

Synthesis and Characterization of [2-Oxo-2-(4-methyl)phenyl amino]ethylene Methacrylate–styrene Copolymers and Determination of Monomer Reactivity Ratios

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ABSTRACT: Some copolymers of [2-oxo-2-(4-methyl)phenyl amino]ethylene methacrylate (PEMA) with styrene (ST) have been prepared in the presence of benzoylperoxide (BPO) in 1,4-dioxane solvent at 65 °C. The copolymers have been characterized by Infrared, ¹H and ¹³C NMR techniques. The percentages of PEMA and ST in the copolymers have been established by elemental analysis. The glass transition temperatures and thermal stability of copolymers were obtained and discussed. The monomer reactivity ratios of copolymerizations are calculated by using both Kelen–Tüdös and Fineman–Ross equations.

KEY WORDS Ethylene Methacrylate / Styrene / Monomer / Reactivity Ratios / Thermal Analysis /

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}

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.^{10,11} The calculation of the monomer reactivity ratios requires the mathematical treatment of experimental data on the compositions of copolymers and monomer feed mixtures.

In this article we report the synthesis of a new methacrylate monomer derived from the reaction of

α -chloro *N*-(*p*-methyl)phenyl acetamide with sodium methacrylate as well as its free-radical copolymerization behavior.

EXPERIMENTAL

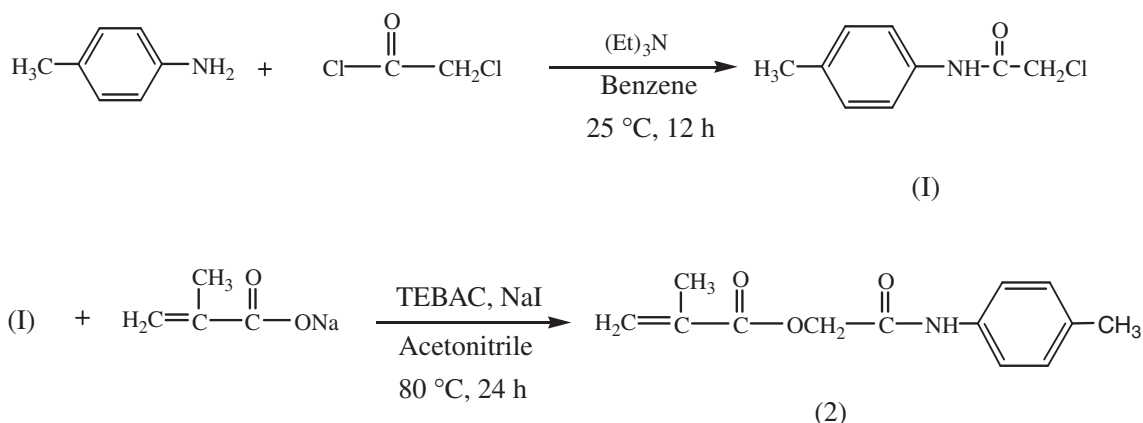
Materials

P-Toluidine and chloroacetylchloride (MERCK & Co., INC.) were used as received. Ethanol, methanol, chloroform, *n*-hexane and benzene were freshly distilled over molecular sieves prior to use. Formic acid, *n*-heptane, diethyl ether, triethylamine, 1,4-dioxane, acetonitrile (MERCK & Co., INC.) and sodium methacrylate (Aldrich Chemical Company, Inc) were used as received. Styrene (ST) was freed from inhibitor by washing with 5% NaOH solution followed by distilled water, drying over anhydrous MgSO₄, and distillation under vacuum. Benzoyl peroxide (BPO) was recrystallized from a chloroform–methanol mixture.

Monomer Synthesis

The first *N*-(4-methyl)phenyl chloroacetamide was prepared by reacting *p*-toluidine with chloroacetyl chloride using triethylamin.¹² The monomer [2-oxo-2-(4-methyl)phenyl amino]ethylene methacrylate was synthesized as follows: 1 mol *N*-(4-methyl)phenyl chloroacetamide, 1.1 mol sodium methacrylate, 0.1 mol TEAC and 0.1 mol NaI as catalyst were stirred in 75 mL acetonitrile at 75–80 °C in a reflux condenser for 24 h. Then mixture was cooled, filtrated and evaporated. The resulting monomer purified by re-

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Scheme 1.

crystallization from ethanol (yield 75%).

