Copolymerization of Two New Kinds of Methacrylate Monomers and Determination of Monomer Reactivity Ratios

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ABSTRACT: New methacrylate monomers 2-(*p*-methoxyphenoxy)-2-oxo-ethyl methacrylate (pMPOEMA), 2-(*p*-chlorophenoxy)-2-oxo-ethyl methacrylate (pClPOEMA), and 2-oxo-2-phenylamino ethylene methacrylate (PAMA) were synthesized for the first time. The free-radical-initiated copolymerization of pMPOEMA and pClPOEMA with PAMA was carried out in 1,4-dioxane solution at 65°C using 2,2′-azobisisobutyronitrile (AIBN) as an initiator with different monomer-to-monomer ratios in the feed. The monomers and copolymers were characterized by Fourier transform infrared, ^{1}H and ^{13}C NMR spectral studies. The copolymer compositions were evaluated from nitrogen content in polymers. The reactivity ratios of the monomers were determined by applying Fineman–Ross and Kelen–Tüdös methods. The analysis of reactivity ratios revealed that pMPOEMA and pClPOEMA are less reactive than PAMA is, and copolymers formed are statistically in nature. The molecular weights ($\bar{M}_w$ and $\bar{M}_n$) and polydispersity index of the polymers were determined using gel permeation chromatography. Thermogravimetric analysis of the polymers reveals that the thermal stability of the copolymers increases with an increase in the mole fraction of pMPOEMA and pClPOEMA in the copolymers. Glass transition temperatures of the copolymers were found to decrease with an increase in the mole fraction of PAMA in the copolymers. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1864–1874, 2006

Key words: methacrylate; monomer reactivity ratios; thermogravimetric analysis; glass transition temperatures

INTRODUCTION

Nowadays there exists a strong demand for "functional polymers" with very specific properties. In polymer science, the improvement of the mechanical properties has been the center of interest for many years, but today special electrical and optical properties of polymers receive an increasing interest. Functional groups give the polymer structure special character, substantially different from the inherent properties of the basic polymer chain.[1] In recent years, some comprehensive work has been published on functional monomers and their polymers.[2–4] The effect of polymer structure on the reactivity and properties of reactive moieties is very important for the chemical modifications and for the eventual applications of reactive polymers.[5–7] Functionalized polymers have wide applications for various biological and technological purposes.[8,9]

Acrylate and methacrylate vinyl esters are readily polymerized by free radical polymerization (FRP) to form linear, branched, or network polymers.[10]

Reactivity ratios are among the most important parameters for composition equation of copolymers, which can offer information such as relative reactivity of monomer pairs and estimate the copolymer composition. Knowledge of the copolymer composition is an important step in the evaluation of its utility. Copolymer composition and its distribution are dependent on the reactivity ratios. The most common mathematical model of copolymerization is based on finding the relationship between the composition of copolymers and the composition of the monomer feed in which the monomer reactivity ratios are the parameters to be determined.[11,12] The calculation of the monomer reactivity ratios requires the mathematical treatment of experimental data on the compositions of copolymers and monomer feed mixtures. [Monomer reactivity ratios are generally determined at low conversion. In the classic terminal model of copolymerization, it has been suggested that, for a given pair of monomers, the instantaneous copolymer composition is a function of instantaneous feed only. Among several methods available to determine monomer reactivity ratio values, the Finemann–Ross and Delen–Tudos methods are appropriate for the determination of monomer reactivity ratios at low conversions.]

pMPOEMA and pClPOEMA are new methacrylate esters having pendant oxycarbonyl group. PAMA is

TABLE I
Monomer Composition in Feed and in Copolymer[a]

Sample	Feed composition in mole fraction		Conversion (%)	Elemental N %	Coplymer composition in mole fraction	
	PAMA (M_1)	pClPOEMA (M_2)			PAMA (m_1)	pClPOEMA (m_2)
1	0.200	0.800	11.023	2.051	0.354	0.646
2	0.300	0.700	10.250	2.751	0.468	0.532
3	0.400	0.600	7.625	3.055	0.515	0.485
4	0.500	0.500	9.214	3.201	0.539	0.461
5	0.600	0.400	8.063	3.425	0.573	0.427
6	0.700	0.300	9.078	3.682	0.613	0.387
7	0.800	0.200	10.045	4.521	0.737	0.263

[a] Solvent, 1,4-dioxane; temperature, (65 ± 1)°C; initiator, AIBN (1% weight of the monomers); nonsolvent, ethanol.

also a new methacrylate ester having pendant amide group. In a previous study, the synthesis, characterization, and copolymerization of such monomers and their polymers have been described.[13,14] However, no studies on reactivity ratios in the copolymerizations of pMPOEMA and pClPOEMA with PAMA are available in the literature.

The present article investigates the synthesis, and structural and thermal characterization of copolymers of PAMA with pMPOEMA and pClPOEMA as well as the reactivity ratios in the copolymerization. For this purpose, reactivity ratios r_1 for the classical copolymerization model were determined using the linearization methods of Finemann–Ross (FR method) and Kelen–Tüdös (KT method).[15,16]

EXPERIMENTAL

Materials

p-chloro phenol, *p*-methoxy phenol, aniline, and chloroacetylchloride, (Merck) were used as received. Sodium methacrylate, 1,4-dioxane, potassium carbonate, acetonitrile, and anhydrous magnesium sulfate (Aldrich) were also used as received. 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from chloroform–methanol. pMPOEMA, pClPOEMA, and PAMA were prepared as previously reported.[13,14]

Copolymerization

Copolymerizations of pClPOEMA and pMPOEMA with PAMA using different proportions of PAMA were carried out, in glass ampoules under N_2 atmosphere, in 1,4-dioxane solution with AIBN (1%, based on the total weight of monomers) as an initiator. The reacting components were degassed by threefold freeze–thawing cycles and then immersed in an oil bath at 65°C ± 0.1°C for a given reaction time. The reaction time was selected to give conversions less than 10% to satisfy the differential copolymerization

equation.[17] After the desired time, the copolymers were separated by precipitation in ethanol and reprecipitated from CH_2Cl_2 solution. The polymers were purified by reprecipitation to avoid the formation of homopolymers. The polymers were finally dried under vacuum, at 45°C, to constant weight. The amounts of monomeric units in the copolymers were determined by elemental analysis. The feed composition and copolymer composition for the copolymerization of pClPOEMA–PAMA and pMPOEMA-*co*-PAMA are presented in Tables I and II.

