.70)	3.48 (3.55)	6.96 (6.80)	-	53
O-2-TMAP-Cu	56.95 (56.71)	13.80 (13.68)	2.58 (2.41)	6.04 (5.86)	13.70 (13.47)	65
O-2-TMAP-Zn	56.72 (56.59)	13.75 (13.63)	2.57 (2.38)	6.02 (5.89)	14.05 (13.76)	61
O-2-TMAP-Cd	51.52 (51.37)	12.48 (12.32)	2.34 (2.21)	5.46 (5.33)	21.94 (21.63)	57
O-2-TMAP-Pb	43.47 (43.29)	10.54 (10.38)	1.98 (1.78)	4.61 (4.46)	34.12 (33.86)	77
O-2-TMAP-Co	57.52 (57.39)	13.94 (13.75)	2.61 (2.44)	6.10 (5.84)	12.84 (12.65)	66
O-2-TMAP-Fe	57.90 (57.73)	14.03 (13.82)	2.63 (2.50)	6.14 (6.00)	12.25 (12.11)	75
O-2-TMAP-Zr	53.74 (53.59)	13.02 (12.86)	2.44 (2.35)	5.70 (5.58)	18.57 (18.37)	76
O-2-TMAP-Ni	57.55 (57.39)	13.95 (13.81)	2.61 (2.47)	6.10 (5.95)	12.79 (12.59)	55

Table 5. FT-IR spectral data of 2-TMAP, O-2-TMAP and oligomer-metal complexes

	Wave number (cm^{-1})						
Compounds	**-OH**	**-CH=N**	**-C-S**	**-C=C**	**-C-O**	**Metal-O**	**Metal-N**
2-TMAP	3298	1610	744	1590, 1578,1482	1217	----	----
O-2-TMAP	3312	1618	745	1594, 1574,1482	1224	----	----
O-2-TMAP-Cu	3332	1600	745	1565, 1530, 1477	1250	560	641
O-2-TMAP-Zn	3326	1602	751	1552, 1496, 1417	1256	572	630
O-2-TMAP-Cd	3352	1602	750	1548, 1487, 1416	1246	570	621
O-2-TMAP-Pb	3336	1600	751	1574, 1532, 1484	1246	550	660
O-2-TMAP-Co	3340	1600	752	1592, 1497, 1455	1253	580	665
O-2-TMAP-Fe	3314	1595	751	1545, 1484, 1462	1243	580	640
O-2-TMAP-Zr	3310	1598	753	1551, 1493, 1464	1250	576	640
O-2-TMAP-Ni	3320	1590	749	1570, 1545, 1490	1253	572	635

In order to identify the structures of monomer and oligomer, the ^{1}H-NMR spectra were recorded in DMSO-d_6. ^{1}H-NMR and ^{13}C-NMR spectra of the monomer are given in Figs. 1-3, respectively. In the ^{1}H-NMR spectra of 2-TMAP and O-2-TMAP, the signals of phenyl –OH and –CH=N groups were observed in 9.12 and 8.84 ppm and 10.17 and 9.55 ppm, respectively. The ^{1}H-^{13}C-NMR spectra results of the O-2-TMAP confirm the formation of oligomer units. The substitute phenols and azomethine group contains derivatives were polymerized, and the results are reported in the literature[23, 22]. The peak values for C1-*ipso*, C7, C2 and C4 observed in δ=151.15, 153.74, 116.60 and δ=127.53 ppm in the monomer and δ=160.24, 174.76, 126.19 and δ=129.95 ppm in the oligomer, respectively. It is seen that Figure 2a, the new a peak observed in 134.29 ppm. The oxyphenylene are involved in the formation of free radicals leading to oligomer formation and they appeared to be involved in bond formation. Thus, the phenyl rings in the oligomer appears to be linked primarily at *ortho* and *para* positions and oxyphenylene. The ^{1}H-NMR and ^{13}C-NMR results showed that the polymerization of 2-TMAP proceeded by C-C and C-O-C coupling from *ortho* and *para* positions according to –OH group and oxyphenylene, respectively. According to spectral analyses, a segment of O-2-TMAP chain may be formulated as Scheme 2.