IR (KBr pellet), cm^{-1} : 3254 (N–H stretching), 1680 (C=O amide carbonyl), 1726 (C=O ester carbonyl), 1630 (C=C), 1255 (C–O–C), 3100 (Ar–H), 2960 (C–H aliphatic).

^1H NMR (δ , ppm): 5.6 and 6.2 (CH_2 = vinylic protons), 4.8 (OCH_2 –C=O protons), 10.1 (NH –C=O protons), 7.2–7.5 (Ar–H protons), 2.2 (Ar– CH_3 protons), 1.9 (C=C– CH_3 protons).

^{13}C NMR (δ , ppm): 167 (NH–C=O carbons), 169 (O=C–O carbons), 18 (CH_3 –C=C methyl carbons), 22 (Ar– CH_3 carbons), 64 (OCH_2 –C=O carbons), 120–130 (aromatic and C=C carbons).

Polymerization of the PEMA

Poly(PEMA) was prepared by free radical polymerization of PEMA with 1% BPO (total weight of monomer) in 1,4-dioxane solution (monomer/solvent, 1:4, w/v) in a sealed tube under nitrogen atmosphere at 65 °C for 15 h. with 90% conversion. The polymer was precipitated in excess ethanol. After a three reprecipitations from acetone solution using ethanol, the polymer was dried under vacuum at 40 °C for 24 h.

Copolymerization

The appropriate quantities of PEMA and ST in 1,4-dioxane (monomer/solvent: 1/4 w/v) and BPO (Bz_2O_2) were placed in a standard reaction tube and the mixture was purged with nitrogen gas for deoxygenating. The tube was then tightly stoppered and maintained in a thermostatic oil bath at 65 ± 1 °C. The copolymerization was allowed to proceed for about 3–5 h to achieve a conversion of about 10%. The polymerization mixture was then poured into ethanol and purified by at least two precipitations by ethanol from dichloromethane solution to ensure complete removal of unreacted monomers. The precipitated polymers were then filtrated, washed with the same precipitant and dried under vacuum at 45 °C for 24 h.

Characterization Techniques

Infrared Spectra were recorded by using a Perkin Elmer FTIR spectrometer. The ^1H and ^{13}C NMR spectra were run on a Bruker GmbH DPX-400 400 MHz FT-NMR spectrometer. Spectra were recorded at room temperature in $\text{DMSO}-d_6$ using TMS as internal standard. Elemental analysis were carried out by a Leco-932 microanalyzer. Thermal data were obtained by using a seteram instrument and a seteram thermobalance. Solubility parameters of the copolymers were estimated from the solubility test using 1,4-dioxane and non-solvents. The density of the polymers was determined by the flotation method.

RESULTS AND DISCUSSION

As shown in Scheme 1, we propose a new route for a new methacrylate ester having pendant amide moieties. The yields of the reactions in Scheme 1 are of medium quantity (80%). The keto group was introduced into the amine by a Schotten-Baumann reaction with acyl halide using triethylamine catalyst. The esterification of sodium methacrylate with α -chloro acetamide was also examined using TEBAC.

Characterization of Monomer and Its Polymer

The ^1H and ^{13}C NMR spectrums of the monomer are shown in Figure 1a,b. The ^1H and ^{13}C NMR spectra of the monomer has the characteristic peaks of the monomeric units. The main evidence of polymer formation is certainly the disappearance of some characteristic signals of the double band in the spectra, which was effectively observed in our case.

