Turkish Journal of Chemistry

Volume 25 | Number 1 Article 2

1-1-2001

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Recommended Citation
KAYA, İSMET and DEMİRELLİ, KADİR (2001) "Determination of the Thermodynamic Properties of Poly [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] at Infinite Dilution by Inverse Gas Chromatography," *Turkish Journal of Chemistry*: Vol. 25: No. 1, Article 2. Available at: https://journals.tubitak.gov.tr/chem/vol25/iss1/2

Turk J Chem
25 (2001) , 11 – 18.
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Determination of the Thermodynamic Properties of Poly [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] at Infinite Dilution by Inverse Gas Chromatography

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Received 20.04.1998

Some thermodynamic quantities were obtained for the interactions of poly [2-(3-phenyl -3- methylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] Poly (PCHEMA-co-MA) with alcohols, ketones, acetates, aromatics and n-alkanes by inverse gas chromatography in the temperature range of 150-180°C. The specific retention volumes, Vg°, weight fraction activity coefficients of solute probes at infinite dilution, Ω_1^∞ and Flory-Huggins thermodynamic interaction parameters, χ_{12}^∞ between polymers and solvents were determined. The partial molar free energy, ΔG_1^∞, the partial molar heat of mixing, ΔH_1^∞, at infinite dilution and the solubility parameters of the polymer, δ_2, were calculated. The copolymer was characterized by ^{1}H-NMR, FT-IR and DSC analyses

Key Words: Poly [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid], inverse gas chromatography, polymer-solvent interactions.

Introduction

The inverse gas chromatography, (IGC), method has been used extensively to study the structure of polymers, the interactions of various liquids and gases with polymeric materials, and polymer-polymer miscibility. The method is simple, fast and economical and provides valuable thermodynamic information for characterization of polymeric materials[1−6].

In this study, we examined the interactions of poly [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] (PPCHEMA-co-MA) with solvents and the solubility parameters of PPCHEMA-co-MA by using IGC in the temperature range 150-180°C.

The probe specific retention volumes, Vg°, corrected to 0°C were calculated from the standard chromatographic relation

$$V_2^\circ = \Delta t\ G273.2/wT_r\ 3/2[P_i/P_o)^2 - 1/(P_i/P_o^3 - 1] \tag{1}$$

where $\Delta t = t_p - t_g$ is the difference between the retention times of the probe, t_p, and the methane, t_g; F is the flow rate of the carrier gas measured at room temperature, T_r; w is the mass of the polymeric stationary phase; and P_i and P_o are the inlet and outlet pressures, respectively[7−10].

The weight fraction activity coefficient, Ω_1^∞, the partial molar free energy, ΔG_1^∞, and the average partial molar enthalpy, ΔH_1^∞, at infinite dilution of the organic solvents were calculated according to the following equations[3]:

$$\Omega_1^\infty = 273.2R/V_g^o P_1^o M_1 \exp[-P_1^o(B_{11} - V_1)/RT] \tag{2}$$

$$\Delta G_1^\infty = RT \ln \Omega_1^\infty \tag{3}$$

$$\Delta H_1^\infty = R\partial \ln(\Omega_1^\infty)/\partial(1/T) \tag{4}$$

where B_{11} is the second virial coefficient of the organic solute in the gaseous state; P_1° is the vapour pressure of the probes at temperature $T(K)$; and M_1 is the molecular weight of the probe. The values of P_1° and B_{11} have been calculated as in the literature[11].

The molar volume of the solute, V_1, was calculated using the following relation[12]:

$$V_1 = V_c/\rho_r \tag{5}$$

where V_c is the critical molar volume and ρ_r is the reduced density of the solute given as

$$\rho_r = 1.20 + (5.565 - 11.03z_c)(1 - T/T_c)^{(0.8z_c+0.31)} \tag{6}$$

where z_c is the critical compressibility factor and T_c is critical temperature.