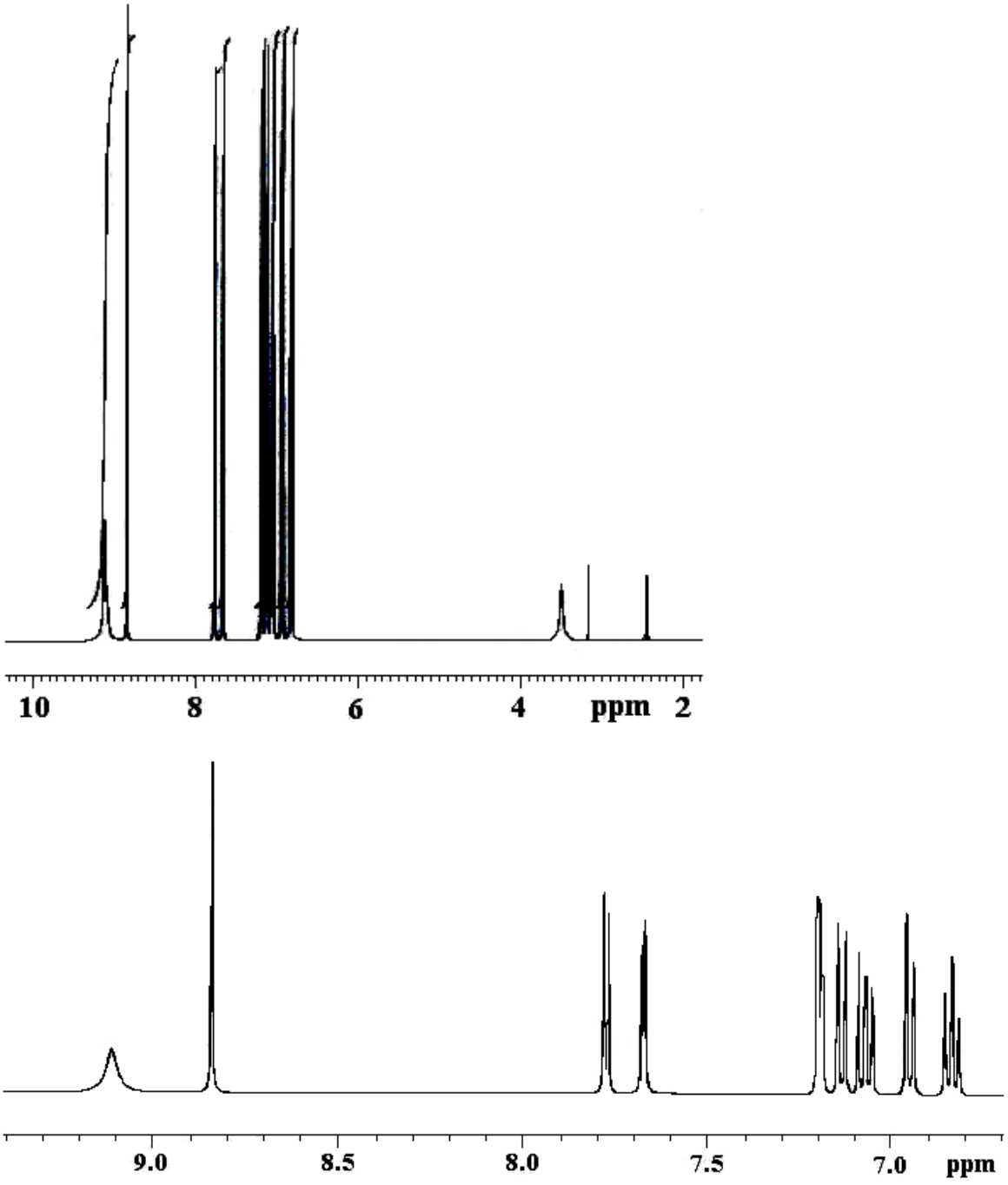


Fig. 1. ^{1}H-NMR spectrum of 2-[(thien-2-yl-methylene)]aminophenol

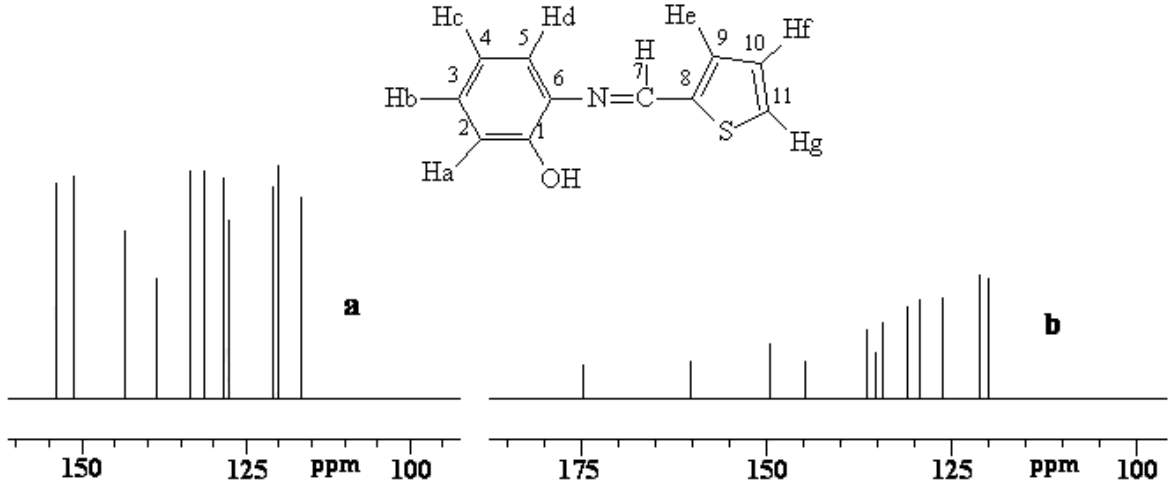


Fig. 2. ^{13}C-NMR spectrum of 2-[(thien-2-yl-methylene)]aminophenol (a) and oligo-2-[(thien-2-yl-methylene)]aminophenol (b)