Thus, two bands vanished in the IR spectrum: the absorption band at 930 cm^{-1} assigned to the C–H bending of geminal $=\text{CH}_2$, and the stretching vibration band at $\text{C}=\text{C}$ at 1630 cm^{-1} . From ^1H NMR spectroscopy the formation of the polymer is also clearly evident from the vanishing of the two singlets at 5.6

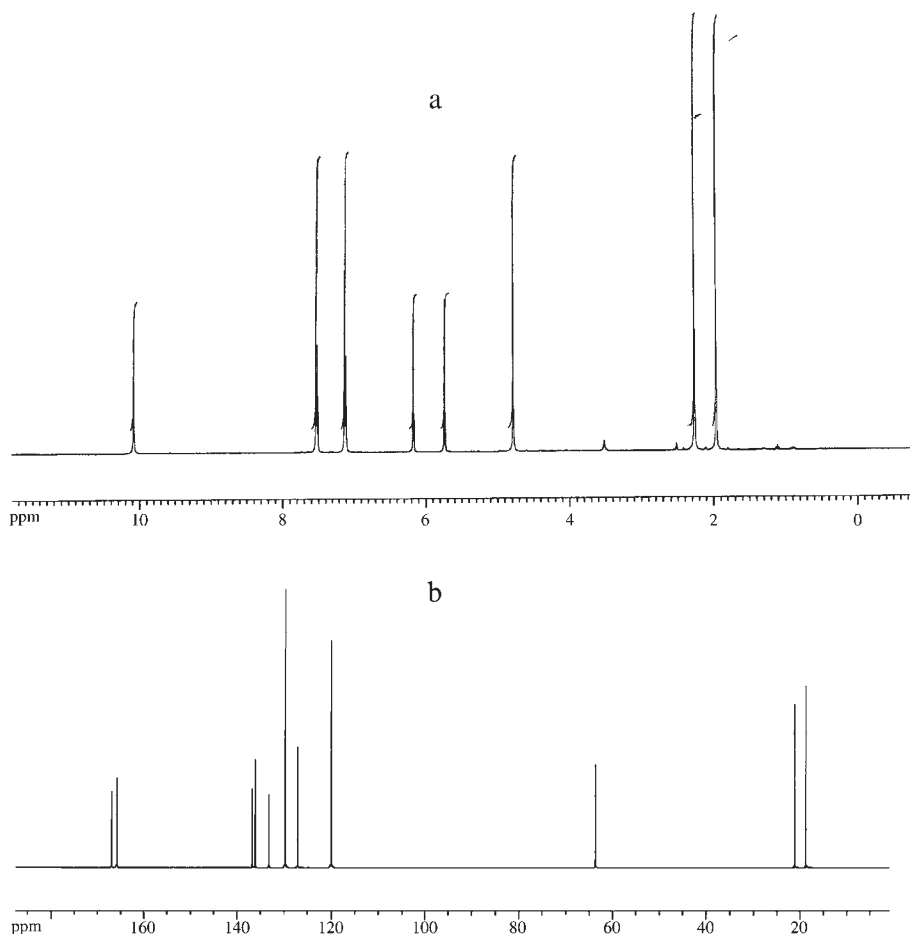


Figure 1. ^1H NMR (a) and ^{13}C NMR (b) spectrum of (PEMA) monomer.

Table I. Monomer compositions in feed and in copolymer^a

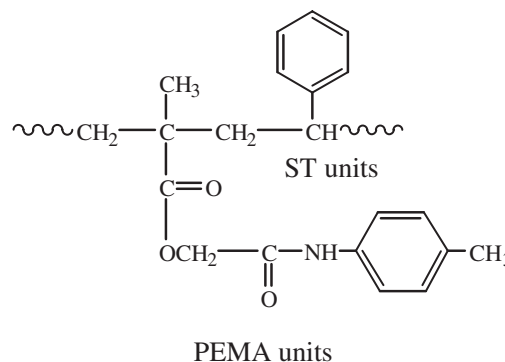
Sample no.	Feed composition in mole fraction		Conversion (%)	Elemental N%	Copolymer composition in mole fraction	
	PEMA (M_1)	ST (M_2)			PEMA (m_1)	ST (m_2)
1	0.250	0.750	7.510	2.910	0.296	0.704
2	0.400	0.600	9.301	3.770	0.432	0.568
3	0.500	0.500	11.217	4.160	0.505	0.495
4	0.650	0.350	8.408	4.610	0.599	0.401
5	0.800	0.200	9.103	5.060	0.708	0.292

^aTemperature, 65 ± 1 °C; solvent, 1,4-dioxane; initiator, benzoyl peroxide (2%); non solvent for precipitation, ethanol.

and 6.2 ppm of the vinyl protons and the appearance of the broad signal at 1.3–1.4 ppm, assigned to an aliphatic $-\text{CH}_2$ -group. All the other spectroscopic signals for the macromolecule appeared in a normal mode.