The Flory-Huggins parameters, χ_{12}^∞, characterizing the interactions of a vapour-phase probe with a polymer are determined by the following equation:

$$\chi_{12}^\infty = Ln(273.2R\nu_2/Vg^\circ V_1 P_1^\circ) - 1[-P_1^\circ/RT(B_{11} - V_1)] \tag{7}$$

where R is the gas constant and ν_2 is the specific volume of the polymer. The solubility parameter of the probe is calculated from the relation[13−16].

$$\delta_1 = [(\Delta H_v - RT)/V_1]^{0.5} \tag{8}$$

The solubility parameter of the polymer, δ_2, can be calculated by the following relation:

$$[(\delta_1^2/RT) - \chi_{12}^\infty/V_1] = (2\delta_2/RT)\delta_1 - \delta_2^2/RT \tag{9}$$

If the left-hand side of this equation is plotted against δ_1, a straight line having a slope of $2\delta_2/RT$ and an intercept of $(-\delta_2^2/RT)$ is obtained. The solubility parameter of the polymer, δ_2, can be determined from both the slope and the intercept of the straight line[9].

Experimental

Materials

Ten polar and non-polar probes were used in this study. They were selected to provide several groups of chemically different nature and polarity. N-dodecane was supplied by Aldrich Chemical Co., and methanol, ethanol, acetone, ethyl methyl ketone, methyl acetate, ethyl acetate, benzene, toluene and o-xylene of chromatographic grade were supplied by Merck Chemical Co. Chromosorb W (45-60 mesh) was supplied by Sigma Chemical Co. 1,4-Dioxane and n-hexane (Aldrich) were dried over anhydrous $MgSO_4$ before use. Methacrylic acid and KOH (Aldrich) were used as received. 1-chloro-2,3-epoxy-5-methyl-5-hexene was obtained from the Institute of Polymeric Materials in the Academy of Sciences of Azerbaijan and freshly distilled before use. [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] was synthesized via the method given for the epoxy-carboxy reactions[17−21].

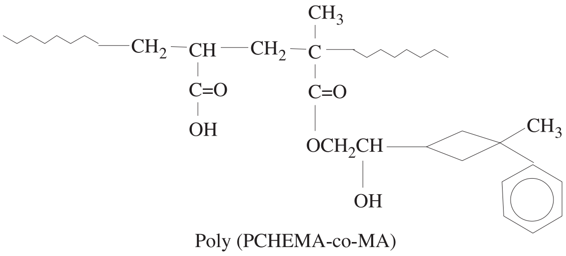
Copolymerization of the monomers

The monomer [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] and methacrylic acid were freed from inhibitor by washing with dilute KOH solution followed by reacting with distilled water and drying over anhydrous MgSO4. Appropriate amounts of [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] and methacrylic acid and 1,4-dioxane and benzoyl peroxide (0.2% of the weight of the monomer) were placed into a reaction tube and purged with Ar for about 10 min. The sealed tube was kept at 60°C for 15 h. The PPCHEMA-co-MA was purified by reprecipitation in n-hexane from 1,4-dioxane solution and finally dried under vacuum. The yield was about 75% for PPCHEMA-co-MA.

Analysis

The molecular weight of the PPCHEMA-co-MA was determined by gel permeation chromatography using polystyrene and tetrahydrofurane as the standard and solvent, respectively. The weight-average molecular weight was found to be 45 000 g/mol (polydispersity:2.62) for PPCHEMA-co-MA. The block copolymer composition was determined by ^{1}H-NMR measurement. In the block copolymer, the composition of [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate] and methacrylic acid found to be 55% and 45%, respectively. The glass transition temperature, Tg, of PPCHEMA-co-MA is found to be about 105°C by Shimadzu differential scanning calorimeter (DSC) (DSC-50 model). Density is measured by determining the weight of a volume-calibrated pycnometer filled with a liquid of known density in which a certain quantity of the polymer sample[22]. Density of PMCHEMA was found as 1.18 g/cm^3 by pycnometric measurement. The monomer and copolymer were characterized by using Mattson FT-IR-1000 spectrometer and Varian ^{1}H-and ^{13}C-NMR spectra (200 MHz) at 25°C with $CDCl_3$ as solvent.