Characterization techniques

Infrared spectra were measured on a Jasco 460 Plus FTIR spectrometer. The ^{1}H and ^{13}C NMR spectra of the monomer and copolymers were recorded, in $CDCl_3$ with tetramethylsilane as the internal standard, using a Bruker GmbH DPX-400 400-MHz FT-NMR spectrometer. Thermal data were obtained using a Setaram DSC-131 instrument and Labsys TGA thermobalance, under N_2 atmosphere. Molecular weight ($\bar{M}_w$ and $\bar{M}_n$) of the polymers were determined using Waters 410 gel permeation chromatography equipped with a differential refractive index detector and calibrated with polystyrene standards. Elemental analysis was carried out by a LECO-932 microanalyzer.

RESULTS AND DISCUSSION

Structural characterization of the copolymers

The constituent monomeric units of the copolymer are shown in Scheme 1.

The FTIR spectrum of poly(pMPOEMA-*co*-PAMA) is shown in Figure 1(a).

The absorption peak at 3080 cm^{-1} is due to aromatic C—H stretching. The peaks at 2950 and 2860 cm^{-1} are due to C—H stretching of methyl and methylene groups. The strong absorptions at 1740, 1770, and 1680 cm^{-1} in the IR spectra of poly(pMPOEMA-*co*-PAMA)s

Sample	Feed composition in mole fraction		Conversion (%)	Elemental N %	Coplymer composition in mole fraction	
	PAMA (M_1)	pMPOEMA (M_2)			PAMA (m_1)	pMPOEMA (m_2)
1	0.200	0.800	9.213	2.102	0.358	0.642
2	0.300	0.700	9.410	2.600	0.440	0.560
3	0.400	0.600	10.113	2.851	0.479	0.521
4	0.500	0.500	8.712	3.352	0.557	0.443
5	0.600	0.400	9.513	3.500	0.580	0.420
6	0.700	0.300	11.078	3.752	0.619	0.381
7	0.800	0.200	9.891	4.621	0.748	0.252

[a] Solvent, 1,4-dioxane; temperature, $(65 \pm 1)°C$; initiator, AIBN (1% weight of the monomers); nonsolvent, ethanol.

are due to the carbonyl stretching of ester carbonyl(in both the monomeric units), oxycarbonyl, and amide carbonyl stretching groups, respectively. The band at 3230 cm^{-1}(—NH in the PAMA unit) is the most characteristic for the copolymer. The aromatic C=C stretching appears at about 1590 and 1465 cm^{-1}. The medium absorption peaks at 1180 cm^{-1} is attributed to the C—O stretch of the ester group. Peaks at 750–780 cm^{-1} may be assigned to the aromatic C—H out-of-plane bending, and those at 1450 cm^{-1} may be assigned to CH$_3$ bending vibrations.

The ^{1}H NMR and ^{13}C NMR spectra of poly(pMPOEMA-*co*-PAMA) are shown in Figures 2(a) and 2(b) respectively. The ^{1}H NMR spectrum of poly(pMPOEMA-*co*-PAMA) is consistent with its chemical structure. Multiplet resonance absorptions at 6.8–7.7 ppm are due to the aromatic protons of pMPOEMA and PAMA. The NH protons of PAMA resonance appear at 8.4 ppm. The signals at 4.8 ppm are due to —OCH$_2$ protons of two monomeric units. The methoxy protons of pMPOEMA resonance appear at 3.8 ppm. The backbone methylene protons of the two comonomer units are observed between 2.2 and 1.8 ppm. The α-methyl protons of monomer units are observed at 1.1–1.4 ppm. The chemical shift assignments were made from the off-resonance decoupled spectra of the

copolymers. In the proton decoupled ^{13}C NMR spectrum of copoly(pMPOEMA-*co*-PAMA), the resonance signals at 166.1 and 168.4 ppm are due to the aryloxy carbonyl and amide ester carbonyl carbons respectively. The ester carbonyl carbon of both the monomeric units appears at 173.3 ppm. The group of signals at 115.5–155.3 ppm arises from aromatic carbons in the pMPOEMA and PAMA units. The signals at 58.5 ppm are due to the OCH$_2$ carbons of pMPOEMA and PAMA units. The methoxy carbon signal is observed at 48.2 ppm.

Although the IR spectra of the pClPOEMA-PAMA [Fig. 1(b)] copolymers show characteristic bands at 1740 cm^{-1} (C=O of ester of both the polymers) and 1760 cm^{-1} (C=O of aryloxycarbonyl), 1680 cm^{-1} (amide ester carbonyl), 3235 cm^{-1} (—NH in the PAMA unit), 3100–3000 cm^{-1}, 1590 cm^{-1} (phenyl), 1160 cm^{-1} (C—O). The ^{1}H NMR and ^{13}C NMR spectra of poly(pClPOEMA-*co*-PAMA) are shown in Figures 3(a) and 3(b) respectively. The ^{1}H NMR spectrum of poly(pClPOEMA-*co*-PAMA) is consistent with its chemical structure. The signals at 8.5 ppm are due to —NH protons of the PAMA. The broad peaks at 7.1–7.8 ppm are attributed to phenyl protons of two monomeric units; 4.8 ppm, —OCH$_2$ protons; 2.9 ppm, methylene protons of two monomeric units; and 0.9–2.2 ppm, other aliphatic protons, including those in the backbone. ^{13}C NMR peak assigments of this copolymer are 48.0 ppm (—OCH$_2$— carbons), 121.4–148.3 ppm (aromatic ring carbons), and 165.2 and 167.8 ppm (—C=O for aryloxycarbonyl and amide ester carbonyl carbons). The ester carbonyl carbon of both the monomeric units appears at 172.8 ppm.