Characterization of the Copolymer

Five new copolymers of PEMA-*co*-ST having different copolymer composition were prepared according to the experimental details given in Table I, using BPO as initiator in 1,4-dioxane solution under nitrogen atmosphere. The formula of poly(PEMA-*co*-ST) is illustrated in Scheme 2.



Scheme 2.

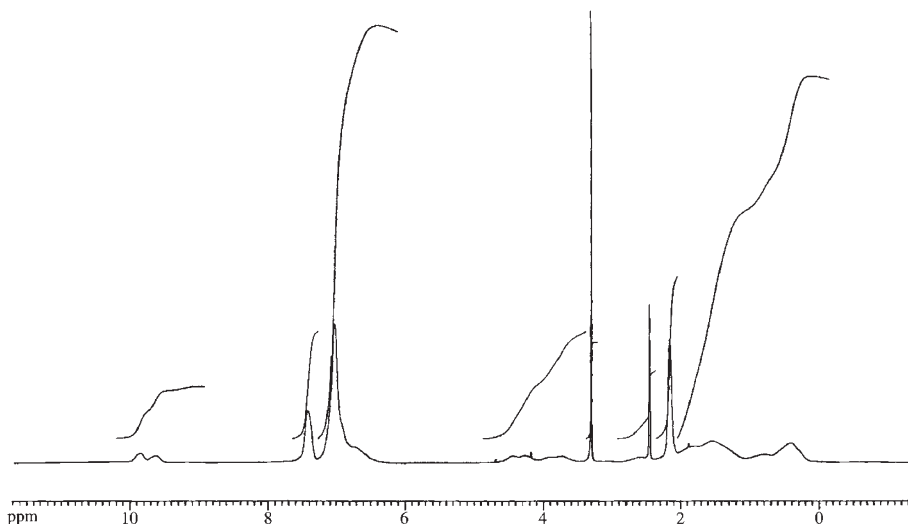


Figure 2. ^1H NMR spectrum of poly(PEMA-co-ST) (PEMA: 50.5 by mole%).

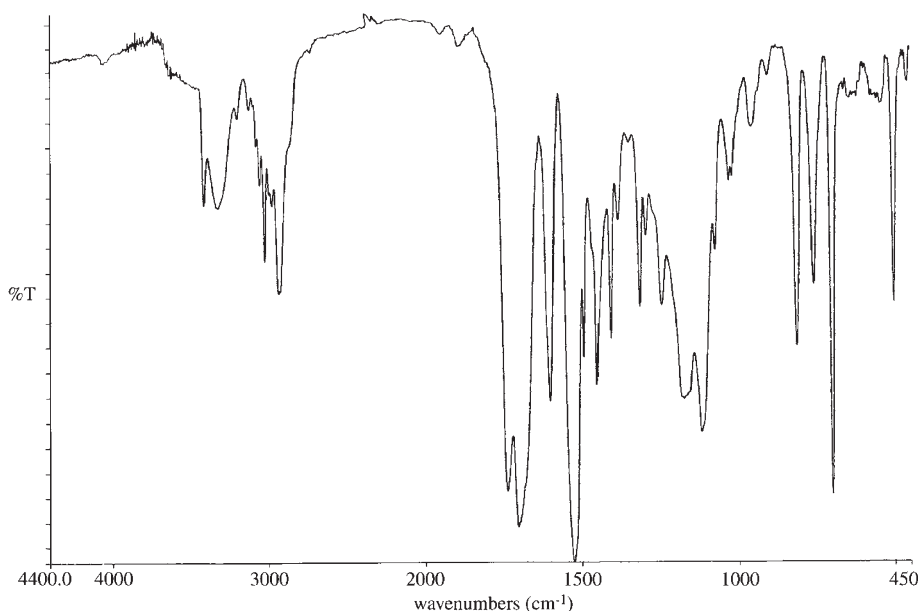


Figure 3. Infrared spectrum of poly(PEMA-co-ST) (PEMA: 50.5 by mole%).

