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Polymer 42 (2001) 5181–5188

polymer

www.elsevier.nl/locate/polymer

3, 4-Dichlorobenzyl methacrylate and ethyl methacrylate system: monomer reactivity ratios and determination of thermodynamic properties at infinite dilution by using inverse gas chromatography

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Received 8 June 2000; received in revised form 30 November 2000; accepted 18 December 2000

Abstract

Copolymers with various contents of 3,4-dichlorobenzyl methacrylate (BzMA) and ethyl methacrylate (EMA) were prepared in 1,4-dioxane solution using 2,2′-azobisisobutyronitrile (AIBN) as initiator at 60°C. The copolymer compositions were determined by ^{1}H NMR analysis. The monomer reactivity ratios were calculated by both Fineman–Ross, and Kelen–Tüdös methods. The monomer reactivity ratios were found to be $r_{\mathrm{BMA}} = 0.521 \pm 0.019$, $r_{\mathrm{EMA}} = 0.847 \pm 0.221$ (Kelen–Tüdös) and $r_{\mathrm{BMA}} = 0.677 \pm 0.008$, $r_{\mathrm{EMA}} = 1.117 \pm 0.209$ (Fineman–Ross). The FT-IR, ^{13}C NMR spectra of the copolymers have been discussed. In all other samples thermal degradation proceeded in a single step. A slight increase in thermal stability of the copolymers was observed with increase in BzMA content. Some thermodynamic quantities such as the specific retention volumes, V_g^0, weight fraction activity coefficients of solute probes at infinite dilution, Ω_1^∞, Flory–Huggins intereaction parameters, χ_{12}^∞, between polymers and solvents, the partial molar free energy, ΔG_1^∞ the partial molar heat of mixing, ΔH_1^∞, at infinite dilution were determined from the interactions of poly(BzMA-*co*-EMA) with alcohols, ketones, acetates, aromatics and *n*-alkanes by inverse gas chromatography method at 130–150°C. All probes are non-solvent for poly(BzMA-*co*-EMA) (7:93%) and poly(BzMA-*co*-EMA) (87:13%) at 130–150°C. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Monomer reactivity ratios; NMR; Inverse gas chromatography

1. Introduction

Incorporation of activated acrylates or methacrylates into polymers provides a versatile route for the preparation of reactive polymer [1]. Copolymers of these activated monomers have been employed to study the kinetic aspects of macromolecular reactions, preparation of macromolecular drug carriers, immobilized enzymes and polymeric reagents for peptide synthesis and transition metal catalysis [2,3]. The uses of acrylics in textile finishing [4–6] and acrylic ester emulsions in leather finishing [7] are well documented. Estimation of the copolymer composition and determination of the reactivity ratios of its constituents assume importance in evaluating and applications of copolymer. The NMR spectroscopy is well established as a convenient method for determining the compositions of constituent monomer units in a copolymer [8,9]. The use of ^{1}H NMR spectroscopy has become more important not only for the determination of sequence distributions but also of copolymer compositions in methacrylate systems [10–12].

The inverse gas chromatography (IGC) method has been used extensively to study the structure of polymers, the interaction of various liquids and gases with polymeric materials and to investigate polymer–polymer miscibility. The method is simple, fast, economical and provides valuable thermodynamic information for characterization of polymeric materials [13–18].

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

$$V_g^0 = \Delta t F 273.2/wT r 3/2/[(P_i/P_o)^2 - 1/(P_i/P_o)^3 - 1], \qquad (1)$$

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 [19–22].

The weight fraction activity coefficient, Ω_1^∞, the partial molar free energy, ΔG_1^∞ and the average partial molar

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PII: S0032-3861(01)00019-2

enthalphy, ΔH_1^∞ at infinite dilution of the organic solvents were calculated according to the following equations [15].

$$\Omega_1^\infty = 273.2R/V_g^0 P_1^0 M_1 \exp[-P_1^0(B_{11} - V_1)/RT] \quad (2)$$

$$\Delta G_1^\infty = RT\ln \Omega_1^\infty \quad (3)$$

$$\Delta H_1^\infty = R\partial\ln(\Omega_1^\infty)/\partial(1/T), \quad (4)$$

where B_{11} is the second virial coefficient of the organic solution in the gaseous state and P_1^0 is the vapour pressure of the probes at desired temperature, T K and M_1 is the molecular weight of the probe. The values of P_1^0 and B_{11} have been calculated as in the literature [23].