The FT-IR spectrum of the copolymer was the same as the characteristic peaks of the monomeric units. The stretch vibration bands of C=O group were observed for ester and acid in 1738 cm^{-1}. The stretching vibration band of -COOH was observed in 3500-2850 cm^{-1} at acid units (broad). The ^{1}H-NMR spectrum of the copolymer showed peaks at 6.8-7.3 ppm, revealing the phenyl ring protons of PCHEMA units as a double. The signals at 4.2-3.1 ppm are assigned to $-OCH_2-CH(OH)-$ for PCHEMA units. The signals at 1.2-2.0 ppm are due to $-CH_3$ of the cyclobutane ring and $-CH_2-CH-$ and $-CH_3$ protons on the copolymer backbone. The signals of cyclobutane ring protons are at 2.2-2.9 ppm on the copolymer. The signal of -OH proton in methacrylic acid unit was shown at 11.5 ppm as singlet.



Poly (PCHEMA-co-MA)

Instrumentation and procedure

A Shimadzu GC-14B model gas chromatography equipped with a dual flame ionization detector was used in the analysis. Dried nitrogen gas (research grade) was used as a carrier gas. Methane was used as a noninteracting marker to correct for dead volume in the column. The net retention time was determined from the positions of the peak maxima for methane and for the probe molecule at each temperature. Pressures at the inlet of the column, read from a mercury manometer, were used to compute corrected retention volumes by the usual procedures. Flow rates were measured from the end of the column with a soap bubble flow meter. A flow rate of about 20 ml min^{-1} was used throughout our experiment. Spiral glass (3.2 mm I.D.×1.1m.) tubing was washed with methylene chloride and was annealed prior to use. A column of packing material was prepared by coating 60-80 mesh size Chromosorb W (DMCS) treated with PPCHEMA-co-MA. Then, 0.1415 g of PPCHEMA-co-MA was dissolved in 25 ml of tetrahydrofurane and 2.6308 g of the solid supporting materials were added to this solution and stirred. The solvent was removed by continuous stirring and slow evaporation under partial vacuum in a rotary evaporator.The prepared material was packed into a spiral glass tubing[14]. The column was conditioned at a temperature above the glass transition temperature and at the fast carrier gas (N_2) flow rate for 24 h prior to use. The probes were injected onto the column with 1μL Hamilton syringes. Three consecutive injections were made for each probe during each set of measurements. An injection volume of 0.2μL was selected. The retention times of the probes were measured by using a Shimadzu CR6A Chromatopac model integrator. Methane was synthesized in the laboratory by the reaction of sodium acetate with sodium hydroxide[23].

Results and Discussion

The specific retention volumes, Vg°, of 10 probes were obtained by using one loading PPCHEMA-co-MA at a series of temperatures (150, 160, 170 and 180°C). The values of specific retention volumes, Vg°, of these probes were calculated according to equation (1) and are given in Table 1. As it is shown in Table 1, Vg°, values changed for each group solvents with temperature. That is, the specific retention volumes, Vg° of the probes decreased with increasing temperature for each group of solvents.

Table 1. Variation of specific retention volumes, Vg° (ml/g), of some alcohols, ketones, acetates, aromatics and n-dodecane with temperature using poly [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] as stationary phase.

Probe/T(°C)	150	160	170	180
Methanol	6.73	6.52	6.01	5.76
Ethanol	6.98	6.65	6.06	6.10
Acetone	6.88	6.19	6.45	6.39
Ethyl methyl ketone	8.94	7.44	6.98	6.73
Methyl Acetate	8.80	6.42	6.06	5.89
Ethyl Acetate	9.00	7.57	6.93	6.81
Benzene	13.37	12.30	7.24	6.73
Toluene	16.21	15.14	13.61	11.25
o-Xylene	40.51	35.93	32.17	26.08
n-Dodecane	82.27	73.96	58.77	44.50

The values for Ω_1^∞ and χ_{12}^∞ obtained using equations (2) and (7), respectively, are also shown in Table 2. The ΔH_1^∞ values of the probes were found from the slope of straight lines in Fig.1. The partial molar free energy of mixing ΔG_1^∞ and the partial molar heats of mixing at infinite dilution of the solutes, ΔH_1^∞ calculated from equations (3) and (4) are shown in Table 3. The ΔH_1^∞ values of alcohols, ketones, acetates, and aromatics ranged from 6.36 to 7.10 kcal/mol, from 2.50 to 6.55 kcal/mol, and from 3.02 to 3.78 kcal/mol, respectively (Table 3). The ΔH_1^∞ value for n-dodecane was found to be 4.37 kcal/mol.

