Free-Radical Copolymerization of 2-[3-(6-Tetralino)-3-methylcyclobutyl]-2-ketoethyl Methacrylate with Acrylonitrile and Styrene: Synthesis, Characterization, and Monomer Reactivity Ratios

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ABSTRACT: The copolymerization of the monomer 2-[3-(6-tetralino)-3-methylcyclobutyl]-2-ketoethyl methacrylate with acrylonitrile and styrene was carried out in a 1,4-dioxane solution at 60°C with 2,2′-azobisisobutyronitrile as an initiator. The copolymers were characterized with Fourier transform infrared, ^{1}H-NMR, and ^{13}C-NMR spectroscopy techniques. The thermal properties of the polymers were also studied with thermogravimetric analysis and differential scanning calorimetry. The copolymer compositions were determined with elemental analysis and ^{1}H-NMR techniques. The monomer reactivity ratios were calculated by the application of conventional linearization methods (Fineman–Ross and Kelen–Tüdös) to be less than 1 for both monomers. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1979–1986, 2007

Key words: copolymerization; radical polymerization; thermogravimetric analysis (TGA)

INTRODUCTION

Many polymers with reactive functional groups are now being synthesized, tested, and used not only for their macromolecular properties but also for the properties of their functional groups. In polymer science, the improvement of mechanical properties has been the center of interest for many years, but today special electrical and optical properties of polymers are receiving increasing interest. Functional groups give the polymer structure special character substantially different from the inherent properties of the basic polymer chain.[1–3]

Polymers containing a cyclobutane ring, which is a small, strained carbon ring, are generally decomposed by irradiation with deep ultraviolet light.[4,5] However, polymethacrylates with keto side chains are readily transformed into other derivatives and have some photosensitive properties.[6,7] There are many reports concerning polymers with a cyclobutane ring[8–11] and a cyclobutane ring and hydroxy and keto ethyl groups together.[12–14]

Reactivity ratios are among the most important parameters for composition equations of copolymers and can offer information about the relative reactivity of monomer pairs and be used to estimate the copolymer composition. Knowledge of a copolymer's composition is an important step in the evaluation of its utility. The 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 the copolymer and the composition of the monomer feed, in which the monomer reactivity ratios are the parameters to be determined.[15,16] The calculation of the monomer reactivity ratios requires the mathematical treatment of experimental data on the compositions of the copolymer and monomer feed mixtures. No studies on reactivity ratios in the copolymerization of 2-[3-(6-tetralino)-3-methylcyclobutyl]-2-ketoethyl methacrylate (TKEMA) with any commercial monomer can be found in the literature. TKEMA is a new methacrylate monomer having pendant cyclobutane and keto groups. In a previous study,[17] the synthesis and characterization of TKEMA monomers and their polymers were described.

This article investigates the synthesis and structural and thermal characterization of copolymers of TKEMA with acrylonitrile (AN) and styrene (ST) as well as the determination of the reactivity ratios in the copolymerization. The constituent monomeric units of the copolymers are presented in Scheme 1.

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Scheme 1
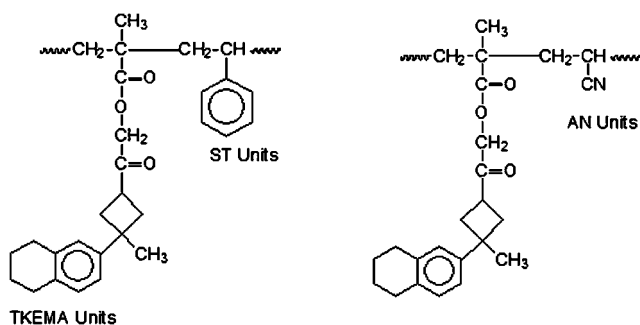
EXPERIMENTAL

Materials

1,4-Dioxane, chloroform, methanol, and ethanol (Merck) were used as received. TKEMA was prepared as reported.[13] AN (Aldrich) was freed from the inhibitor by distillation under reduced pressure, and ST was freed from the inhibitor through washing with a 5% NaOH solution followed by distilled water, drying over anhydrous $MgSO_4$, and distillation *in vacuo*. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from a chloroform–methanol (1 : 1) mixture.