The molar volume of the solute, V_1 was calculated using the following relation [24].

$$V_1 = V_c/\rho_r \quad (5)$$

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

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

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

The Flory–Huggins parameters, characterizing the interactions of a vapour-phase probe with a polymer are determined by the following equation:

$$\chi_{12}^\infty = \ln(273.2Rv_2/V_g^0 V_1 P_1^0) - 1 - P_1^0/RT(B_{11} - V_1) \quad (7)$$

where R is the gas constant, v_2 is the specific volume of the polymer.

In this study, the copolymer compositions were determined by ^{1}H NMR analysis. The monomer reactivity ratios were calculated by both Fineman–Ross, and Kelen–Tüdös methods. On the other hand, we examined the interactions of poly(3,4-di-chloro benzyl methacrylate-*co*-ethyl methacrylate, poly(BMA-*co*-EMA), with alcohols, ketones, acetates, aromatics and alkane solute probes by using the IGC method in the temperatures range 130–150°C.

2. Experimental

2.1. Materials

3,4-Dichlorobenzylmethacrylate (BzMA) (monomer) by reaction of sodiummethacrylate with 3,4-dichlorobenzylchloride and inhibited by hydroquinone (Merck) and ethylmethacrylate (EMA) monomers were washed with 5% NaOH solution and then by distilled water; it was dried over anhydrous magnesiumsulphate and distilled under vacuum. 2,2′-Azobisisobutyronitrile (AIBN, Merck) was recrystallized from the chloroform–methanol mixture.

Fourteen polar and non-polar probes were used to test the solubility of the copolymers in this study. They were selected to provide several groups of chemically different nature and polarity. *N*-octane, *n*-nonane, *n*-decane, *n*-undecane and *n*-dodecane were supplied from Aldrich Chemical Co. and methanol, ethanol, acetone, ethyl methyl ketone, methyl acetate, ethyl acetate, benzene, toluene and *o*-xylene were supplied from Merck Chemical Co. as chromatographic grade. All probes were used as received. Chromosorb W (45–60 mesh) was supplied from Sigma Chemical Co.

2.2. Copolymerization

Appropriate quantities of BzMA and EMA with 1,4-dioxane (monomer/solvent = 2:5 w/v) and AIBN were placed in a standard reaction tube and the mixture was flushed with oxygen-free nitrogen for 10 min. In all cases, the initial total monomer concentration was 0.01 mol/l and the initiator (AIBN) was used as 2% of the total weight of monomers. The tube was then tightly sealed and immersed in a thermostatic oil bath at 60°C.

The copolymerizations were restricted to below 15% conversion in order to satisfy the usual copolymerization equation. The copolymers were precipitated in *n*-hexane, purified by at least two reprecipitations with *n*-hexane from dichloromethane solution. It was then dried in a vacuum oven at 40°C for 24 h.

2.3. Characterization

2.3.1. IR spectroscopy

A Mattson 1000 FTIR spectrometer was used. Thin films of poly(BzMA) and poly(BzMA-*co*-EMA), (40:60%), were prepared from dichloromethane solution. The solutions were cast on a clear sodium chloride windows and the solvent was completely evaporated and the films were dried by heating to remove trace amounts of solvent before characterization.

2.3.2. ^{1}H and ^{13}C NMR spectroscopy

Fourier-Transform (FT) ^{1}H and ^{13}C NMR spectra were recorded using Jeol FX 90Q, 89.55 and 22.45 MHz, respectively. The homo and copolymer samples were examined in about 20% (w/v) solutions of $CDCI_3$ using tetramethylsilane (TMS) as internal reference.

2.4. Thermal analysis

Thermogravimetric analysis (TGA) curves were recorded with a Shimadzu TGA-50 thermobalance. An aliquot sample weighing 6 mg was used at a temperature rise of 10°C/min under nitrogen. The glass transition temperatures of poly(BzMA), poly(EMA) and poly(BzMA-EMA9) (40:60 mol%) were determined by differential scanning calorimetry (DSC) using a Shimadzu DSC-50 thermal analyser. Samples of 10 mg were heated at rate of 20°C/min in the presence of air.

2.5. Instrumentation and procedure of thermodynamic studies

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 non-interacting 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 with a soap bubble flow meter at the end of the column. A flow rate of about 20 ml/min was used throughout the experiment. The spiral glass (3.2 mm i.d. × 1.1 m.) tubing was washed with methylene chloride and was annealed prior to use. A column packing material was prepared by coating 45–60 mesh size Chromosorb W treated with poly(PCHEMA-*co*-MA). An amount of 0.2786 and 0.2760 g of poly-(BzMA-*co*-EMA) (7:93%) and poly(BzMA-*co*-EMA) (87:13%) were dissolved in 25 ml of tetrahydrofurane and an amount of 2.6112 and 2.5647 g of the solid supporting materials were, respectively, then 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 [25]. The column was conditioned at a temperature above the glass transition temperature under fast carrier gas (N_2) flow rate for 24 h prior to use. The probes were injected into the column with 1 μl Hamilton syringes. Three consecutive injections were made for each probe at each set of measurements. An injection volume was selected as 0.2 μl. 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 [25].