The main evidence of the polymer formation is certainly the disappearance of some characteristic signals of the double bond in the spectra, and this fact was effectively observed in our case. Thus, two bands vanished from the IR spectrum: the absorption band at 920 cm^{-1} assigned to the C—H bending of geminal =CH$_2$ and the stretching vibration band
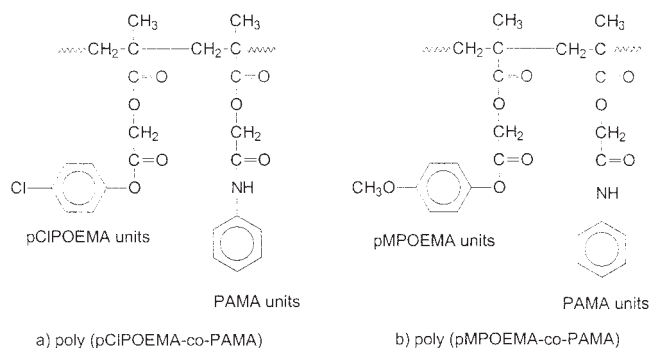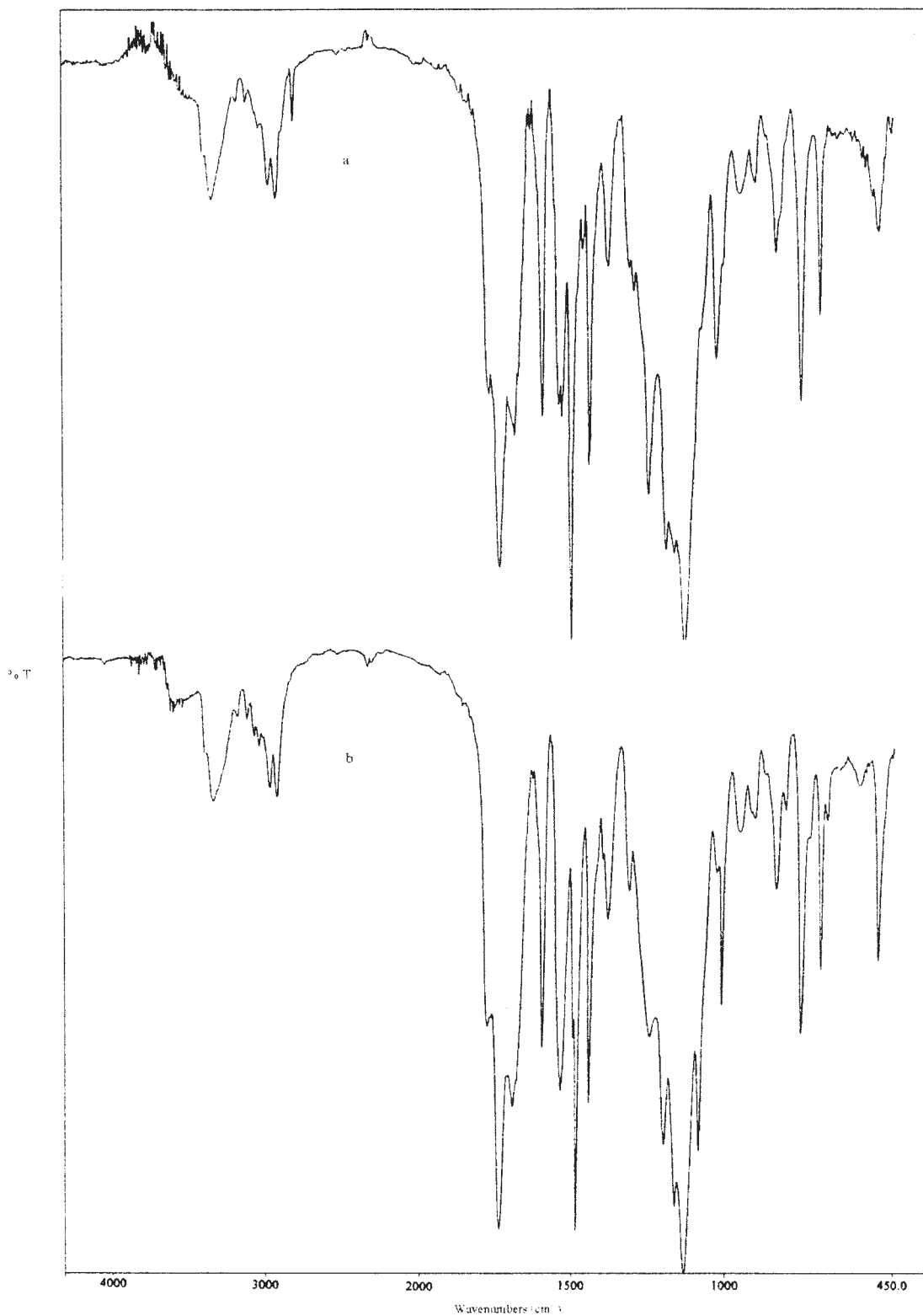

Scheme 1

Figure 1 FTIR spectrum of (a) copoly(pMPOEMA–PAMA) [$m_1 : m_2$, 52.1 : 47.9] and (b) copoly(pClPOEMA–PAMA) [$m_1 : m_2$, 48.5 : 51.5].