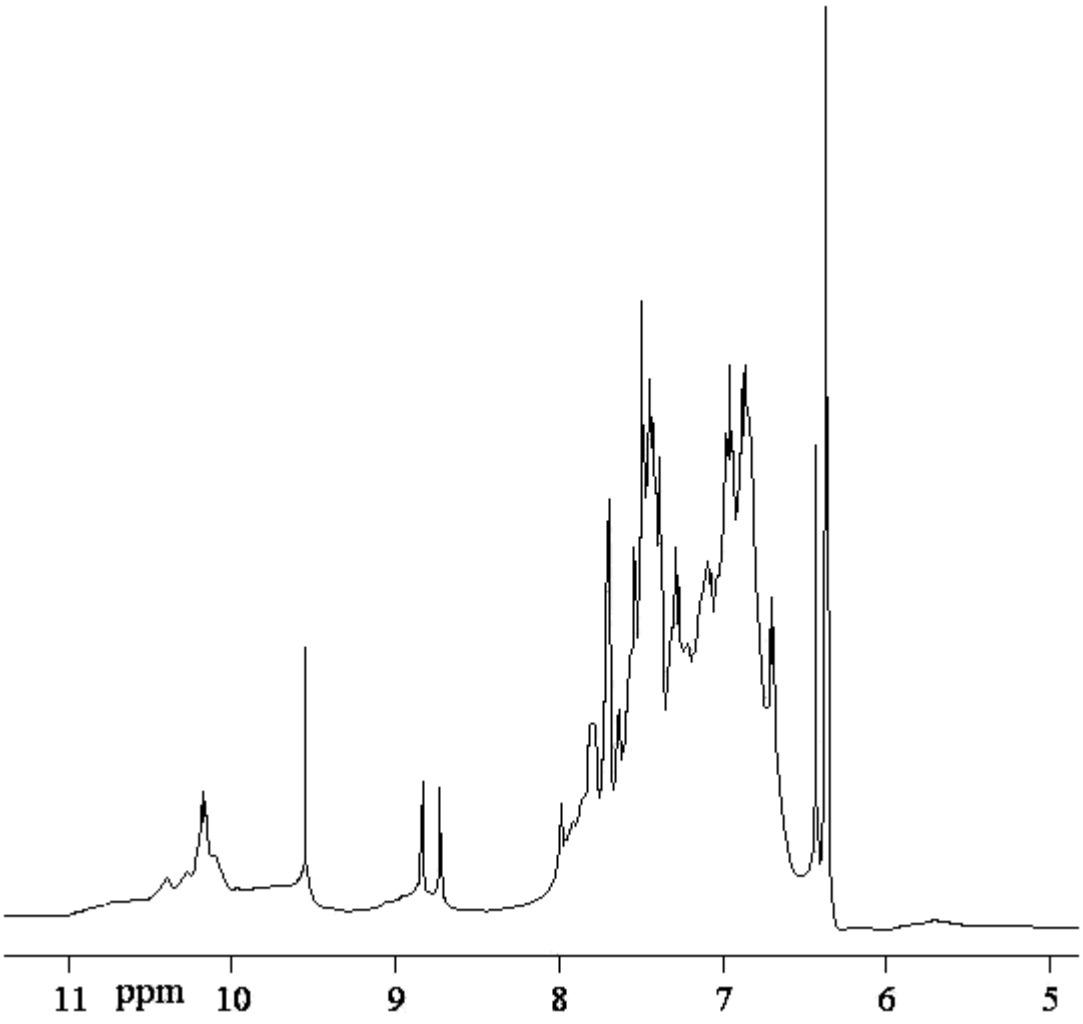


Fig. 3. ^{1}H-NMR spectrum of oligo-2-[(thien-2-yl-methylene)]aminophenol

Thermal analyses of 2-TMAP and O-2-TMAP

TGA, DTG and DTA curves of monomer, oligomer and oligomer-metal complex compounds were given in Figs. 4, 5 and 6 and Table 6. The initial degradation temperature and 50% weight loss of 2-TMAP was found to be 212, 244°C, respectively. According to DTG curve, thermal degradation of 2-TMAP completed in 440°C. According to DTA analysis, endothermic peak observed in 83 and 263°C. The initial degradation temperature, 50% and 69.24% weight loss of O-2-TMAP was found to be 176, 400°C and 1000°C, respectively. According to DTG curve, thermal degradation of O-2-TMAP occurred in one step and it weight loss was found as 69.24% between 175-1000°C. Because of long conjugated band systems, oligomer demonstrated higher resist against high temperature than monomer. According to TG analysis, although initial degradation temperature of O-2-TMAP was lower than monomer, it was more stable than monomer through to temperature and thermal decomposition. Because was formed carbines residue at high amount such as 30.76% at 1000°C. Because of C-O-C coupling formation, initial degradation temperature of oligomer was lower than monomer from TGA measurements. C-O-C bond has degradated at lower temperature than C-C bond. O-2-TMAP-Zr compound demonstrated higher thermal stability according to other oligomer-metal complex compounds. The initial degradation temperature and 41.82% weight loss of O-2-TMAP-Zr compound was found to be 242 and 1000°C, respectively. According to TG curves, to be high of thermal stability of oligomer-metal complex compounds may be indicate the formation of metal-oxygen valance and metal-nitrogen coordination bond between oligomer-metal ions. The presence of water can be seen in TGA curves of oligomer-metal complex compounds (Fig. 4), showing between 10.78 and 1.50% wt losses in the 50-150°C and 50-190°C range, respectively, and corresponding to the loss of water of crystallization (50-150°C) and coordination water (150-200°C)[24, 25].