3. Result and discussion

3.1. Characterization of the copolymers

The feed composition of monomers and the copolymer compositions obtained by ^{1}H NMR analysis are summarized in Table 1.

The FT-IR spectra of poly(BzMA) and poly(BzMA-*co*-EMA) show absorbtion bands typical of the constituent monomeric units and their relative intensity depending on composition. Thus, as a function of BzMA in copolymer, the band at 1732 cm^{-1} (C=C stretching) became strong gradually from 1 to 7. Also, the bands at 1732 (C=O) and 3000–3100, 720–780, 1680–1920 cm^{-1} are the characteristics of BzMA units in the copolymer.

The ^{13}C NMR spectrum of copolymer (BzMA 40%) has the characteristic peaks of the monomeric units at: 176 (C=O), 129, 132 (the ipso carbon of the phenyl ring), 128, 130 ppm (the other carbons of the phenyl ring), 65.2 (O–CH_2-Ar), 60.7 (–OCH_2–CH_3). The ^{1}H NMR spectrum of the copolymer with the same composition is shown in Fig. 1. The peaks at 7.1–7.4 ppm reveal the phenyl ring protons of BzMA units, the signal at 4.9 and 4.0 ppm are assigned to methylene in –OCH_2-Ar and –OCH_2CH_3, respectively.

3.2. Glass transition temperature

The glass transition temperatures of poly(BzMA) and poly(BzMA-*co*-EMA) were determined by a Shimadzu DSC-50 thermal analyser. The T_g of poly(BzMA) is 67°C and that of poly(BzMA-*co*-EMA) (40:60%) is 61°C. The T_g of poly(EMA) was 54°C under conditions similar to that of poly(BzMA).

Table 1
Parameters of Eqs. (8) and (9) for the copolymerization data of BzMA with EMA ($\alpha = \sqrt{H_{\max}H_{\min}} = 0.75$)

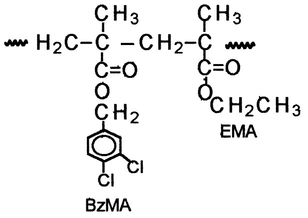
Sam. No	Feed composition[a]		Copoly. composition[a]		F	f	G^b	H^c	η^d	ξ^e
	BzMA (M_1)	EMA (M_2)	(m_1)	EMA (m_2)						
1	0.06	0.94	0.07	0.93	0.06	0.07	−0.79	0.05	−0.98	0.06
2	0.18	0.82	0.18	0.82	0.20	0.21	−0.75	0.19	−0.79	0.20
3	0.31	0.69	0.30	0.70	0.45	0.42	−0.62	0.48	−0.50	0.39
4	0.45	0.55	0.40	0.60	0.60	0.66	−0.43	1.06	−0.23	0.58
5	0.61	0.39	0.50	0.50	1.63	1.00	0.47	2.66	0.01	0.78
6	0.79	0.21	0.73	0.27	3.95	2.33	2.25	6.69	0.30	0.89
7	0.89	0.11	0.87	0.13	8.70	6.69	7.26	11.31	0.60	0.93

[a] Mole fraction.
[b] $F(f-1)/f$.
[c] F^2/f.
[d] $G/(\alpha + H)$.
[e] $H/(\alpha/H)$.

3.3. Copolymerization reactivity ratios

The compositions of copolymer samples obtained from various feed ratios of BzMA and EMA were estimated by ^{1}H NMR analysis, and are given in Table 1.

he plot of copolymer composition (m_1) vs feed composition (M_1) is shown in Fig. 2. The diagram shows an azeotropic composition at 40:60% (BzMA/EMA). The monomer reactivity ratios of BzMA and EMA were computed by two graphical methods according to Eq. (8) (Fineman–Ross method) [26] and Eq. (9) (Kelen–Tüdös method) [27].



$$\frac{F}{f}(f-1) = r_1\frac{F^2}{f} - r_2 \qquad (8)$$

$$\eta = \left(r_1 + \frac{r_2}{\alpha}\right)\xi - \frac{r_2}{\alpha} \qquad (9)$$

F and f are the molar ratios of the monomers in feed and in the copolymer, respectively; and r_1 and r_2 are reactivity ratios of BzMA and EMA monomers, respectively, η and ξ are mathematical functions of F and f, as defined in Table 1, α is an arbitrary denominator having any positive value, but produces more homogeneous distribution of data along the ξ-η axes in Eq. (8), a plot of $F/f(f-1)$ vs. F^2/f should produce a straight line, with r_1 as its slope and $-r_2$ as its intercept. A similar plot of ξ vs. η (in Eq. (9)) provides $[r_1 + (r_2/\alpha)]$ as the slope and $(-r_2/\alpha)$ as its intercept. The parameters of Eqs. (8) and (9) for the monomer pair BzMA/EMA are given in Table 1.