Copolymerization of 2-[3-mesityl-3-methylcyclobutyl]-2-ketoethyl methacrylate with AN and ST

Copolymerizations of TKEMA with AN and ST with different proportions of TKEMA were carried out in glass ampules under an N_2 atmosphere in 1,4-dioxane solutions with AIBN (1% based on the total weight of the monomers) as an initiator. The reacting components were degassed by three freeze–thaw cycles and then immersed in an oil bath at 65 $\pm$ 0.1°C for a given reaction time. The reaction time was selected to give conversions lower than 10% to satisfy the differential copolymerization equation.[18] The resulting copolymers were purified by dissolution in CH_2Cl_2 and reprecipitation from ethanol. To check for the possible formation of homopolymers, TKEMA–ST copolymer samples were extracted in a Soxhlet extraction apparatus with cyclohexane, which is a solvent for polystyrene, and then with acetonitrile, which is a solvent for poly(TKEMA). The isolated TKEMA–AN copolymers were purified by Soxhlet extraction for 8 h in ethanol. The copolymers were finally dried *n vacuo* at 45°C to a constant weight. The feed compositions and copolymer compositions for the copolymerization of TKEMA-*co*-AN and TKEMA-*co*-ST are presented in Tables I and II.

TABLE I
Monomer Feed Ratios and Copolymer Compositions

Sample	Feed composition in the molar fraction		Conversion (%)	N (%)	Polymerization time (h)	Copolymer composition in the molar fraction		I_A/I_a
	AN (M_1)	TKEMA (M_2)				AN (m_1)	TKEMA (m_2)	
1	0.25	0.75	9.5	1.68	8.0	0.29	0.71	0.125
2	0.40	0.60	10	2.83	7.0	0.43	0.57	0.118
3	0.50	0.50	7.0	3.51	6.5	0.49	0.51	0.112
4	0.60	0.40	8.0	4.80	5	0.58	0.42	0.110
5	0.70	0.30	9.0	6.25	3	0.66	0.34	0.102
6	0.80	0.20	8.0	8.22	1.5	0.74	0.26	0.095

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

TABLE II
Monomer Compositions in the Feed and in the Copolymer

Sample	Feed composition in the molar fraction		Conversion (%)	I_A/I_a	Copolymer composition in the molar fraction		Polymerization time (h)
	ST (M_1)	TKEMA (M_2)			ST (m_1)	TKEMA (m_2)	
1	0.25	0.75	10	0.27	0.40	0.60	8.0
2	0.40	0.60	9.0	0.35	0.55	0.45	7.5
3	0.50	0.50	9.0	0.46	0.67	0.33	6.0
4	0.60	0.40	7.0	0.50	0.70	0.30	5.0
5	0.70	0.30	8.0	0.62	0.78	0.22	3.5
6	0.80	0.20	10	0.72	0.82	0.18	2.0

Solvent = 1,4-dioxane; temperature = 65 $\pm$ 1°C; initiator = AIBN (1 wt % of the monomers); nonsolvent = ethanol.
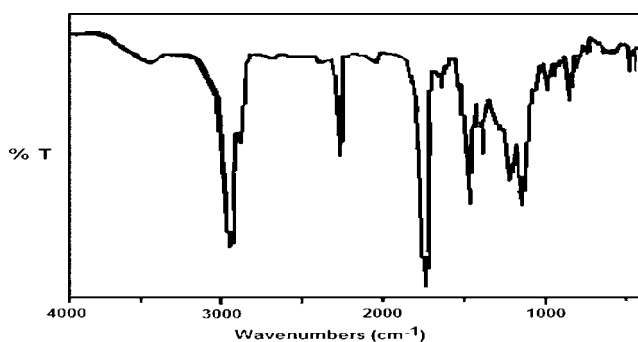
Figure 1 FTIR spectrum of copoly(TKEMA–AN) (m_1/m_2 = 26 : 74).