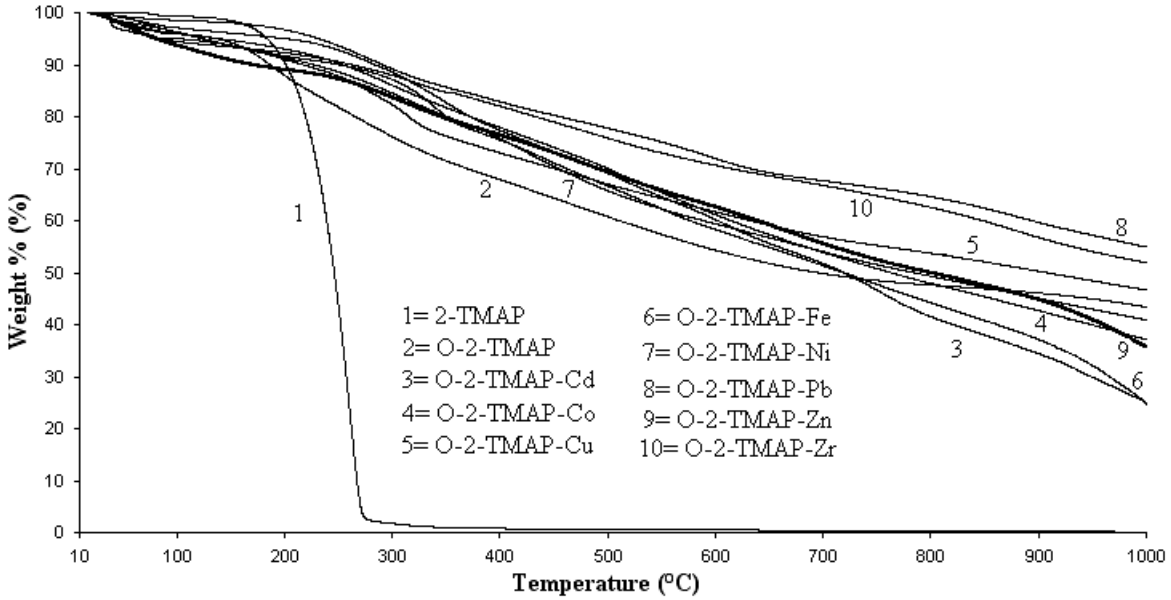


Fig. 4. TG curves of monomer, oligomer and oligomer-metal complex compounds

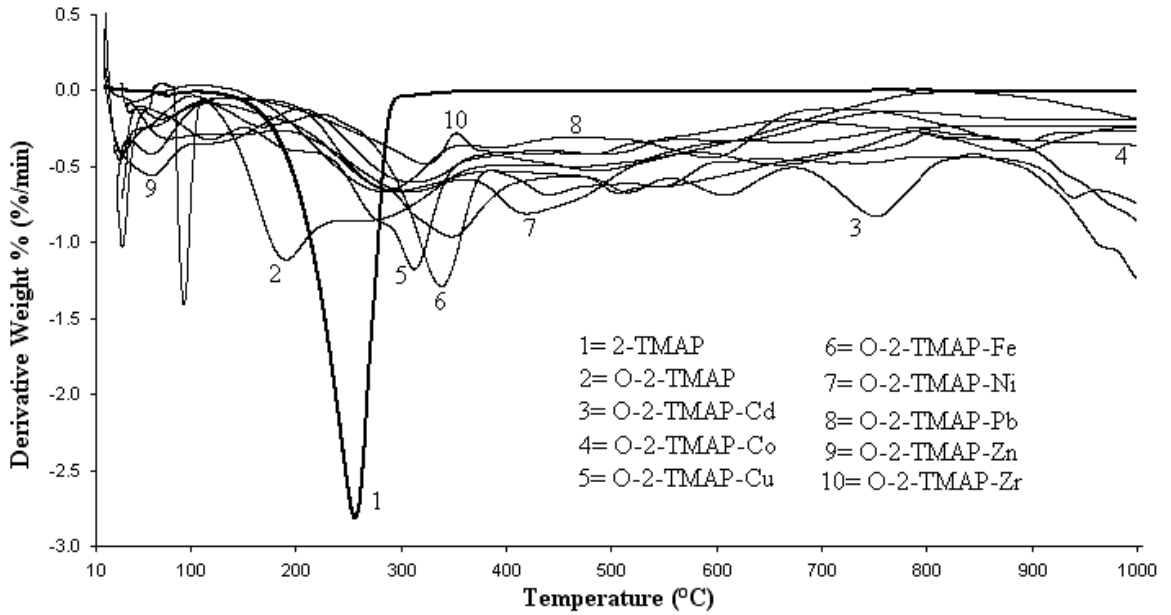


Fig. 5. DTG curves of monomer, oligomer and oligomer-metal complex compounds

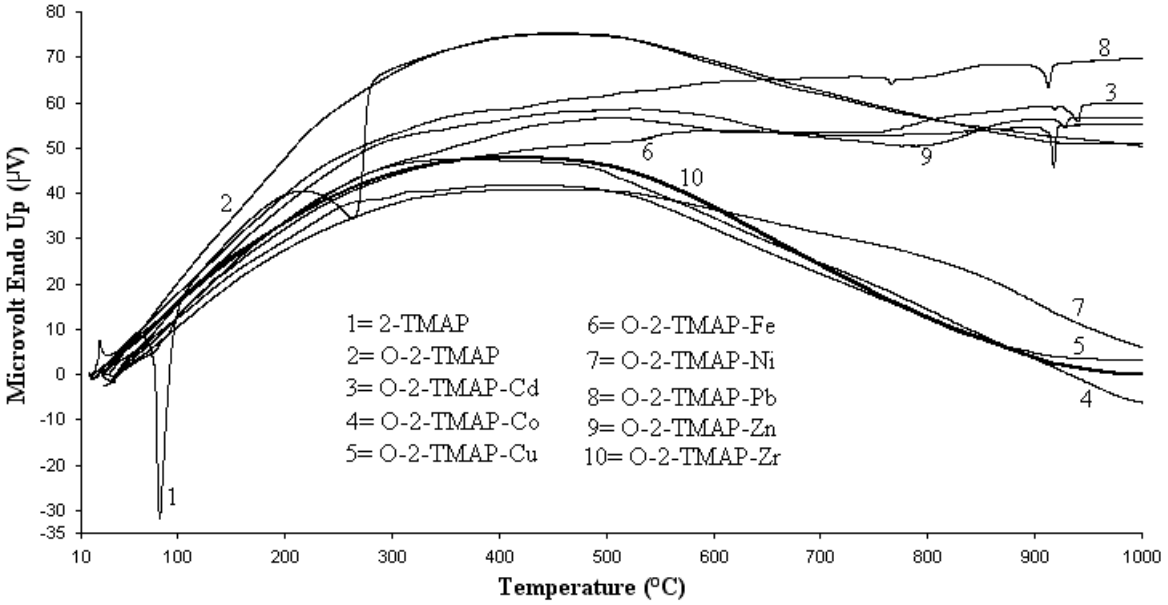


Fig. 6. DTA curves of monomer, oligomer and oligomer-metal complex compounds

Table 6. Thermal decomposition values of 2-TMAP, O-2-TMAP and oligomer-metal complex compounds

Compounds	TGA					DTA	
	[a]T_{on}	[b]T_{max}	20% wght Loss	50% wght Loss	% Carbine Resi. at 1000°C	exo	endo
2-TMAP	212	256	225	244	0.0	-	82, 263
O-2-TMAP	176	867	205	400	30.76	-	-
O-2-TMAP-Cu	251	312, 484	395	908	52.90	-	-
O-2-TMAP-Zn	238	310, 482, 658	482	802	46.03	-	-
O-2-TMAP-Cd	255	347, 514, 606, 749, 938	363	707	28.72	-	-
O-2-TMAP-Pb	204	281, 593, 884	429	-	56.44	-	-
O-2-TMAP-Co	230	290, 503	442	771	41.69	368	-
O-2-TMAP-Fe	296	337, 440, 546	401	722	33.36	-	-
O-2-TMAP-Zr	242	320, 429, 895	493	-	58.18	404	-
O-2-TMAP-Ni	254	302, 418	436	791	48.84	-	-

[a]The onset temperature. [b]Maximum Weight Loss Temperature.