The corresponding graphs are shown in Figs. 3 and 4, and the copolymerization reactivity ratios of BzMA and EMA

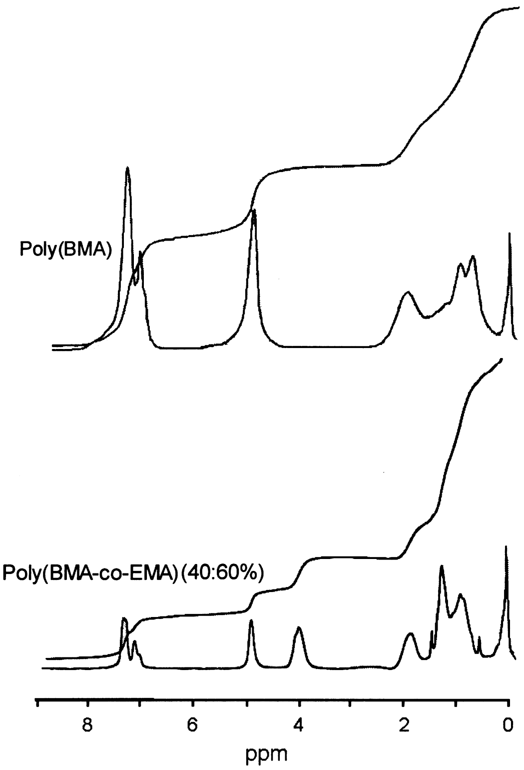


Fig. 1. The ^{1}H-NMR spectra of poly(BzMA) and poly(BzMA-*co*-EMA).

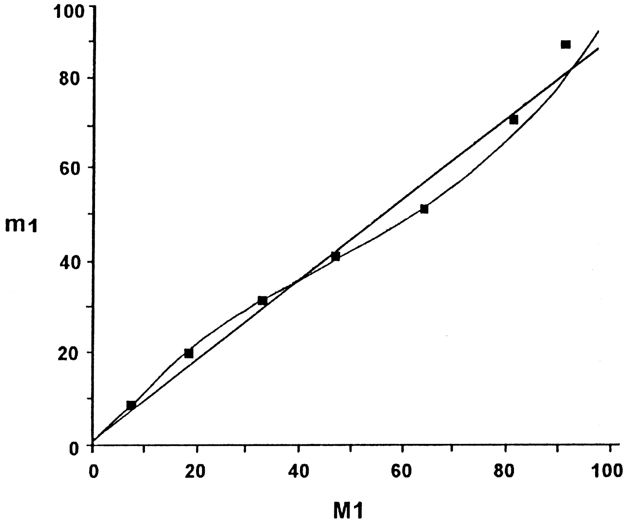


Fig. 2. The copolymerization diagram of BzMA/EMA (copolymer composition vs. feed composition).

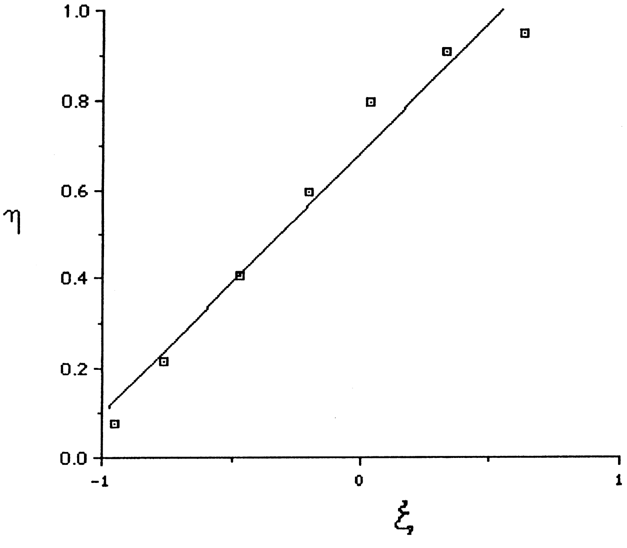


Fig. 3. Kelen–Tüdös plot for the BzMA–EMA copolymer system.