Measurements

Infrared spectra were measured on a Mattson 1000 Fourier transform infrared (FTIR) spectrometer (USA). The ^{1}H- and ^{13}C-NMR spectra of the monomers and copolymers were recorded in CDCl$_3$ with tetramethylsilane as the internal standard with a Varian Gemini 200-MHz spectrometer (USA). The thermal data were obtained with a Shimadzu DSC-50 instrument and a TGA-50 thermobalance in an N$_2$ atmosphere (Japan). The weight-average and number-average molecular weights (M_w and M_n, respectively) of the polymers were determined with a Waters 410 gel permeation chromatograph equipped with a differential refractive-index detector and calibrated with polystyrene standards (USA). Elemental analyses were carried out with a Leco 932 microanalyzer (USA).

RESULTS AND DISCUSSION

Structural characterization of the copolymers

The constituent monomeric units of the copolymer are as follows. The FTIR spectra of the TKEMA–AN copolymers (KBr discs) show characteristic bands at 2200 (—C≡N), 1738 (—OC=O and —C=O), 1510 (aromatic C=C stretching), 3100 (aromatic C—H stretching vibrations), and 1150 cm^{-1} (—C—O) The FTIR spectrum of poly(TKEMA-co-AN) is shown in Figure 1. Figure 2 shows the ^{1}H-NMR spectrum (δ, ppm): 6.5–6.73 (ArH), 4.16 (OCH$_2$C=O), 2.2–3.3 (cyclobutane ring protons and CH$_2$ protons on the tetraline), and 1.1–1.7 (—CH$_3$ on the cyclobutane ring and methylene protons in the polymer backbone). Figure 3 shows the ^{13}C-NMR spectrum (δ, ppm): 205 (ketone carbonyl), 167 (ester carbonyl), 132–117 (ArC in the polymer backbone), 75 (OCH$_2$), 81 (—C≡N), 42.5–38.9 (carbons in the cyclobutane ring and tetraline), 28.6 (CH$_3$ in the cyclobutane ring), and 20.1 and 22.0 (CH$_3$ on the polymer backbone).
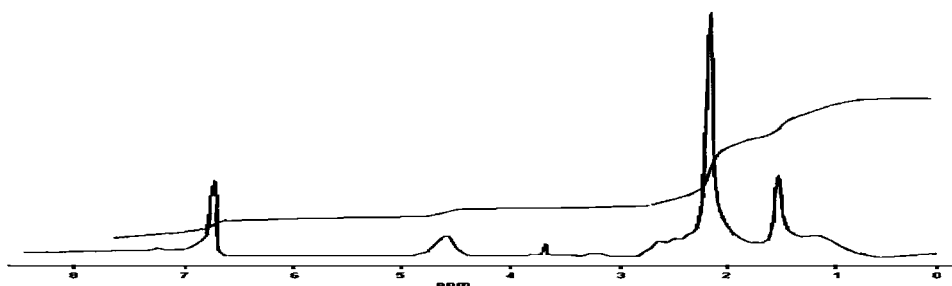