The FTIR spectrum of poly(PEMA-co-ST) is shown in Figure 3. The amide and ester carbonyl groups of the PEMA unit have sharp bands at 1680 and 1736 cm^{-1} respectively. The bands at 3000–3100 and 1595 cm^{-1} (Aromatic) show the characteristic for ST and PEMA. The N–H stretching bands for PEMA was at 3250 cm^{-1} . The ^1H NMR spectra of the copolymers have the characteristic peaks of the monomeric units. The ^1H NMR spectra (Figure 2) of poly(PEMA-co-ST) show resonances at 7.2–7.5 ppm corresponding to the phenyl ring protons. The signals at 4.4 ppm are a result of the OCH_2 group of PEMA. The signals of $-\text{CH}_2$ and $-\text{CH}$ protons in the backbone are between 1.2–1.6 ppm. The N–H protons of PEMA units are shown at 9.8 ppm.

Copolymer Composition and Monomer Reactivity Ratios

The compositions of the poly(PEMA-co-ST) samples were determined by elemental analysis. The monomer reactivity ratios of PEMA and ST were estimated by graphical methods according to the Fineman–Ross¹³ equation and the Kelen–Tüdös^{14,15} equation.

$$G = r_1 F - r_2 \quad (1)$$

$$\eta = (r_1 + r_2/\alpha)\varepsilon - r_2/\alpha \quad (2)$$

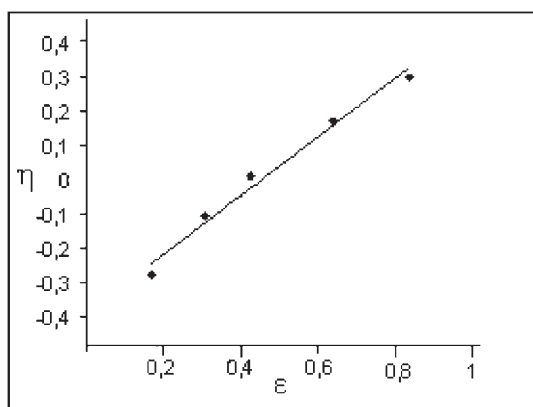
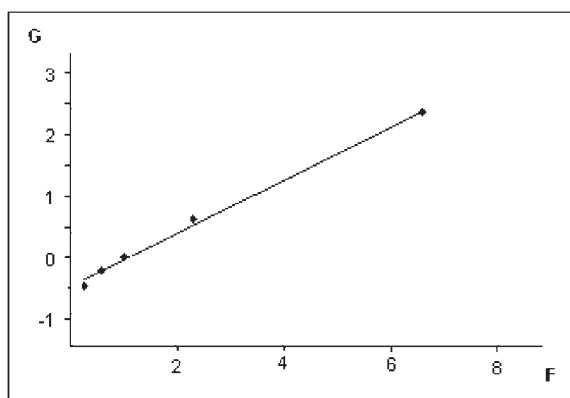
Here $\eta = G/(\alpha + F)$, $\varepsilon = F/(\alpha + F)$, $G = x(y - 1)/x$, $F = x^2/y$, $x = M_1/M_2$, $y = m_1/m_2$ and $\alpha = (F_{\text{max}} \cdot F_{\text{min}})^{1/2}$.