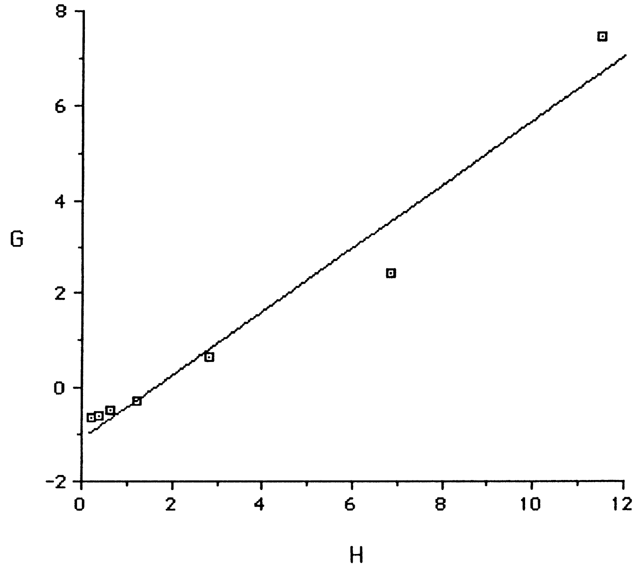


Fig. 4. Fineman–Ross plot for the BzMA–EMA copolymer system.

were found to be:

$r_1 = 0.521 \pm 0.019$, $r_2 = 0.847 \pm 0.221$, $r_1r_2 = 0.441$ (from Eq. (8))

$r_1 = 0.677 \pm 0.008$, $r_2 = 1.117 \pm 0.209$, $r_1r_2 = 0.756$ (from Eq. (9))

The results from both the Fineman–Ross (Eq. (8)) and Kelen–Tüdös (Eq. (9)) methods are in good agreement. Although the copolymerization of BzMA its EMA an alternating tendency shows, BzMA, and the copolymer sequence will be statistical in structure with more EMA. The reactivity ratios determined up to 1990 were collected by Müller [28]. The recent work of Çatalgil and Jenkins agrees with the values reported for the methyl methacrylate, somewhat higher r_2 value of EMA confirms the higher reactivity of EMA compared with that of -ethyl methacrylate (MMA–EMA) system. In that system the smaller monomer (MMA) was the more active one ($r_{\mathrm{MMA}} = 1.58 \pm 0.23, r_{\mathrm{EMA}} = 0.40 \pm 0.14$) [29]. In our case, the smaller monomer (EMA) was also more active. The copolymer will have a statistical arrangement of units in which EMA will tend to predominate.

3.4. Thermal behavior

Thermogravimetric traces of poly(BzMA), poly(EMA) and one poly(BzMA-*co*-EMA) (40:60%) are shown in Fig. 5. The relative thermal stabilities of the various samples were assesed by comparing the initial decomposition temperature (T_i), final decomposition temperature (T_f) and temperature of maximum rate of weight loss ($T_{\max}$). The results of thermal behavior are summarized in Table 2. The homopolymers and all the copolymer samples showed a single decomposition step.

Table 2
Results of thermal analysis of homopolymer and copolymer

Polymer (%)	T_i (°C)	$T_{\max}$ (°C)	T_f (°C)
Poly(BzMA)	225	230	410
Poly(EMA)	216	305	393
Poly(BzMA-*co*-EMA)			
(7:93%)	220	308	395
(40:60%)	222	310	399
(73:27%)	228	313	408

Increasing in the thermal stability of EMA upon incorporation of BzMA as copolymer could be attributed to the blocking effect of these monomers on depropagating poly(ethyl methacrylate) radicals.

3.5. Specific retention volumes

The specific retention volumes, V_g^0 of 14 probes were obtained by using two columns loading poly(BzMA-*co*-EMA) (7:93%) and poly(BzMA-*co*-EMA) (87:13%) at a series of temperatures (130, 140 and 150°C). The values of specific retention volumes, V_g^0 of these probes were calculated according to Eq. (1) and are given in Table 3. As shown in Table 3, V_g^0 values changed for each group solvents with temperature. That is, the specific retention volumes, V_g^0 of the probes decreased with increasing temperature.

The values of Ω_1^∞ and χ_{12}^∞ obtained from Eqs. (2) and (7), respectively, are also collected in Table 4. The values of ΔH_1^∞ of the probes were found from the plot of $\ln \Omega_1^\infty$ against $1/T$ in the Fig. 6.