Table 2. Weight fraction activity coefficients, Ω_1^∞ and interaction parameters, χ_{12}^∞ of poly [2-(3-methyl-3-phenylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] with some alcohols, ketones, acetates, aromatics and n-dodecane systems.

	Ω_1^∞					χ_{12}^∞				
Probe/T(°C)	150	160	170	180	170*	150	160	170	180	170*
Methanol	7.62	6.29	5.51	4.67	6.98	0.689	0.479	0.331	0.144	0.523
Ethanol	7.06	5.81	4.96	3.82	5.95	0.577	0.367	0.192	-0.096	0.485
Acetone	5.17	4.74	3.86	3.34	4.70	0.329	0.227	-0.004	-0.178	0.154
Ethyl methyl ketone	5.39	5.22	4.92	4.39	5.03	0.446	0.381	0.253	0.089	0.193
Methyl acetate	3.70	3.26	3.35	2.96	3.80	0.076	-0.044	-0.148	-0.201	0.036
Ethyl acetate	4.42	4.29	3.91	3.37	4.30	0.238	0.196	0.088	-0.088	0.139
Benzene	4.91	4.36	4.05	3.88	6.09	0.508	0.367	0.319	0.190	0.478
Toluene	5.63	4.86	4.36	4.26	6.62	0.468	0.315	0.199	0.166	0.575
o-Xylene	4.55	4.02	3.58	3.53	8.42	0.233	0.088	-0.037	-0.060	0.781
n-Dodecane	10.76	8.53	7.88	7.72	21.60	0.990	0.748	0.661	0.632	1.622

*References 26

It has been proposed that values for Ω_1^∞ greater than 5 are indicative of poor polymer-solute systems, while lower values indicate good solubility for such a system[24]. Values for χ_{12}^∞ greater than 0.5 represent unfavourable polymer-solvent interactions, while values lower than 0.5 indicate favourable interactions in dilute polymer solutions[25]. It will be seen that these values (in Table 2) according to Ω_1^∞ and χ_{12}^∞, acetates, aromatics, alcohols and ketones are good solvents, but that n-dodecane is non-solvent for PPCHEMA-co-MA. The interaction parameters, χ_{12}^∞, the partial molar free energy of mixing, ΔG_1^∞, the weight fraction activity coefficients, Ω_1^∞, and the partial molar heats of mixing at infinite dilution of the solutes, ΔH_1^∞, were dependent on the number of carbons in the series (except alcohols). That is, these values χ_{12}^{∞}, Ω_1^{∞}, ΔG_1^{∞} and ΔH_1^{∞} increased with increasing in the number of carbons in the series. But, in all series, χ_{12}^{∞}, Ω_1^{∞} and ΔG_1^{∞} the values decreased with increasing the column temperature.

Table 3. The partial molar free energies of mixing, ΔG_1^{∞} (kcal/mole), and partial molar enthalpy, ΔH_1^{∞}, (kcal/mole) of poly [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] with some alcohols, ketones, acetates, aromatics and n-dodecane systems at 150-180°C.

	ΔG_1^{∞} (kcal/mole)				ΔH_1^{∞} (kcal/mole)
Probe/T(°C)	150	160	170	180	(150-180°C)
Methanol	1.71	1.58	1.50	1.39	6.36
Ethanol	1.64	1.51	1.41	1.21	7.10
Acetone	1.38	1.34	1.19	1.09	5.96
Ethyl methyl ketone	1.42	1.42	1.40	1.33	6.55
Methyl acetate	1.10	1.02	1.06	0.98	2.50
Ethyl acetate	1.25	1.25	1.20	1.09	3.62
Benzene	1.34	1.27	1.23	1.22	3.02
Toluene	1.45	1.36	1.30	1.30	3.78
o-Xylene	1.27	1.20	1.12	1.14	3.54
n-Dodecane	2.00	1.84	1.82	1.84	4.37