Electrochemical properties of 2-TMAP and O-2-TMAP

The voltammetric measurements of 2-TMAP and O-2-TMAP were carried out in acetonitrile and DMSO, respectively. The HOMO, LUMO energy levels and electrochemical band gaps ($E_g^{'}$) were calculated from oxidation and reduction onset values and voltammograms are shown in Fig. 7. The HOMO, LUMO energy levels and electrochemical energy gaps ($E_g^{'}$) of 2-TMAP and O-2-TMAP were found to be -6.34, -6.17; -2.83, -2.78; 3.51 and 3.39 eV, respectively. According to UV-vis measurements, the absorption spectra of 2-TMAP, O-2-TMAP, O-2-TMAP-Co, O-2-TMAP-Ni and O-2-TMAP-Cu were recorded by using methanol and DMSO at 25°C and are given Table 7.

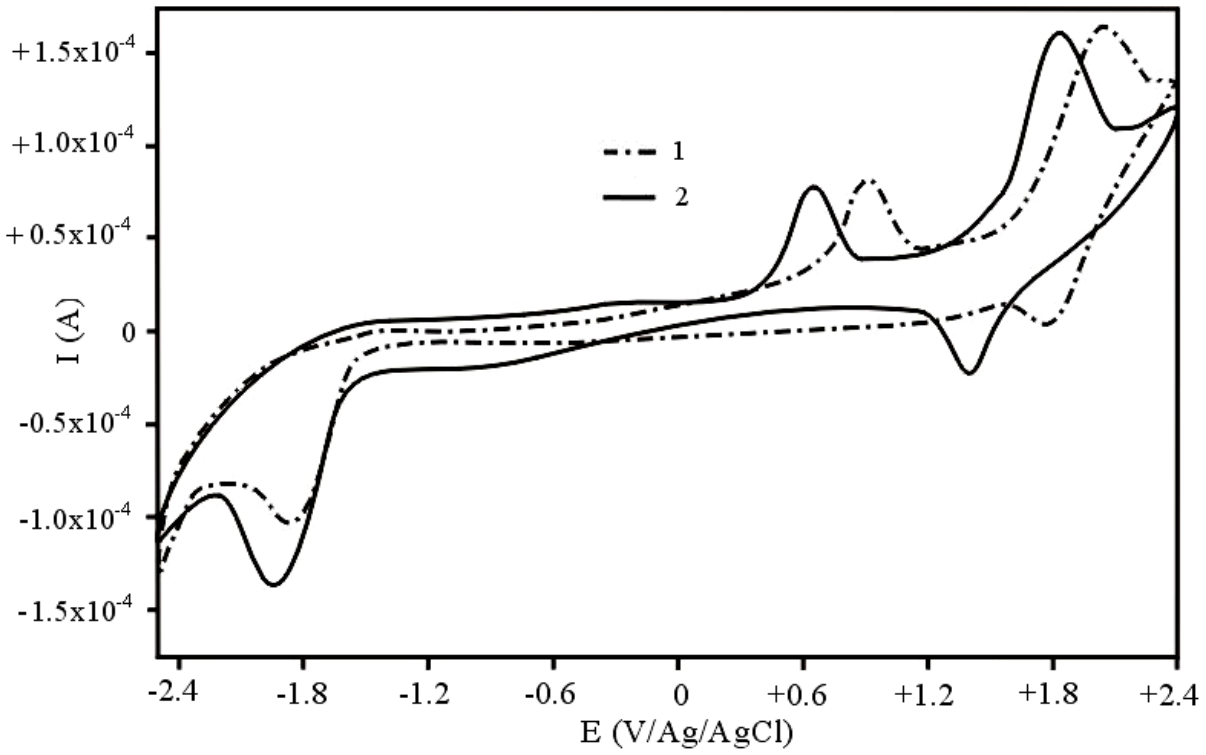


Fig. 7. Cyclic voltammograms of 2-TMAP (1) and O-2-TMAP (2)

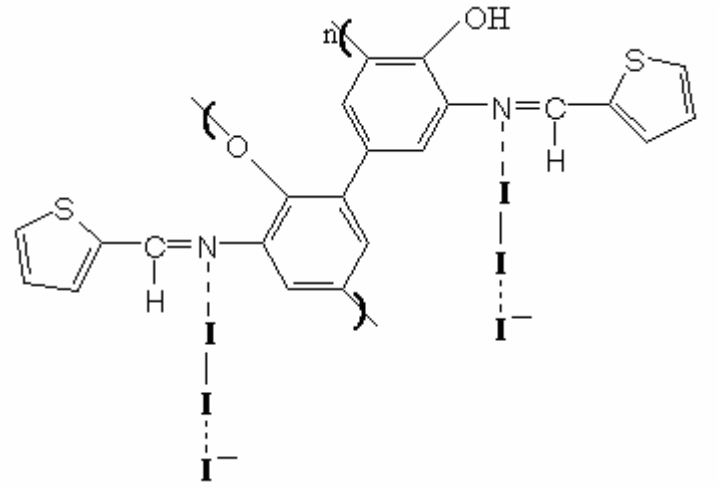
Table 7. λ_{max} (nm) and band gap values of 2-TMAP, O-2-TMAP and oligomer-metal complexes