of C=C at 1633 cm^{-1}. From ^{1}H NMR spectroscopy, the formation of the polymer is also clearly evident from the vanishing of the two singlets at 6.2 and 5.6 ppm of the vinyl protons and the appearance of the broad signal at 2.2–1.7 ppm assigned to an aliphatic —CH$_2$— group. All the other spectroscopic
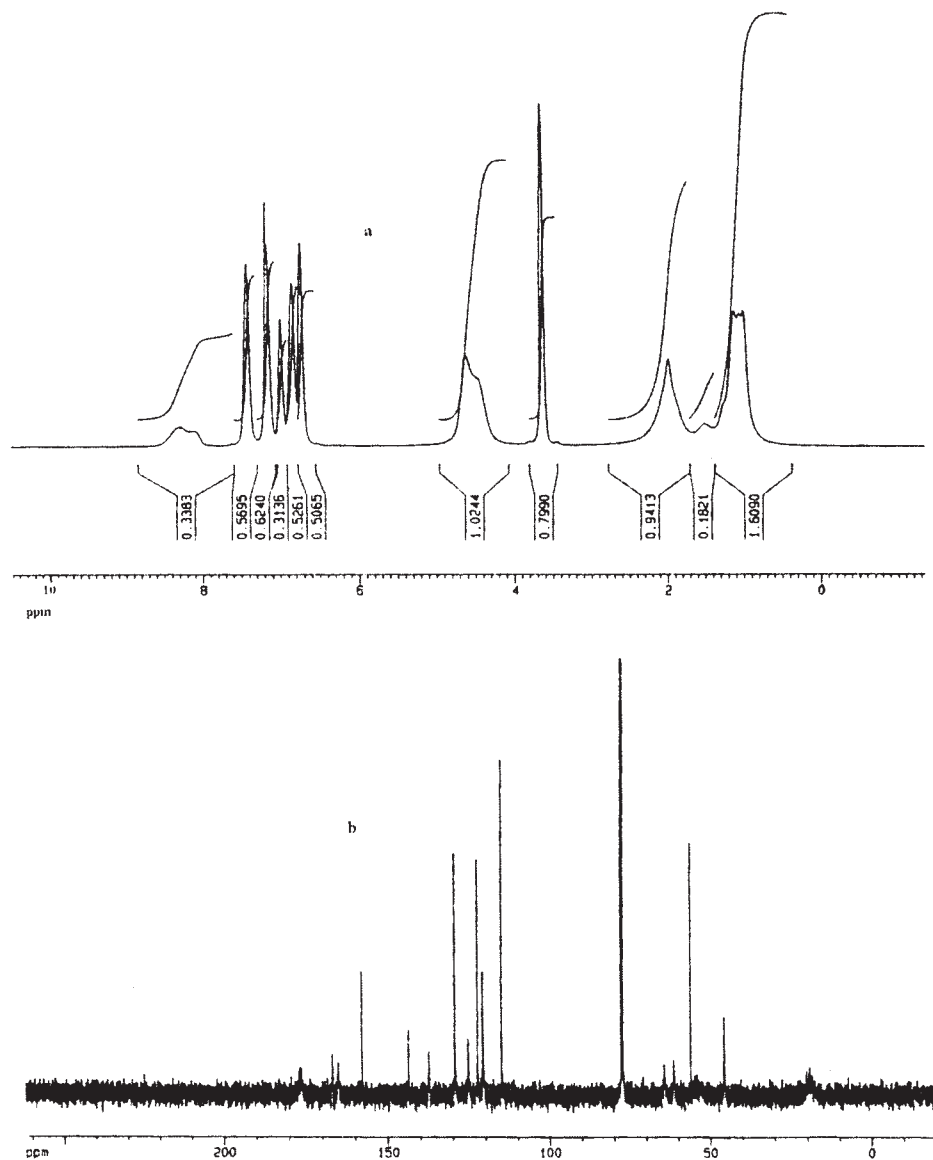
Figure 2 ^{1}H NMR (a) and ^{13}C NMR (b) spectra of copoly(pMPOEMA–PAMA) [m$_1$:m$_2$, 52.1:47.9].

signals appeared in a normal mode for the macromolecules.

Molecular weights of the polymers

The molecular weights of the polymers were determined by GPC with polystyrene and tetrahydrofuran as the standard and the solvent, respectively. The weight–average ($\bar{M}_w$) and number–average ($\bar{M}_n$) molecular weights, and the polydispersity indexes ($\bar{M}_w/\bar{M}_n$) of polymer samples are presented in Table III. The PDIs of the polymers are close to 2.0. The theoretical values of PDI for polymers via radical recombination and disproportionation are 1.5–2.0, respectively.[18] The value of PDI in homopolymerization is also known to depend on chain termination.

Determination of the physical parameters of the polymers

Some physical parameters such as density (d), solubility parameter (δ), and inherent viscosity (η_{inh}) of the polymers were determined in this study. The densities of the polymers were determined experimentally by the flotation method,[19] at 25°C, using mixtures of methanol and formic acid as the floating agent, and many glass beads of known densities. The solubility parameters of the polymers were determined by using a titration method[19] at 25°C from a solubility test using CH_2Cl_2 as a solvent and n-hexane and ethanol as nonsolvents. Solutions of the polymers in $CHCl_3$ at the concentration of 0.5 g dL^{-1} were used to determine inherent viscosities (η_{inh} = ln η_r/C). Measurements were performed by an Ubbelohde viscometer thermo-
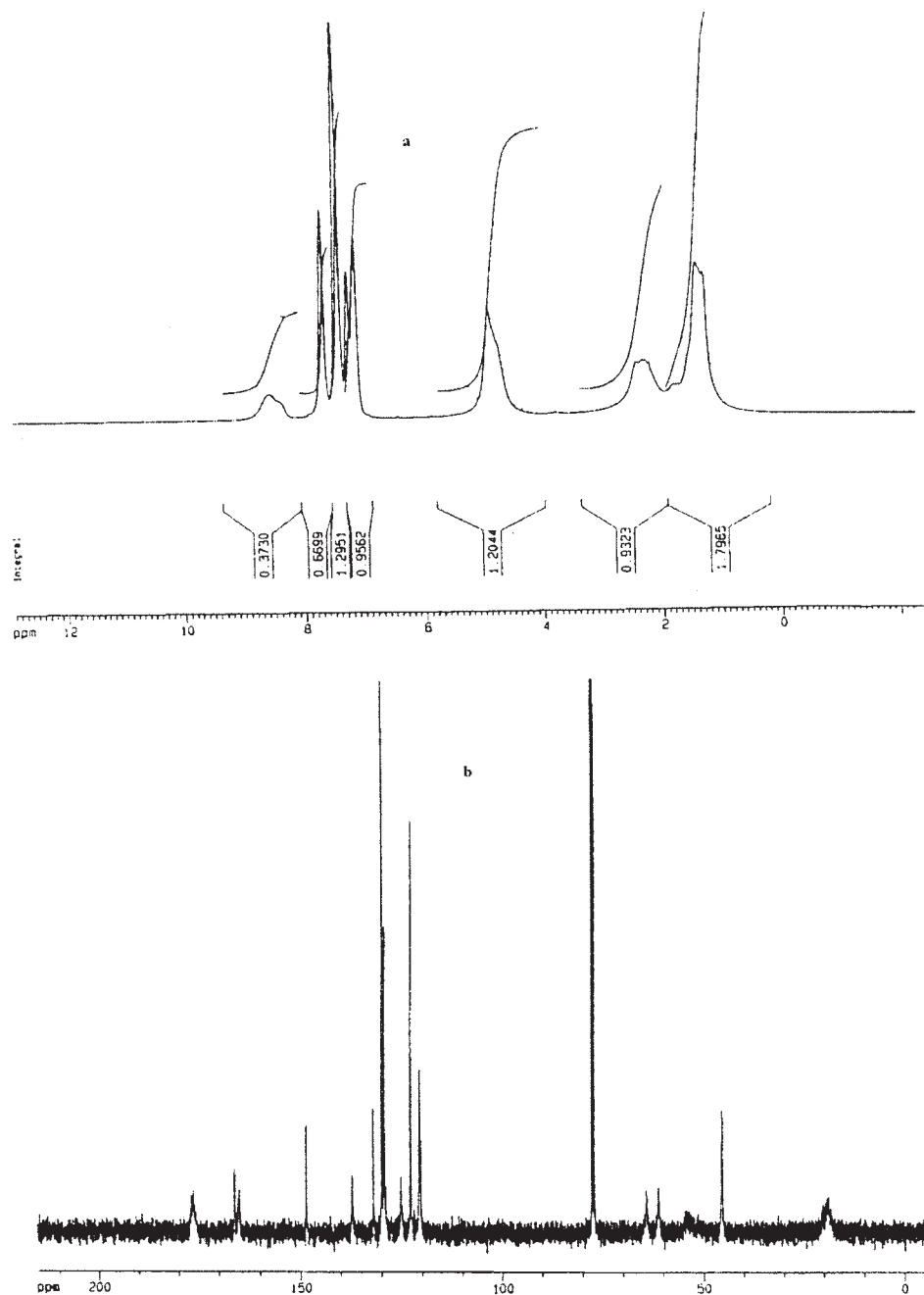
Figure 3 ^{1}H NMR (a) and ^{13}C NMR (b) spectra of copoly(pClPOEMA–PAMA) [m_1:m_2, 48.5:51.5].