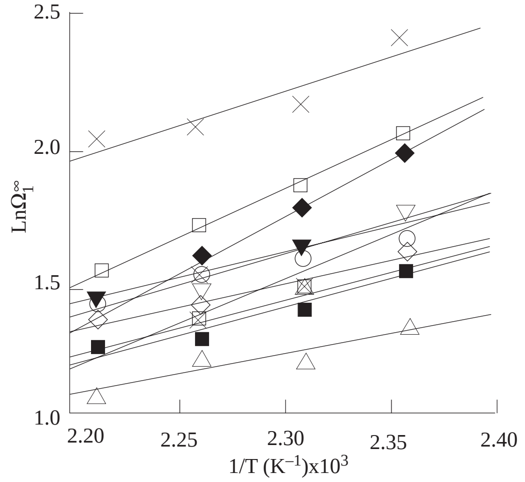


Figure 1. Variation of logarithm of weight fraction activity coefficients, Ω_1^{∞}, with reciprocal of absolute column temperature, 1/T(K^{-1}) for poly [2-(3-phenyl -3- methylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] and some solutes: □: methanol, ♦: ethanol, ◯: acetone, ⊗: EMK., △: methyl acetate, ⊠: ethyl acetate, ◊: benzene, ▽: toluene, ■: *o*-xylene, ×: n-dodecane

It may be seen from χ_{12}^{∞} and Ω_1^{∞} values that aromatics and alcohols are poor solvents for PPCHEMA[26] (homopolymer) (see Table 2). In constrast, they are good solvents for PPCHEMA-co-MA (co-polymer) at 170°C.

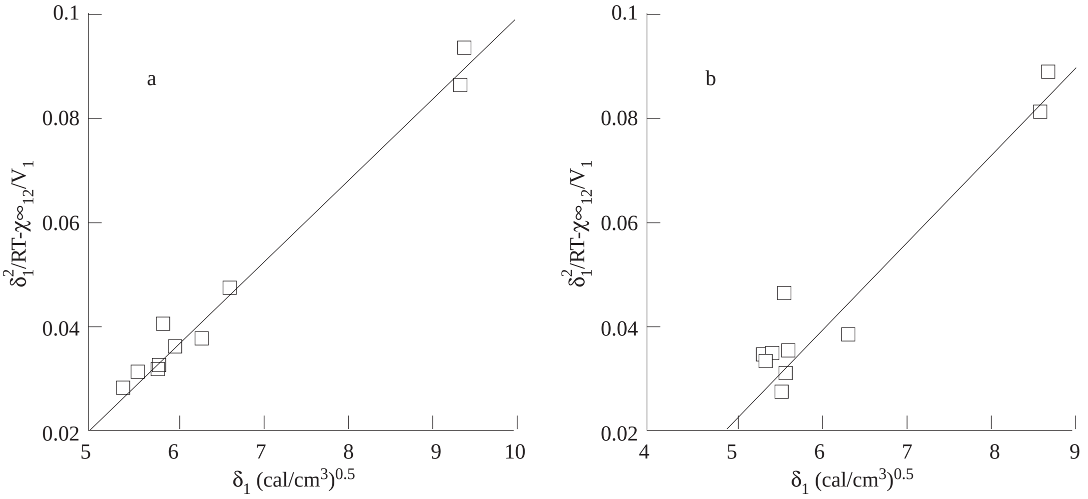


Figure 2. Variation of the term $[(\delta_1^2/RT) - \chi_{12}^\infty/V_1]$ with solubility parameters of the solutes, δ_1 (cal/cm^3)$^{0.5}$, at temperatures (a)= 170°C (b)=180°C

Table 4. The solubility parameter, δ_2 (cal/cm^3)$^{0.5}$, of poly [2-(3-phenyl-3-methylcyclobutyl)-2-hydroxyethyl methacrylate-co-methacrylic acid] at 170 and 180°C.

T(°C)	slope	intercept	from slope, δ_2	from intercept, δ_2	r
170	0.0158	-0.0547	6.95	6.94	0.9964
180	0.0152	-0.0515	6.84	6.81	0.9922

The solubility parameter of a polymer, δ_2, can be determined by equation (9)[9,16]. The solubility parameter δ_2 is determined from either the slope or the intercept of a straight line obtained by plotting the left-hand side of equation (9) versus δ_1. The solubility parameter of PPCHEMA-co-MA was evaluated from either the slope or the intercept of Fig. 2 as 6.95 (cal/cm^3)$^{0.5}$ or 6.94 (cal/cm^3)$^{0.5}$, respectively, at 170°C. The values of the solubility parameters of PPCHEMA-co-MA, δ_2, decreased with increasing temperature (see Table 4). Kaya et al.[22,26] and Yılmaz et al.[27] have determined the solubility parameters, δ_2, of poly methyl methacrylate (PMMA), poly (ethyl methacrylate) (PEMA), poly[2-(3-phenylcyclobutyl)-2-hydroxyethylmethacrylate] (PPCHEMA) and poly (p-chlorostyrene) to be 6.85 (cal/cm^3)$^{0.5}$, 5.99 (cal/cm^3)$^{0.5}$, 6.92 (cal/cm^3)$^{0.5}$ and 7.90 (cal/cm^3)$^{0.5}$ by equation (9) at 180°C and 162°C, respectively.