It has been proposed that the values of Ω_1^∞ greater than 5 are indicative of poor polymer–solute systems while lower values characterize good solubility for such a system [30]. The values of χ_{12}^∞ greater than 0.5 represent unfavourable polymer–solvent interactions, while the values lower than

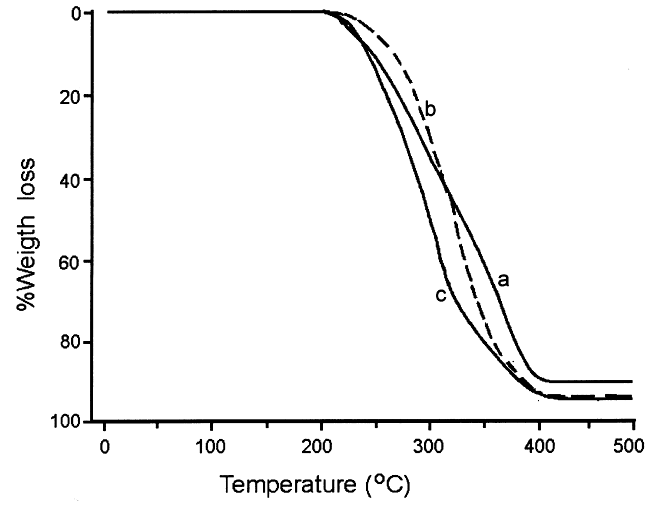


Fig. 5. TGA curves of (a) poly(BzMA-*co*-EMA) (40:60%), (b) poly(BzMA), (c) poly(EMA).

Table 3
Variation of specific retention volumes. V_g^0 (ml/g) of some alcohols, ketones, acetates, aromatics and *n*-alkanes between 130–150°C using poly(BzMA-*co*-EMA) (7:93%) and poly(BzMA-*co*-EMA) (87:13%) as stationary phase

	Poly(BzMA-*co*-EMA) (7:93%)			Poly(BzMA-*co*-EMA) (87:13%)		
Probe/*T* (°C)	130	140	150	130	140	150
Methanol	2.87	2.85	2.47	3.02	2.77	2.43
Ethanol	3.43	3.38	3.05	3.02	2.98	2.67
Acetone	2.63	2.71	2.49	2.73	2.51	2.33
Ethyl methyl ketone	3.39	3.17	2.97	3.66	3.29	2.95
Methylacetate	2.36	2.54	2.32	2.84	2.63	2.35
Ethylacetate	3.16	2.95	2.68	3.45	3.20	2.90
Benzene	3.58	3.40	3.14	4.18	3.86	3.40
Toluene	4.72	3.86	3.41	5.28	4.71	4.05
O-xylene	6.57	6.14	4.84	8.85	7.13	6.04
n-Octane	3.03	2.92	2.71	3.46	3.22	3.00
n-Nonane	3.45	3.29	3.06	4.36	4.07	3.69
n-Decane	4.48	4.37	3.82	6.56	5.66	4.46
n-Undecane	6.95	5.44	4.27	7.97	7.41	5.87
n-Dodecane	10.76	6.52	5.74	15.12	12.33	9.79

0.5 indicate favourable interactions in dilute polymer solutions [31].

The values of Ω_1^∞ and χ_{12}^∞ (in Table 4) have shown that acetates, aromatics, alcohols, ketones and alkanes are non-solvent for poly(BzMA-*co*-EMA) (7:93%) and poly(BzMA-*co*-EMA) (87:13%). According to Ω_1^∞ and χ_{12}^∞ methanol, acetone, ethyl methyl ketone, methylacetate, ethylacetate, *o*-xylene, *n*-octane, *n*-nonane, *n*-decane, *n*-undecane and *n*-dodecane had been reported as non-solvents for poly(ethyl methacrylate) at 150°C [32]. 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^∞ showed difference depending on change in the number of carbons in the series. 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, the values of χ_{12}^∞, Ω_1^∞, ΔG_1^∞ decreased with increasing in the column temperature.

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 Eqs. (3) and (4) are collected in Table 5. The ΔH_1^∞ values of alcohols, ketones, acetates, aromatics and *n*-alkanes changed from 28.41 to 73.4, 54.04 to 22.86, 27.71 to 23.56, 20.09 to 18.01, 29.79 to 21.48, 20.79 to 18.71, 24.94 to 14.55, 19.40 to 13.16, 7.62 to 33.26,

Table 4
The weight fraction activity coefficients, Ω_1^∞ and interaction parameters, χ_{12}^∞ of poly(BzMA-*co*-EMA) (7:93%) and poly(BzMA-*co*-EMA) (87:13%) with some alcohols, ketones, acetates, aromatics and *n*-alkane systems between 130–150°C