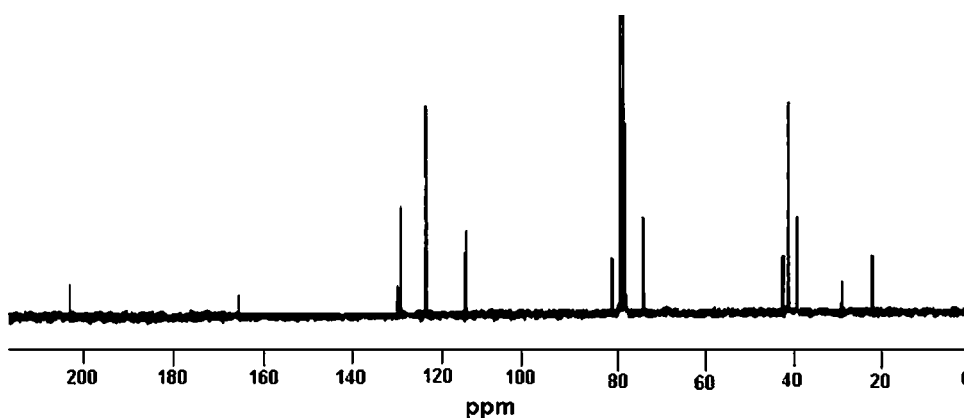**Figure 2** ^{1}H-NMR spectrum of copoly(TKEMA–AN) (m_1/m_2 = 51 : 49).

Figure 3 ^{13}C-NMR spectrum of copoly(TKEMA–AN) (m_1/m_2 = 51 : 49).
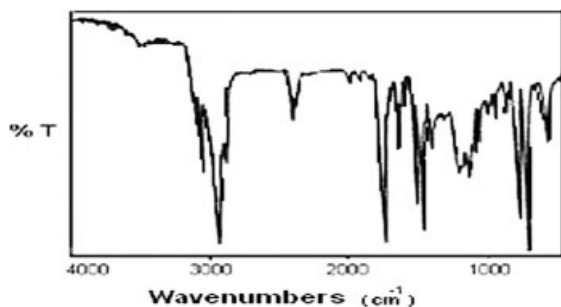
Figure 4   FTIR spectrum of copoly(TKEMA–ST) ($m_1/m_2 =$ 45 : 55).

Although the FTIR spectra of the TKEMA–ST copolymers (Fig. 4.) show characteristic bands at 1740 (—OC=O and C=O), 3100–3000 and 1590 (phenyl), and 1160 cm^{-1} (C—O), the ^{1}H-NMR spectra show broad peaks at 6.8–7.2 (ArH), 4.16 (OCH$_2$C=O), 2.3–3.5 (cyclobutane ring protons and CH$_2$ protons on the tetraline), and 0.9–1.6 ppm (other aliphatic protons including those in the backbone). The ^{1}H-NMR spectrum of poly(TKEMA-co-ST) is shown in Figure 5. The ^{13}C-NMR peak assignments of this copolymer (Fig. 6) are 125–148 (aromatic ring protons), 203 (ketone carbonyl), 171 (ester carbonyl), 44.2–41.6 (carbons in the cyclobutane ring and tetraline), 76.5 (—OCH$_2$), and 37.2–40.5 ppm (—C— and CH protons in the backbone).

Molecular weights of the polymers

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) with polystyrene and tetrahydrofuran as the standard and solvent, respectively. The M_w, M_n, and polydispersity index (PDI = M_w/M_n) values of the polymer samples are presented in Table III. The theoretical values of PDI for the polymers via radical recombination and disproportionation are 1.54–1.60. The PDI value in the homopolymerization is also known to depend on chain termination.[19]

Copolymer compositions

The copolymerization of TKEMA with AN in a 1,4-dioxane solution was studied for TKEMA molar fractions of approximately 0.75–0.25 in the feed. The number of monomeric units in the copolymers was determined by elemental analysis. In addition, the copolymer compositions for this system were determined by ^{1}H-NMR spectroscopy analysis. Let m be the molar fraction of TKEMA and $1 - m$ be that of AN in the copolymer. There are 3 aromatic protons (3H in TKEMA) and 26 aliphatic protons (23H in TKEMA and 3H in AN) in all:

$$3m_1/23m_1 + 3m_2 = I_A/I_a \qquad (1)$$

where I_A is the intensity of the aromatic protons and I_a is the intensity of the aliphatic protons. Upon simplification, this leads to