Compounds	λ_{max} (nm)	E_g (eV)
2-TMAP	353	3.01
O-2-TMAP	371	2.65
O-2-TMAP-Cu	473	2.63
O-2-TMAP-Zn	473	2.63
O-2-TMAP-Cd	476	2.61
O-2-TMAP-Pb	509	2.44
O-2-TMAP-Co	490	2.53
O-2-TMAP-Fe	464	2.67
O-2-TMAP-Ni	483	2.57
O-2-TMAP-Zr	480	2.56

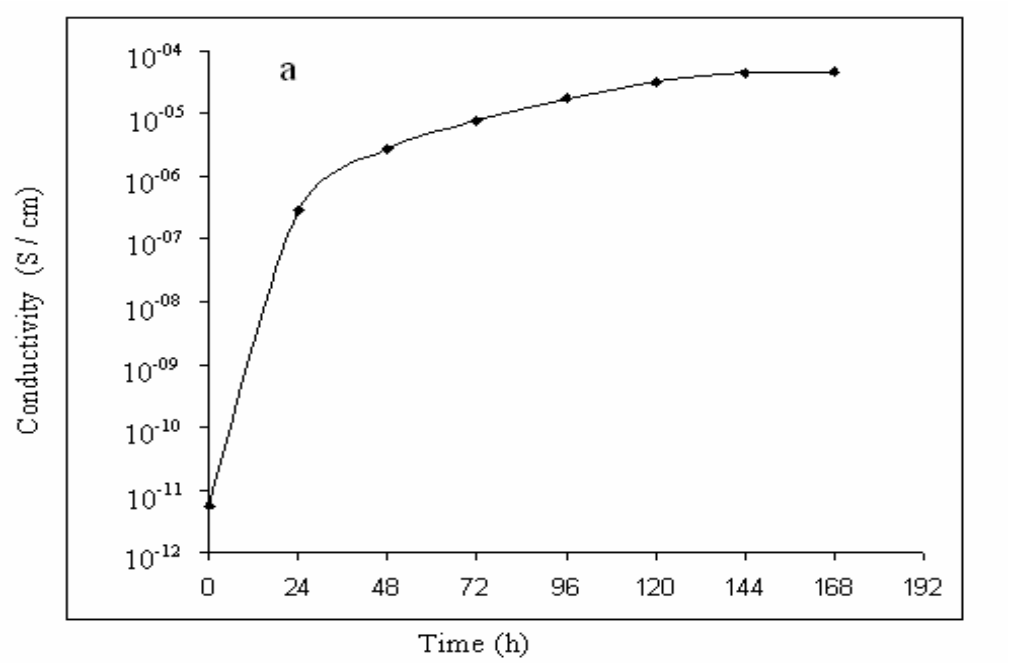
Conductivity of O-2-TMAP and oligomer-metal complex compounds

O-2-TMAP and oligomer-metal complex compounds have conductivities of 10^{-l2}-10^{-11} and 10^{-ll}-10^{-10} S/cm, respectively. Fig. 8 shows the doping results for O-2-TMAP, O-2-TMAP-Co, O-2-TMAP-Ni, O-2-TMAP-Cu, O-2-TMAP-Cd, O-2-TMAP-Pb, O-2-TMAP-Zn, O-2-TMAP-Fe and O-2-TMAP-Zr complex compounds with iodine for the various times at 25°C. Although the structure of O-2-TMAP, O-2-TMAP-Co, O-2-TMAP-Ni, O-2-TMAP-Cu, O-2-TMAP-Cd, O-2-TMAP-Pb, O-2-TMAP-Zn, O-2-TMAP-Fe and O-2-TMAP-Zr differ, little significant difference in conductivity was observed. This effect may possibly be due to all of them actually belonging to the same class of oligomer and oligomer-metal complex compounds. In the doping of O-2-TMAP with iodine, it was found that the conductivity of O-2-TMAP first increases greatly with doping time, but then tends to level-off. The maximal (or saturated) conductivity values of O-2-TMAP, O-2-TMAP-Co, O-2-TMAP-Ni, O-2-TMAP-Cu, O-2-TMAP-Cd, O-2-TMAP-Pb, O-2-TMAP-Zn, O-2-TMAP-Fe and O-2-TMAP-Zr were found to be 4.46 x 10^{-10}, 1.41 x 10^{-10}, 6.48 x 10^{-10}, 8.34 x 10^{-11}, 6.25 x 10^{-11}, 1.12 x 10^{-10}, 6.24 x 10^{-11}, 2.55 x 10^{-10} and 1.20 x 10^{-10} S/cm. According to the values, the highest conductivity was observed in O-2-TMAP-Ni compound. The increasing conductivity could indicate that a charge-transfer complex between O-2-TMAP and its oligomer-metal complex compounds with dopant iodine is continuously formed. Consequently, Fig. 8 not only shows the conductivity/doping time relationship but also indicate how quickly the doping reaction takes