statted at 25°C. The change in viscosity with the change in composition of the polymer is random. These values are shown in Table III.

Hyrogen bonding effects on the copolymerization

According to the nature of the conjugation between double bonds and functional groups (C=O of amide, and ester), all three monomers (pClPOEMA, pMPO-EMA, and PAMA) can be considered as electron acceptors. In addition, this fact does not prevent the monomers from having sufficient activity in free-rad-

ical copolymerization of pClPOEMA–PAMA and pM-POEMA–PAMA monomer pairs, thanks to the interaction between functional groups of the comonomers or macroradicals through H-bonding. This effect can be illustrated as shown in Scheme 2.

Determination of monomer reactivity ratios

The monomer reactivity ratios for the copolymerization of pMPOEMA and pClPOEMA with PAMA were determined from the monomer feed ratios and the copolymer composition. The Fineman–Ross (FR) and

TABLE III
Physical Parameters, Molecular Weights, and Polydispersity Index Values of Polymers

	d (g cm^{-3})	η_{inh} (dL g^{-1})	δ (cal/cm^3)$^{1/2}$	$\bar{M}_w \times 10^4$	$\bar{M}_n \times 10^4$	PDI
Poly(pMPOEMA–PAMA)						
64.2/35.8	1.01	0.57	10.55	5.72	3.37	1.70
44.3/55.7	1.07	0.50	11.02	6.68	3.71	1.80
38.1/61.9	1.14	0.45	11.51	5.12	3.15	1.63
25.2/74.8	1.18	0.42	11.97	5.32	2.73	1.95
Poly(pClPOEMA–PAMA)						
64.6/35.4	0.98	0.58	9.81	4.17	2.39	1.74
48.5/51.5	1.07	0.53	10.34	6.48	3.41	1.90
38.7/61.3	1.16	0.45	11.51	7.52	4.58	1.64
26.3/73.7	1.18	0.42	11.98	5.43	3.51	1.55
Poly(pMPOEMA)	0.98	0.59	10.40	5.22	3.01	1.73
Poly(pClPOEMA)	1.02	0.61	9.92	5.79	3.17	1.83
Poly(PAMA)	1.20	0.40	12.09	6.54	3.45	1.90

Kelen–Tüdös (KT) methods were used to determine the monomer reactivity ratios. The significance of parameters of F–R and K–T equations are presented in Tables IV and V. According to the FR method, the monomer reactivity ratios can be obtained by the equation

$$G = Fr_1 - r_2 \qquad (1)$$

where the reactivity ratios, r_1 and r_2, correspond to the pMPOEMA and PAMA monomers respectively. The parameters G and H are defined as follows:

$$G = F(f-1)/f \quad \text{and} \quad H = F^2/f \qquad (2)$$

with

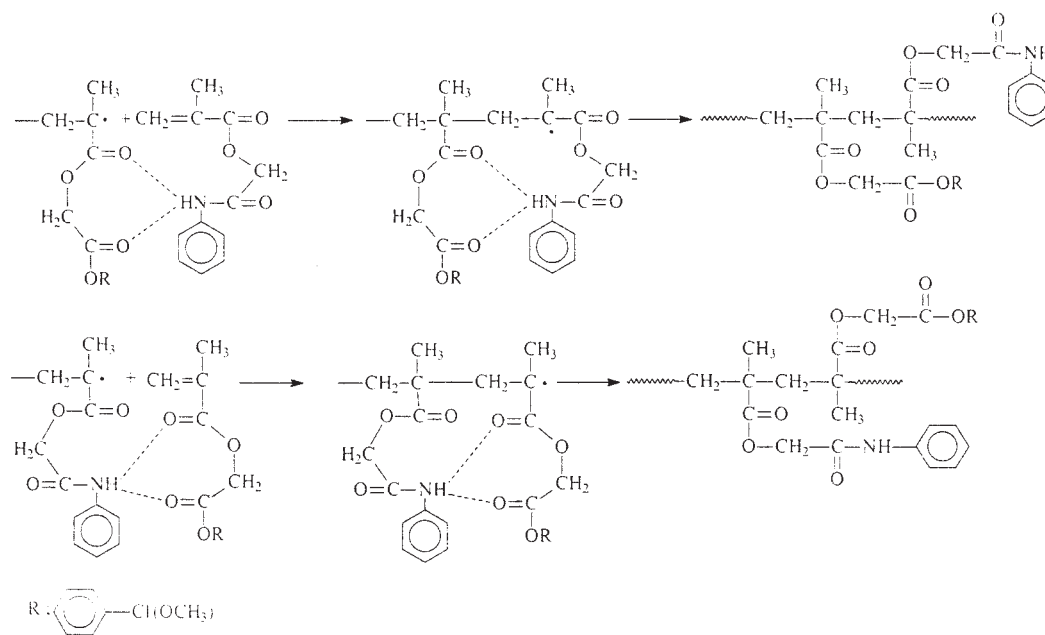$$F = M_1/M_2 \quad \text{and} \quad f = m_1/m_2 \qquad (3)$$

M_1 and M_2 are the monomer molar compositions in feed and m_1 and m_2 the copolymer molar compositions.