$$m_1 = 3I_A/3I_a - 20I_A \qquad (2)$$

where m_1 and m_2 are the copolymer molar compositions. With eq. (2), the molar fractions of TKEMA in the copolymers were determined by the measurement of the integrated peak heights of the total aromatic proton signals and the total aliphatic proton signals of both monomer units.
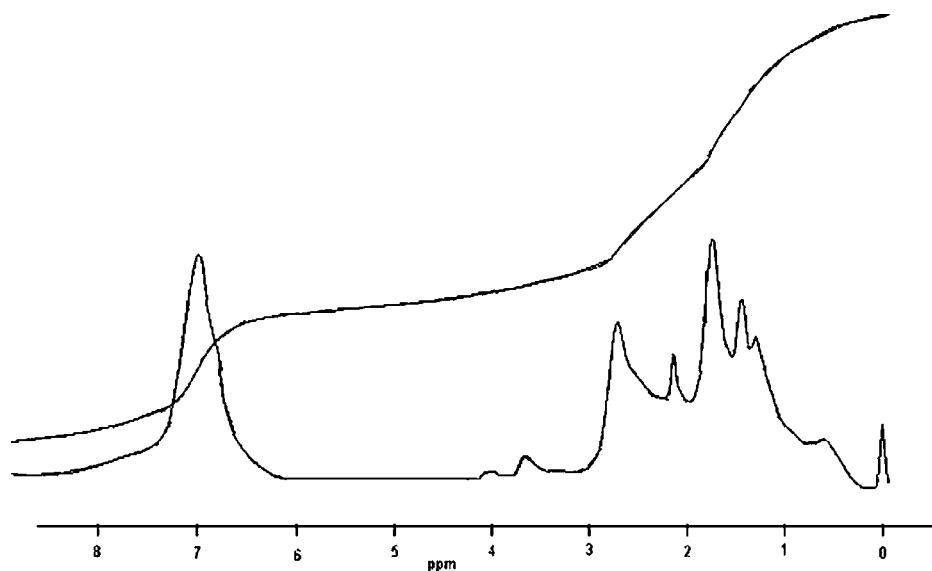

Figure 5 ^{1}H-NMR spectrum of copoly(TKEMA–ST) ($m_1/m_2 =$ 45 : 55).
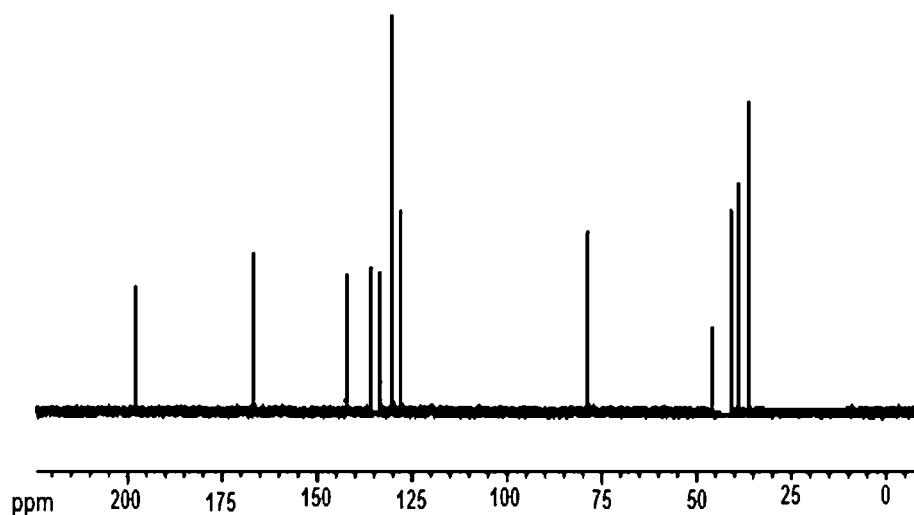
Figure 6 ^{13}C-NMR spectrum of copoly(TKEMA–ST) ($m_1/m_2 = 45 : 55$).