References

1. O. Smidsrod and J.E. Guillet, **Macromolecules, 2,** 272-82 (1969).
2. G.J. Price, J.E. Guillet and J. H. Purnell, **J.Chromatogr., 369,** 273-78 (1986).
3. A. Exteberria et al, **J.Chromatogr., 607,** 227-37 (1992).
4. İ. Kaya K. Ceylan and E. Özdemir, **Tr.J.of Chemistry, 19,** 94-100 (1995).
5. P. Munk, Z.Y. Al-Saigh and T.W. Card, **Macromolecules, 18,** 2196-203 (1985).

6. Y. Al-Saigh, **Polymer Communications, 32 (15),** 459-61 (1991).
7. O. Smidsrod and J.E. Guillet, **Macromolecules, 2,** 272-76 (1976)
8. J.M. Braun and J.E. Guillet, **Macromolecules, 10,** 101-11 (1977).
9. G. DiPaola-Baranyi and J.E. Guillet, **Macromolecules, 11,** 228-35 (1978).
10. M. Galin and L. Maslinco, **Macromolecules, 18,** 2192-98 (1985).
11. R.C. Reid, J.M. Prausnitz and T.K. Sherwood, **The Properties of Gases and Liquids,** McGraw Hill Book Comp., New York 1977.
12. R.C. Reid and T.K. Sherwood, **The Properties of Gases and Liquids,** 2nd Edn, McGraw Hill, New York 1966.
13. J.H. Hildebrand and R.L.Scott, **The Solubility of Non-Electrolytes,** Reinhold, 3rd Ed New York, 1959.
14. İ. Kaya, E. Özdemir and M. Coşkun, **J. of Macromolecular Sciences Pure-Appl. Chem., A33 (1)**, 37-47 (1996).
15. A. Desgupta, Y.R. Santee and H.J. Harwood, **J.Macromol.Sci-Chem., 23 (1)** 97-03 (1986).
16. İ. Kaya and E. Özdemir, **J. of Macromolecular Sciences Pure-Appl. Chem., A32 (3)**, 369-78 (1995).
17. P.J. Madec and E. Mareshal, **Makromol.Chem., 184**, 323-27 (1983).
18. B. Boutevin, Y. Pietrasanta and J.P. Parisi, **Makromol. Chem., 188,** 1621-29 (1987).
19. J.C. Brosse, J.C. Soutif and C.Pirazzi, **Makromol Chem., 180,** 2109-13 (1979).
20. G. Bauduin, B. Boutevin, J.P. Mistral, J.P. Parisi and Y. Pietrasanta, **Makromol.Chem., 188,** 1055-62 (1987).
21. M. Coşkun, K. Demirelli, İ. Erol and M. Ahmedzade, **J. Polym. Sci.A: Polym.Chem. 35,** 2123-28 (1997).
22. J.F. Rabek, **Experimental Methods in Polymer Chemistry, John Wiley and Sons,** P.520, Sweden, 1980.
23. İ. Kaya, PhD Thesis, **Study of Physical and Thermodynamic Properties of Alkyl Methacrylates,** Fırat Univ., Elazığ, 1995.
24. J.E. Guillet and J.H.Purnel, **Advences in Analytical Chemistry and Instrumentation, Gas Chromatograph,** John Wiley and Sons, New York 1973.
25. J. Klein and H.E. Jeberien, **Macromol.Chem., 181**, 1237-49 (1980).
26. İ. Kaya and K. Demirelli, **Polymer, 41**, (8), 2855-63 (2000).
27. F. Yılmaz, Ö.G. Cankurtaran and B.M. Baysal, **Polymer, 33 (21),** 4563-68 (1992).