M_1 is the mole fraction of PEMA in the feed, M_2 is the mole fraction of ST in the feed, r_1 is the reactivity

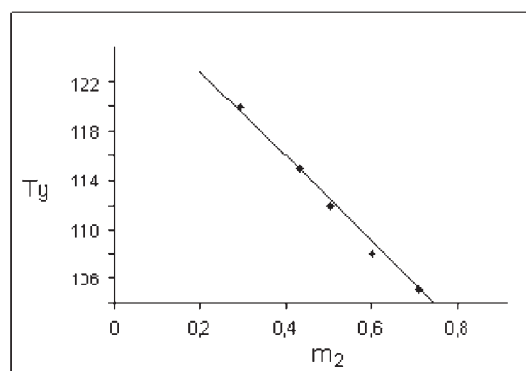
Table II. The Finemann–Ross and Kelen–Tüdös parameters for copolymerization of PEMA with ST

Sample no.	$X = M_1/M_2$	$Y = m_1/m_2$	$G = x(y - 1)/y$	$F = x^2/y$	$\eta = G/(\alpha + F)$	$\varepsilon = F/(\alpha + F)$
1	0.333	0.420	-0.459	0.264	-0.281	0.166
2	0.666	0.759	-0.211	0.584	-0.110	0.306
3	1.000	1.020	0.019	0.980	0.008	0.426
4	1.857	1.495	0.614	2.306	0.169	0.635
5	4.000	2.422	2.348	6.606	0.296	0.833

$$\alpha = \sqrt{F_{\max} \cdot F_{\min}} = 1.320$$


Figure 4. K–T plot for the determination of reactivity ratios of PEMA–ST copolymer system.

Figure 5. F–R plot for the determination of reactivity ratios of PEMA–ST copolymer system.

ratio of PEMA and r_2 is the reactivity ratio of ST. Kelen–Tüdös and Fineman–Ross parameters were calculated from the above equations using the data in Table II. Typical plots are shown in Figure 4 and 5, respectively. The following values were found: $r_1 = 0.43 \pm 0.080$, $r_2 = 0.46 \pm 0.015$ (Fineman–Ross); $r_1 = 0.46 \pm 0.003$, $r_2 = 0.51 \pm 0.075$ (Kelen–Tüdös). The monomer reactivity ratios (r_1 and r_2) of poly(PEMA-*co*-ST) are less than 1. This indicates that the system copolymerizes statistically. Comparing PEMA to ST, it should be stated that two monomers show similar copolymerization behavior. The reactivities of these monomers are close together.


Figure 6. Dependence of T_g on mole fraction of ST in copolymer (m_2), by DSC.

The $r_1 \cdot r_2$ value indicates that the system copolymerizes statistically in the polymer chain, although there is a possible tendency for alternation. Thus, the factors, general reactivity and alternating tendency, are predominant in determining the behavior of monomers in copolymerization.

Thermal Analysis

Differential scanning calorimetry (DSC) was performed at a heating rate of 20 °C/min under nitrogen atmosphere. A plot of copolymer composition versus glass transition temperature of the copolymer is shown in Figure 6. T_g values of poly(PEMA) and poly(ST) obtained under the same conditions with the copolymers were found to be 125 and 103 °C respectively. The T_g values of all the copolymers were between those of the homopolymers of the same monomers, which is predicted by the dotted line in Figure 6. When the mole fraction of PEMA in the copoly(PEMA-*co*-ST) changed from 0.708 to 0.296. The T_g value changed from 105 to 120 °C. The chain flexibility of poly ST was lower than that of poly PEMA. This means that the free volume in poly ST was higher than that in poly PEMA. The *p*-methyl phenyl group on the (PEMA) was caused diminution of the free volume for poly(PEMA). Therefore, an increase of T_g as a function of the number of PEMA units in the copolymer is an expected result.