	Ω_1^∞ (copoly[a])			Ω_1^∞ (copoly[b])			χ_{12}^∞ (copoly[a])			χ_{12}^∞ (copoly[b])		
Probe/*T*(°C)	130	140	150	130	140	150	130	140	150	130	140	150
Methanol	27.60	20.89	18.50	26.05	21.57	18.81	1.600	1.298	1.156	1.638	1.426	1.267
Ethanol	51.29	27.90	17.89	44.22	31.65	20.30	2.429	1.744	1.267	2.324	1.965	1.495
Acetone	17.54	13.55	11.82	16.90	14.63	12.64	1.134	0.852	0.692	1.192	1.024	0.854
EMK[c]	21.35	17.86	15.20	19.78	17.21	15.31	1.350	1.147	0.963	1.368	1.205	1.065
MA[d]	15.35	11.34	9.94	12.76	10.95	9.81	1.168	0.841	0.686	1.078	0.901	0.768
Ethylacetate	17.13	14.32	12.55	15.70	13.20	11.60	1.244	1.041	0.885	1.251	1.055	0.902
Benzene	26.28	21.68	18.35	22.51	19.10	16.95	1.487	1.2.56	1.052	1.427	1.224	1.065
Toluene	35.18	32.87	28.38	31.45	26.94	23.89	2.116	2.033	1.870	2.099	1.929	1.793
O-Xylene	46.28	37.13	35.42	34.36	31.97	28.56	2.111	1.967	1.902	2.008	1.913	1.776
n-Octane	53.97	42.62	35.27	47.26	38.65	31.86	2.142	1.884	1.671	2.105	1.881	1.665
n-Nonane	87.87	68.33	54.91	69.53	55.23	45.54	2.654	2.379	2.139	2.515	2.261	2.047
n-Decane	123.44	91.25	76.72	84.30	70.46	65.71	3.010	2.685	2.490	2.724	2.522	2.430
n-Undecane	144.41	129.36	117.77	125.93	94.97	85.67	3.184	3.051	2.936	3.143	2.837	2.713
n-Dodecane	168.28	159.35	150.80	119.75	100.12	88.42	3.348	3.444	3.193	3.103	2.902	2.754

[a] poly(BzMA-*co*-EMA) (7: 93%).
[b] poly(BzMA-*co*-EMA) (87:13%).
[c] EMK: Ethyl methyl ketone.
[d] MA: Methylacetate.

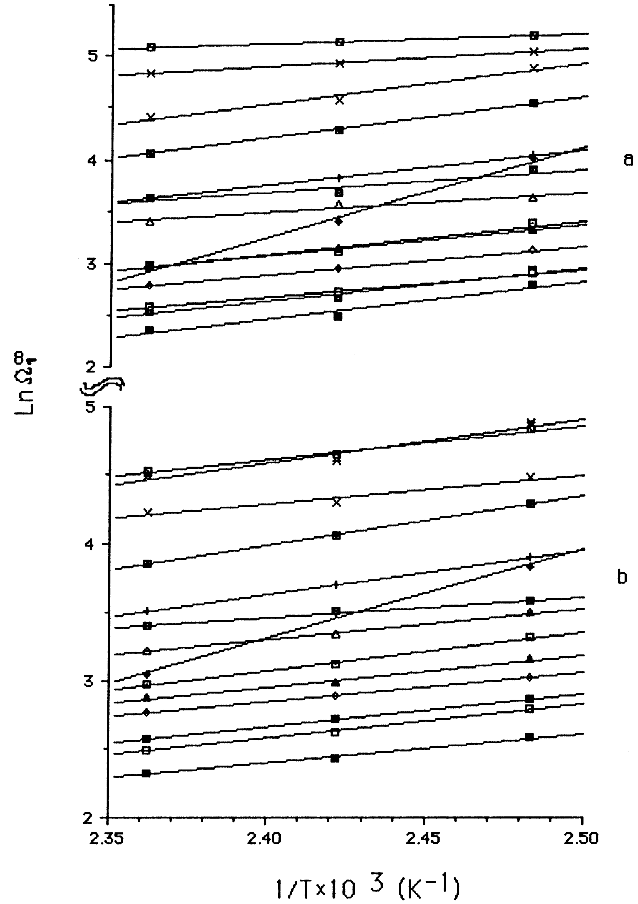


Fig. 6. Variation of logarithm of weight fraction activity coefficients, Ω_1^∞ with reciprocal of absolute column temperature, $1/T$ K^{-1} for poly(BMA-*co*-EMA) (7:93%) (a), poly(BMA-*co*-EMA) (87:13%) (b), and some solutes: □: Methanol, △: Acetone, ⊗ : EMK., ⍓: Methyl Acetate, ◆: Ethyl Acetate, +: Benzene, ▽: Toluene, ■: *o*-Xylene, ●: *n*-Octane, ⊙: *n*-Nonane, ⊠ *n*-Decane, ◇: *n*-Undecane, × : *n*-Dodecane.