Alternatively the reactivity ratios can be obtained using the KT method which is based on the equation

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \qquad (4)$$

where η and ξ are functions of the parameters G and H:

$$\eta = G/(\alpha + H) \quad \text{and} \quad \xi = H/(\alpha + H) \qquad (5)$$

Scheme 2.

TABLE IV
F–R and K–T Parameters for Copoly(pMPOEMA–PAMA) Systems

Sample	$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f-1)/f$	$H = F^2/f$	$\eta = G/(\alpha + H)$	$\varepsilon = H/(\alpha + H)$
1	4.000	2.968	2.652	5.391	0.430	0.874
2	2.333	1.625	0.897	3.349	0.217	0.812
3	1.500	1.381	0.414	1.629	0.185	0.667
4	1.000	1.257	0.204	0.796	0.130	0.506
5	0.667	0.919	−0.059	0.484	−0.047	0.384
6	0.429	0.786	−0.117	0.234	−0.116	0.231
7	0.250	0.558	−0.198	0.112	−0.223	0.126

$\alpha = (H_{max} \cdot H_{min})^{1/2} = 0.777.$

and α a constant that is equal to $(H_{max} \cdot H_{min})^{1/2}$, H_{max} and H_{min} being the maximum and the minimum H values, respectively, from the series of measurements. From the linear plot of η as a function of ξ, the values of η for $\xi = 0$ and $\eta = 1$ are used to calculate the reactivity ratios according to the equations

$$\xi = 0 => \eta = -r_1/\alpha \quad \text{and} \quad \xi = 1 => \eta = r_2 \quad (6)$$

The graphical plots concerning the methods previously reported are given for poly(pClPOEMA-co-PAMA) in Figures 4 and 5, and the reactivity ratios are summarized in Table VI.

In all cases and for all graphical methods the plots were linear, indicating that these copolymerizations follow the conventional copolymerization kinetics and that the reactivity of a polymer radical is determined only by the terminal monomer unit.

For pMPOEMA and PAMA systems, the r_1 values are higher than the r_2 values. The higher r_1 value of PAMA confirms the higher reactivity of PAMA compared with that of pMPOEMA. For pClPOEMA and PAMA systems, the r_1 values are higher than the r_2 ones. The higher r_1 value of PAMA confirms the higher reactivity of PAMA compared with that of pClPOEMA. The reactivity ratio values (r_1 and r_2) of copoly(pMPOEMA–PAMA) and copoly(pClPOEMA–PAMA) are less than 1. The product $r_1.r_2$ indicates that the two systems copolymerize randomly in the polymer chain although there is a possible tendency for alternation. Usually, these results permit us to assume

that the chain growth reactions proceed predominantly by the addition of pClPOEMA or pMPOEMA comonomers to PAMA macroradical through intermediate formation of H-bond between secondary amide and ester carbonyl groups according to Scheme 1. However, this fact is not observed in radical copolymerization between monomers having ester carbonyl groups such as maleic anhydrides and alkyl acrylates and N,N-dialkylacrylamides anologies to PAMA.[20] Such copolymerizations predominantly lead to the formation of random copolymers enriched with acrylic monomer units ($r_1 = 3.5$ and $r_2 = 0.03$ for methyl methacrylate–maleic anhydride pair[12]), also confirming that a H-bond effect is responsible for an increased tendency toward alternation in the radical copolymerization of PAMA with pClPOEMA or pMPOEMA. The relationships between mole fractions of pMPOEMA and pClPOEMA incorporated into the copolymers and pMPOEMA and pClPOEMA in feed are shown in Figure 8.

Glass transition temperatures

The glass transition (T_g) temperatures were determined by a Setaram 131 DSC. Samples of about 4–7 mg held in sealed aluminum crucibles, and at a heating rate of 20°C/min under a dynamic nitrogen flow (5 L h^{-1}), were used for the measurements. From DSC measurements, T_g was taken as the midpoint of the transition region. The T_g values of poly(pMPOEMA),

TABLE V
F–R and K–T Parameters for Copoly(pClPOEMA–PAMA) Systems

Sample	$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f-1)/f$	$H = F^2/f$	$\eta = G/(\alpha + H)$	$\varepsilon = H/(\alpha + H)$
1	4.000	2.800	2.571	5.714	0.394	0.876
2	2.333	1.584	0.860	3.436	0.203	0.810
3	1.500	1.342	0.382	1.667	0.154	0.671
4	1.000	1.169	0.145	0.855	0.088	0.514
5	0.667	1.062	0.039	0.419	0.032	0.342
6	0.429	0.880	−0.058	0.209	−0.057	0.206
7	0.250	0.548	−0.206	0.114	−0.224	0.124

$\alpha = (H_{max} \cdot H_{min})^{1/2} = 0.807.$

Figure 4 TGA curves of the copoly(pMPOEMA–PAMA); heating rate is 10°C/min under a nitrogen atmosphere.
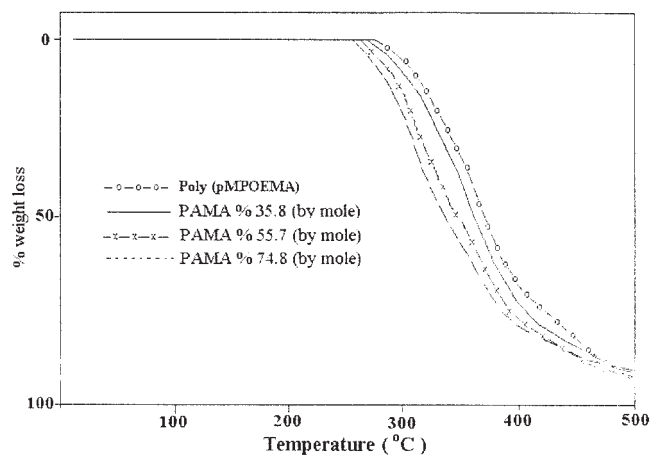

Figure 5 TGA curves of the copoly(pClPOEMA-*co*-PAMA); heating rate is at 10°C/min under a nitrogen atmosphere.

poly(pClPOEMA, and poly(PAMA) obtained under the same conditions with the copolymers were found to be 123, 118, and 101°C, respectively.