The thermal stability of the copolymers was studied by programmed thermogravimetric analysis over a

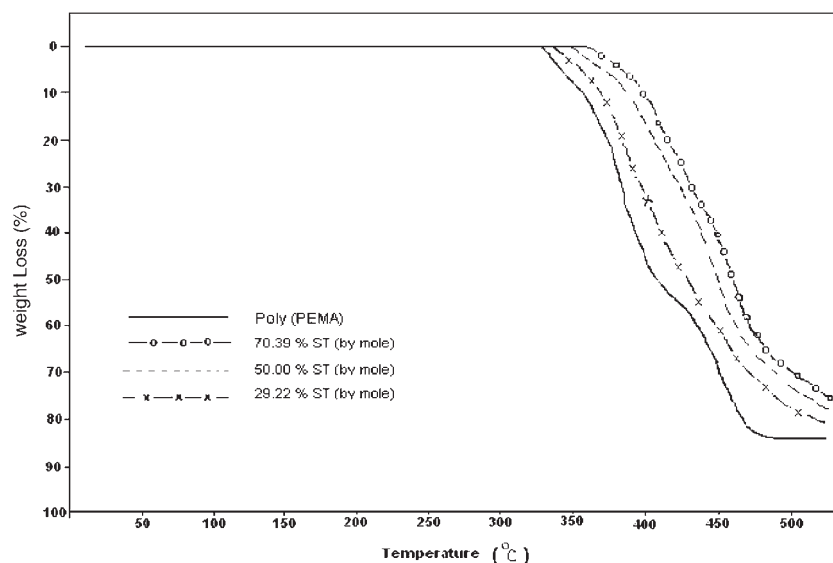


Figure 7. TGA curves of the polymer and copolymers heated in nitrogen at a heating rate of 20 °C/min.

Table III. Some TGA result of the copolymers

Polymer	IDT ^a	The temperature for a weight loss (%) of			The residue (%) at 450 °C
		20	50	70	
Poly(PEMA)	310	360	407	450	28
Poly(ST)	355	380	400	450	2
Poly(PEMA- <i>co</i> -ST)					
(29.6/70.4)	352	411	460	498	55
(50.5/49.5)	348	403	449	490	50
(70.8/29.2)	340	355	435	460	35

^aInitial decomposition temperature

temperature range from room temperature to 500 °C under nitrogen atmosphere. Typical thermograms obtained by plotting percentage of residual weight against temperature for poly(PEMA) and three poly(PEMA-*co*-ST)'s are given in Figure 7. The thermal analysis data show that initial decomposition temperature (IDT) increases with the introduction of ST units. The IDT of poly(PEMA) and poly(ST) are 310 and 355 °C respectively. Some degradation characteristics of the copolymers are given in Table III by comparison with those of the given homopolymers. The thermal stabilities of copolymers are between those of the corresponding homopolymers.

Physical Parameters

Some physical parameters such as density (d), solubility parameters (δ), and inherent viscosity (η_{inh}) of the polymers were determined in the study. The density of the polymers was determined experimentally by the flotation method¹⁶ 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 method¹⁶ at 25 °C from a solubility test using 1,4-dioxane as solvent and *n*-heptane and ethanol

Table IV. Some physical parameters of polymers

Sample	d (g/cm ³)	η_{inh} (dl/g)	δ (cal/cm ³)
Poly(PEMA)	1.135	0.534	11.280
Poly(ST)	1.047	0.612	9.500
29.6% PEMA (by mole)	1.057	0.591	9.818
50.5% PEMA (by mole)	1.073	0.567	10.311
70.8% PEMA (by mole)	1.092	0.543	10.938

as non-solvent. The inherent viscosities of 1% (w/v) solutions of the polymers in 1,4-dioxane were determined at 30 °C using an ubbelohde viscometer.

These values are shown in Table IV. The solubility parameter and density values of the copolymers were between those of the homopolymers. These values were influenced by their composition.

CONCLUSIONS

New methacrylate monomer (PEMA) having pendant amide moiety was synthesized and characterized by IR, ¹H and ¹³C NMR. Copolymers of PEMA with ST were prepared using BPO as an initiator in 1,4-dioxane solution at 65 °C. IR, ¹H and ¹³C NMR spectroscopies revealed the presence of monomeric con-

stituents in the copolymers. Thermal stabilities and T_g 's of the copolymers were between those of the corresponding homopolymers. The monomer reactivity ratios in the copolymerization of PEMA with ST are less than unity, indicating a tendency for the monomer units to attract in the copolymers.

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