16.63 to 29.10 kJ/mol, respectively, using poly(BzMA-*co*-EMA) (7:93%) and poly(BzMA-*co*-EMA) (87:13%) as stationary, as seen from Table 5.

The enthalpy data in Table 5 indicated that most of the solvents showed a stronger interaction with poly(BzMA-*co*-EMA) (7:93%) than that of poly(BzMA-*co*-EMA) (87:13%), except for toluene, *n*-hexane, *n*-dodecane. It may be asserted from these experimental results that BzMA units in the copolymer decreased the polymer solvents interactions, because it is a more bulky group than EMA unit.

The solubility parameter of poly(BzMA-*co*-EMA) were evaluated from either the slope or intercept of variation of the term $[(\delta_1^2/RT) - \chi_{12}^\infty/V_1]$ with solubility parameters of the solutes, δ_1 (cal/cm^3)$^{0.5}$ as 6.73 (cal/cm^3)$^{0.5}$, 7.15 (cal/cm^3)$^{0.5}$ at 140°C, respectively [33].

4. Conclusions

Some copolymers of 3, 4-dichlorobenzylmethacrylate (BzMA) with ethyl methacrylate (EMA) were formed in 1,4-dioxane by using AIBN at 60°C. The copolymers were characterized by FT-IR, ^{1}H–^{13}C NMR and DSC. The percentages of BzMA and EMA in the copolymers were established by ^{1}H NMR analysis. The glass transition temperatures of the copolymer (40:60%) were found to be 61°C. The copolymerization monomer reactivity ratios were calculated by using both Kelen–Tütös and Fineman–Ross Eqs. (8) and (9). Inverse gas chromatography technique was succesfully applied to determine some thermodynamic properties of poly(BzMA-*co*-EMA) such as Flory–Huggins interaction parameters, χ_{12}^∞, the partial molar free energy of mixing, ΔG_1^∞, the weight fraction activity coefficients, Ω_1^∞,

Table 5
The partial molar free energies of mixing, ΔG_1^∞ (kJ/mol) and partial molar entalphy, ΔH_1^∞ (kJ/mol) of poly(BzMA-*co*-EMA) (7:93%) and poly(BzMA-*co*-EMA) (87:13%) with some alcohols, ketones, acetates, aromatics and *n*-alkanes systems between 130–150°C

	ΔG_1^∞ (kJ/mol)			ΔG_1^∞ (kJ/mol)			ΔH_1^∞ (kJ/mol)	
	Copoly[a]			Copoly[b]			Copoly[a]	Copoly[b]
Probe/T(°C)	130	140	150	130	140	150	130–150	130–150
Methanol	11.11	10.44	10.26	10.92	10.55	10.32	28.41	22.86
Ethanol	13.19	11.43	10.14	12.70	11.86	10.59	73.44	54.04
Acetone	9.60	8.95	8.69	9.47	9.21	8.92	27.71	20.09
Ethyl methyl ketone	10.26	9.90	9.57	10.00	9.77	9.60	23.56	18.01
Methylacetate	9.15	8.34	8.08	8.53	8.22	8.03	29.79	18.71
Ethylacetate	9.52	9.14	8.90	9.23	8.86	8.62	21.48	20.79
Benzene	10.95	10.56	10.23	10.43	10.13	9.95	24.94	19.40
Toluene	11.93	11.99	11.77	11.55	11.31	11.16	14.55	14.90
O-Xylene	12.85	12.41	12.55	11.85	11.90	11.80	18.71	13.10
n-Octane	13.36	12.88	12.53	12.92	12.55	12.17	29.79	27.71
n-Nonane	15.00	14.51	14.09	14.21	13.77	13.43	32.56	29.10
n-Decane	16.14	15.50	15.26	14.86	14.61	14.72	33.26	16.63
n-Undecane	16.66	16.70	16.77	16.20	15.64	15.65	13.86	27.02
n-Dodecane	17.17	17.41	17.64	16.03	15.82	15.76	7.62	21.48

[a] poly(BzBMA-*co*-EMA)(7:93%).

[b] poly(BzBMA-*co*-EMA) (87:13%).

and the partial molar heats of mixing, ΔH_1^{∞}, at infinite dilution of the solvents of alcohols, ketones, acetates, aromatics and *n*-alkanes. The results obtained are in good agreement with that of polymer–non-solvents systems. The technique is relatively uncomplicated and the data reduction is carried out by a computer.

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