The copolymer compositions of TKEMA with ST were determined by ^{1}H-NMR spectroscopy analysis. The assignment of the resonance peaks in the ^{1}H-NMR spectrum allowed the accurate determination of both kinds of monomeric units incorporated into the copolymers.

The following expression was derived to calculate the copolymer composition. Let m be the molar fraction of TKEMA and $1 - m$ be that of ST in the copolymer. There are 8 aromatic protons (3H in TKEMA and 5H in ST) and 26 aliphatic protons (23H in TKEMA and 3H in ST) in all:

$$3m_2 + 5m_1/23m_2 + 3m_1 = I_A/I \quad (3)$$

Upon simplification, this leads to

$$m_1 = 23I_A - 3I_a/20I_A + 2I_a \quad (4)$$

With eq. (4), the molar fractions of TKEMA in the copolymers were determined by the measurement of the integrated peak heights of the total aromatic proton signals and the total aliphatic proton signals of both monomer units.

TABLE III
GPC Results for Some Copolymers

	M_w	M_n	M_w/M_n
Poly(TKEMA–AN)			
71/29	42.300	27.500	1.54
51/49	37.380	23.540	1.59
74/26	35.950	22.450	1.60
Poly(TKEMA–ST)			
60/40	38.540	24.340	1.58
33/67	37.640	23.750	1.58
18/82	33.500	20.550	1.63

TABLE IV
F–R and K–T Parameters for the Copoly(TKEMA–AN) Systems

Sample	F^a	f^b	G^c	H^d	η^{ef}	ε^{fg}
1	0.33	0.41	−0.47	0.27	−0.31	0.18
2	0.67	0.74	−0.24	0.61	−0.13	0.33
3	1.00	0.96	−0.04	1.04	−0.02	0.46
4	1.50	1.36	0.40	1.65	0.14	0.57
5	2.33	1.96	1.14	2.77	0.28	0.69
6	4.00	2.81	2.58	5.70	0.37	0.82

^{a} $F = M_1/M_2$.
^{b} $f = m_1/m_2$.
^{c} $G = F(f - 1)/f$.
^{d} $H = F^2/f$.
^{e} $\eta = G/(\alpha + H)$.
^{f} $\alpha = (H_{max} \times H_{min})^{1/2} = 1.24$.
^{g} $\varepsilon = H/(\alpha + H)$.

TABLE V
F–R and K–T Parameters for the Copoly(TKEMA–ST) Systems

Sample	F^a	f^b	G^c	H^d	η^{ef}	ε^{fg}
1	0.33	0.66	−0.17	0.17	−0.18	0.18
2	0.67	1.22	0.12	0.37	0.11	0.32
3	1.00	2.03	0.51	0.49	0.40	0.39
4	1.50	2.33	0.86	0.97	0.49	0.56
5	2.33	3.55	1.67	1.53	0.73	0.67
6	4.00	4.56	3.12	3.51	0.72	0.82

^{a} $F = M_1/M_2$.
^{b} $f = m_1/m_2$.
^{c} $G = F(f - 1)/f$.
^{d} $H = F^2/f$.
^{e} $\eta = G/(\alpha + H)$.
^{f} $\alpha = (H_{max} \times H_{min})^{1/2} = 0.77$.
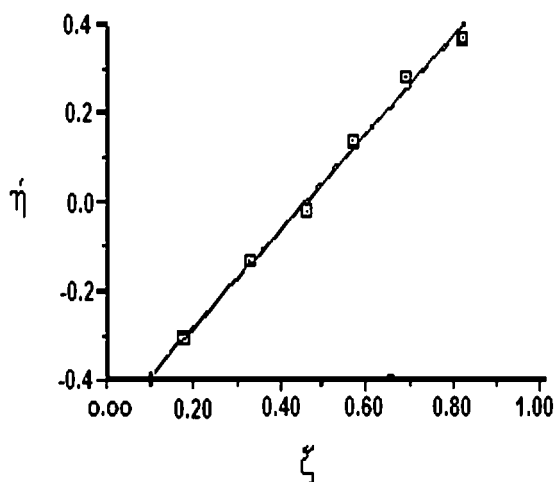^{g} $\varepsilon = H/(\alpha + H)$.