place. The experimental results showed that a longer doping time is needed to obtain the maximal conductivity. As a result, the conductivity/doping time curve varies with doping conditions. In order to exclude the influence of doping conditions, the conductivity of doped O-2-TMAP, O-2-TMAP-Co, O-2-TMAP-Ni, O-2-TMAP-Cu, O-2-TMAP-Cd, O-2-TMAP-Pb, O-2-TMAP-Zn, O-2-TMAP-Fe and O-2-TMAP-Zr have been related with doping extent. The conductivity values of oligo-2-[(4-morpholin-4-yl-phenyl)imino]methylphenol and oligomer-metal complex compounds had been determined with same technique and results were similar with literature[26]. Coordination of iodine during O-2-TMAP doping is as follow at Scheme 4. On the nitrogen atom coordination of iodine ions with Schiff base polymers and pyridine solutions had been suggested at the literatures[27-30] as follows.



Scheme 4. Coordination of iodine ions during O-2-TMAP doping



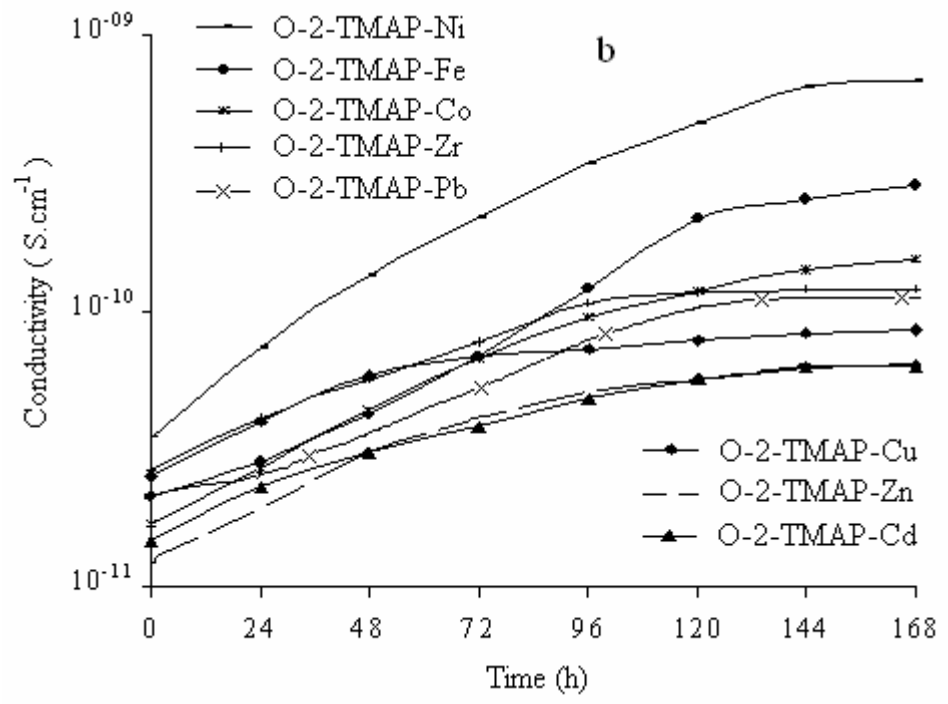


Fig. 8. Electrical conductivity of I_2-doped (a) O-2-TMAP and (b) oligomer-metal complex compounds vs. doping time at 25°C

CONCLUSIONS

Oligo-2-[(thien-2-yl-methylene)]aminophenol was synthesized with oxidative polycondensation by using such as H_2O_2, air O_2 and NaOCl oxidants in an aqueous alkaline medium. In the oxidative polycondensation reaction of 2-TMAP, H_2O_2 demonstrated less activity than the NaOCl and air O_2 oxidants. The spectral analyses such as ^{1}H-NMR and ^{13}C-NMR data of oligomer have showed that the polymerization proceeded with C-C and C-O-C coupling system of *ortho* and *para* positions and oxyphenylene according to –OH group of monomer at the each other of formation oligomers from oxidative polycondensation of 2-TMAP. The results of TG-DTA analyses were shown to have enough resistance against thermal decomposition of oligo-2-[(thien-2-yl-methylene)]aminophenol. According to TG analyses, weight losses of oligomer-metal complex compounds changed at 1000°C as follows: Zr^{+4}> Pb^{+2}> Cu^{+2}> Ni^{+2}> Zn^{+2}> Co^{+2}> Fe^{+2}> Cd^{+2}. As a result, O-2-TMAP-Zr^{+4} has demonstrated higher thermal stability against thermal degradation than monomer, oligomer and oligomer-metal complex compounds.

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