Among the many strategies available for increasing the T_g of methacrylate polymers, the most promising one is the replacement of the methyl group in the ester part of the monomer. Sterically hindered and conformationally rigid cycloalkyl groups cause a significant increase in T_g. For example, T_g varies from 110°C for poly(cyclohexylmethacrylate) to 194°C for poly-(bornyl methacrylate) and 200°C for poly(isobornyl methacrylate).[21] Similarly, an increase in the polarity of the ester group causes an increase in T_g, which is observed in 4-cyanophenyl methacrylate (T_g, 155°C).[22] The T_g of the copolymers showed a gradual increase with an increase in the molar percentage of pMPOEMA and pClPOEMA.

In comparison with that of poly(PAMA), the shift to higher temperature is also noted for all the copolymers studied and its magnitude is dependent on the increase in pMPOEMA and pClPOEMA molar fraction in the copolymer chain. An increase in T_g of copolymers may be due to the introduction of comonomer into PAMA, pMPOEMA, and pClPOEMA, which increases the intermolecular polar inter-
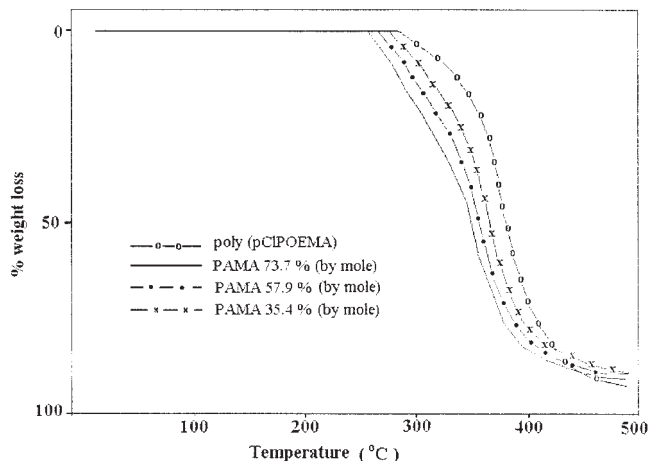
actions between the molecular chains because of structure stretching. The results clearly indicate that T_g values of copolymers depend on the composition of comonomers and increase with increase in pMPOEMA and pClPOEMA contents in the polymer chain. These values are indicated in Table V. It can be seen that the observed T_g increases with increase in pMPOEMA/pClPOEMA and presents a striking positive deviation with respect to linearity, which can be associated with a lower free volume, mobility, and flexibility than a mixture of PAMA and pMPOEMA or pClPOEMA units.

Thermogravimetric measurements of the copolymers

The thermal stability of the copolymers was studied by programmed thermogravimetric analysis over a temperature range from room temperature to 500°C under a nitrogen atmosphere(Table VII). In Figures 6 and 7 the TGA thermograms of polymers are shown. Some degradation characteristics of the copolymers are given in Table V by comparison with those of the homopolymers. [Poly(PAMA) was stable to heat up to

TABLE VI
Comparison of Reactivity Ratios by Various Methods

System	Methods	r_1	r_2	r_1r_2	$1/r_1$	$1/r_2$
Poly(pMPOEMA–PAMA)	FR	0.50 ± 0.22	0.31 ± 0.15	0.16	2.00	3.23
	K–T	0.45 ± 0.28	0.24 ± 0.21	0.11	2.22	4.17
	Average	0.48 ± 0.16	0.28 ± 0.24	0.13	2.08	3.57
Poly(pClPOEMA–PAMA)	F–R	0.45 ± 0.22	0.26 ± 0.26	0.12	2.22	3.85
	K–T	0.40 ± 0.13	0.19 ± 0.21	0.08	2.50	5.26
	Average	0.43 ± 0.11	0.23 ± 0.13	0.10	2.33	4.35

Polymer	IDT[a]	The temperature (°C) for a weight loss of			The residue at 450°C	T_g
		20	50	70		
						10
Poly(PAMA)	250	310	384	445	7	1
Poly(pMPOEMA)	285	305	382	437	8	123
Poly(pMPOEMA–PAMA)						
64.2/35.8	279	314	365	428	7	119
44.3/55.7	270	303	350	398	5	111
25.2/74.8	265	293	321	390	6	104
Poly(pClPOEMA)	280	320	382	403		118
Poly(pClPOEMA–PAMA)						
64.6/35.4	278	290	355	410	9	115
46.1/53.9	272	300	350	406	7	108
26.3/73.7	265	308	342	398	3	103

[a] Initial decomposition temperature.

450°C, and maximum degradation (93%) occurs at 450°C. For the homopolymers of PAMA, pMPOEMA, and pClPOEMA, the degradation occurred in a single
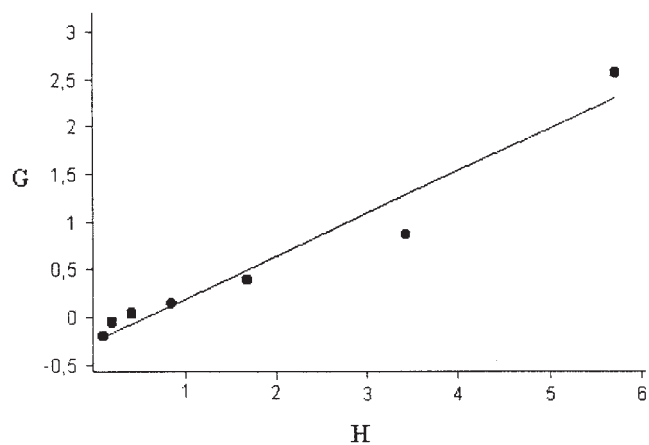

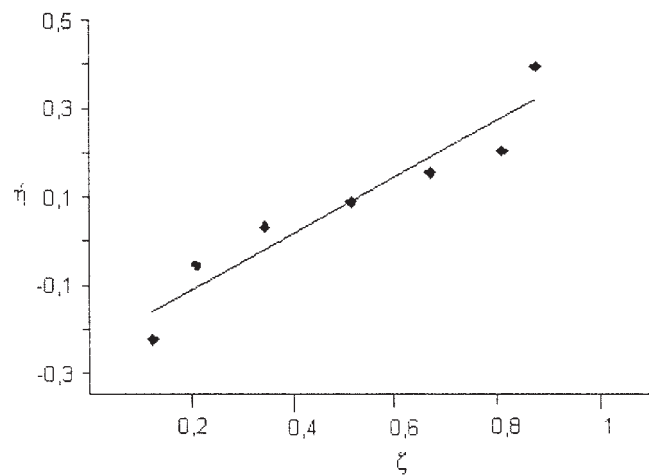**Figure 6** F-R plot for copoly(pClPOEMA–PAMA) system.

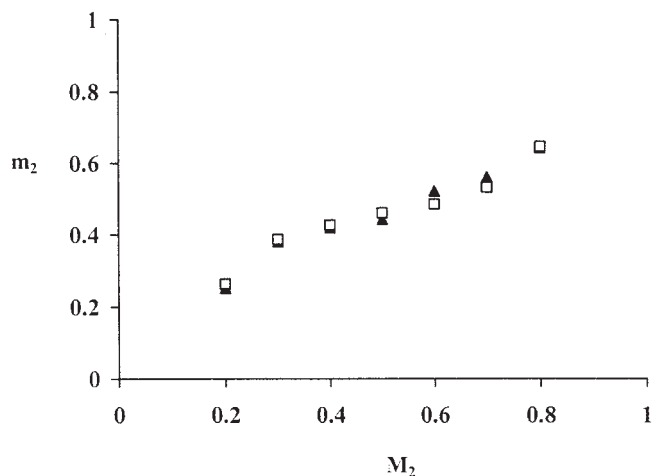**Figure 7** K-T plot for copoly(pClPOEMA–PAMA) system.

Figure 8 Plots of mole fraction of pMPOEMA (▲) and pClPOEMA (□) in copolymers (m_2) measured by elemental analysis versus mole fraction of pMPOEMA and pClPOEMA (M_2).

state. In poly(pMPOEMA), the first degradation occurs at 285°C and complete degradation at 480°C with weight loss at 95%. In poly(pClPOEMA), the first degradation occurs at 280°C and complete degradation at 485°C with weight loss at 92%.] The thermal stabilities of two copolymers are between those of the corresponding homopolymers. The homopolymers and all the copolymer samples showed a single decomposition step. The actual decomposition temperature range depends upon the composition of the constitutional monomeric units in the copolymer. The initial decomposition temperature and thermal stability of the copolymers increase with an increase in pMPOEMA and pClPOEMA monomer concentration. My results are in agreement with those of previous works.[23,24]

CONCLUSIONS

Copolymers of pMPOEMA and pClPOEMA with PAMA have been prepared by FRP in 1,4-dioxane at 65°C. The reactivity ratios of the copolymers were estimated using linear graphical methods. The r_1 values were higher than the corresponding r_2 values in all cases, meaning that a kinetic preference exists for the incorporation of PAMA in the copolymer structure. The T_gs of the pMPOEMA and pClPOEMA with PAMA copolymers were obtained and compared. The TGA studies concluded that the thermal stability of the copolymers increases with an increase of pMPO-EMA and pClPOEMA in the copolymer chain.

References

1. Vogl, O. J Mac Sci Pure Appl Chem 1996, A33, 1571.
2. Sherrington, D. C. Br Polym J 1980, 12, 70.
3. Akelah, A.; Moet, A. Functionalized Polymers and Their Applications. Thompson Press: New Delhi, 1990.
4. Erol, I.; Soykan, C. J Macromol Sci Pure Appl Chem 2002, A39,405.
5. Akelah, A.; Sherrington, D. C. Polymer 1983, 24, 1369.
6. Akelah, A.; Moet, A., Eds. Chapman and Hall: London, 1988.
7. Akelah, A. J Mater Sci 1986, 21, 2977.
8. Vogl, O.; Jaycox G. D. J Polym Sci Part A: Polym Chem 2002, 40, 923.
9. Akelah, A.; Hassanein, M.; Selim, A.; Kebawy, E. R. Eur Polym Mater 1986, 22, 983.
10. Odian, G. In Principles of Polymerization, 3rd ed.; Wiley-Interscience: New York, 1991; p 198.
11. Arshady, R.; Kenner, G. W.; Ledwith, A. Macromol Chem Phys 1981, 182, 41.
12. Ham, G. Copolymerization (High Polymers, Vol. 18); Interscience: New York, 1964.
13. Erol, I.; Soykan, C. React Funct Polym 2003, 56, 147.
14. Soykan, C.; Erol, I. J App Polym Sci 2003, 88, 2331.
15. Finemann, M.; Ross, S. D. J Polym Sci 1950, 5, 259.
16. Kelen, T.; Tüdös, F. J.; Macromol Sci Chem 1981, A16, 1283.
17. Bilmeyer, F. W. Textbook of Polymer Science, 3rd ed.; Wiley: New York, 1984; p 119.
18. Ivan, B.; Kennedy, J. P.; Kelen, T. Polym Bull 1981,6(3/4), 155.
19. McCafferty, E. L. Laboratory Preparation for Macromolecular Chemistry; McGraw-Hill: New York, 1970; p 22.
20. Dinçer, S.; Köseli, V.; Kesim, H.; Rzaev, Z. M. O.; Pişkin, E. Eur Polym Mater 2002, 38, 2143.
21. Matsumoto, A.; Mizuta, K.; Otsu, K. J. J Polym Sci Part A: Polym Chem 1993, 31, 2531.
22. Pizzirani, G.; Magagnini, P. J.; Giusti, P. J Polym Sci Part A-2: Polym Phys 1971, 9,1133.
23. Grassie, N.; Francey, K. F.; MacFarlane, I. G. Polym Degrad Stab 1980, 2, 67.
24. Coskun, M.; Erol, I.; Coşkun, M. F.; Demirelli, K. Polym Degrad Stab 2000, 78, 49.