Figure 7 K–T plot for the copoly(TKEMA–AN) system.

Determination of the monomer reactivity ratios

The monomer reactivity ratios for the copolymerization of TKEMA with AN and ST were determined from the monomer feed ratios and the copolymer composition. The Fineman–Ross (F–R),[20] and Kelen–Tüdös (K–T)[21] methods were used to determine the monomer reactivity ratios. The significance of the parameters of the F–R and K–T equations are presented in Tables IV and V.

According to the F–R method, the monomer reactivity ratios can be obtained as follows:

$$G = Fr_1 - r_2 \tag{5}$$

where the reactivity ratios r_1 and r_2 correspond to the AN and TKEMA monomers, respectively. The parameters G and H are defined as follows:
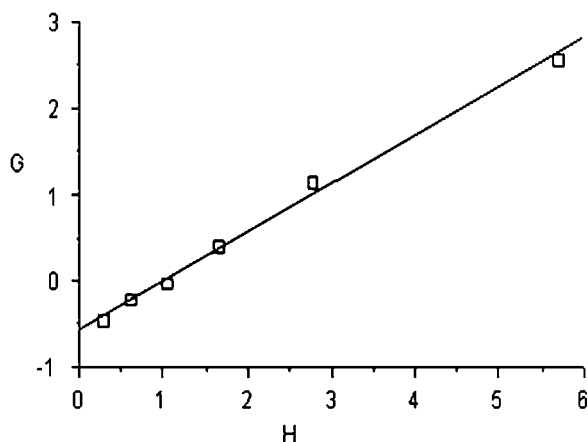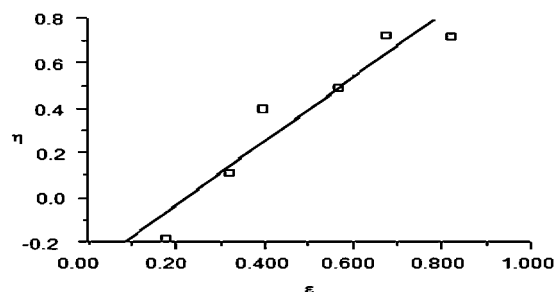
$$G = F(f-1)/f \text{ and } H = F^2/f \tag{6}$$

Figure 9 K–T plot for the copoly(TKEMA–ST) system.

with

$$F = M_1/M_2 \text{ and } f = m_1/m_2 \tag{7}$$

where M_1 and M_2 are the monomer molar compositions in the feed.

Alternatively, the reactivity ratios can be obtained with the K–T method, which is based on the following equation:

$$\eta = (r_1 + r_2/\alpha)\xi - r_2/\alpha \tag{8}$$

where α is a constant that is equal to $(H_{max} \times H_{min})^{1/2}$, H_{max} and H_{min} being the maximum and minimum H values, respectively, from the series of measurements, and η and ξ are functions of parameters G and H:

$$\eta = G/(\alpha + H) \text{ and } \xi = H/(\alpha + H) \tag{9}$$

From a linear plot of η as a function of ξ, the values of η for $\xi = 0$ and $\xi = 1$ are used to calculate the reactivity ratios according to the following equations:

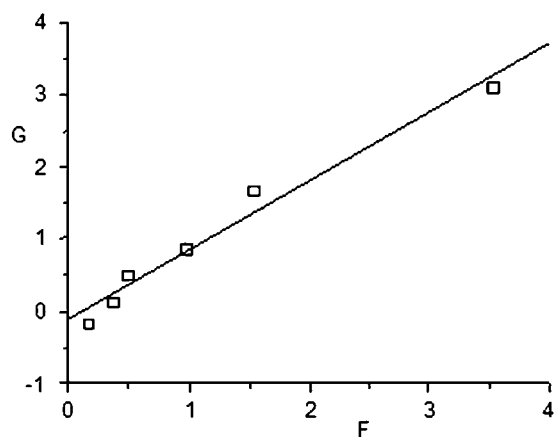$$\xi = 0 \Rightarrow \eta = -r_1/\alpha \text{ and } \xi = 1 \Rightarrow \eta = r_2 \tag{10}$$

Figure 8 F–R plot for the copoly(TKEMA–AN) system.

Figure 10 F–R plot for the copoly(TKEMA–ST) system.

TABLE VI
Comparison of the Reactivity Ratios by Various Methods

System	Method	r_1	r_2	r_1r_2	$1/r_1$	$1/r_2$
Poly(TKEMA–AN)	F–R	0.57	0.57	0.32	1.75	1.75
	K–T	0.59	0.62	0.31	1.69	1.89
	Average	0.58	0.55	0.315	1.72	1.82
Poly(TKEMA–ST)	F–R	0.96	0.11	0.11	1.04	9.09
	K–T	1.11	0.24	0.27	0.90	4.17
	Average	1.04	0.18	0.19	0.97	6.63

The graphical plots concerning the methods previously reported are given for poly(TKEMA-co-AN) in Figures 7 and 8 and for poly(TKEMA-co-ST) in Figures 9 and 10; whereas the reactivity ratios are summarized in Table VI.

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

For the TKEMA and AN systems, the r_1 values are higher than the r_2 values. The higher r_1 value of AN confirms the higher reactivity of AN compared with that of TKEMA. For the TKEMA and ST systems, the r_1 values are higher than the r_2 values. The higher r_1 value of ST confirms the higher reactivity of ST compared with that of TKEMA. The reactivity ratio values (r_1 and r_2) of copoly(TKEMA–AN) and copoly(TKEMA–ST) are less than 1. Consequently, in both copolymerization sequences, there will be an alternating tendency.

Glass-transition temperatures (T_g's)

T_g's were determined with a Shimadzu DSC-50. Samples of about 4–7 mg were held in sealed aluminum crucibles, and a heating rate of 20°C/min from room temperature to 250°C under a dynamic nitrogen flow (5 L/h) was used for the measurements.

From the DSC measurements, T_g was taken as the midpoint of the transition region. The T_g values of poly(TKEMA), poly(AN), and poly(ST), obtained under the same conditions as the copolymers, are 85, 97, and 105°C, respectively.[17] T_g of poly(ST) is considerably higher than that of the other polymers.

The T_g values for the TKEMA–ST copolymers range between the values of the two homopolymers. The introduction of TKEMA units into the ST units leads to a decrease in T_g of poly(TKEMA-co-ST). A decrease in T_g of the TKEMA–ST copolymers may be due to the introduction of the comonomer, TKEMA, into ST, which reduces the intermolecular interactions between the molecular chains because of structure loosening.

The T_g values of the TKEMA–AN copolymers range between the values of the two homopolymers. The high T_g value of the copolymers may be due to the inflexible and bulky pendant tetralino units. Separately, it may especially be suggested that strong dipolar interactions between nitrile groups in the copolymer are restricted by bulky TKEMA units in the copolymer. These values are indicated in Table VII.

Thermogravimetric measurements of the copolymers

The thermal stability of the copolymers was studied by programmed thermogravimetric analysis (TGA) from room temperature to 500°C under a nitrogen

TABLE VII
Some TGA Results and T_g Values of the Copolymers

Polymer	IDT	Weight-loss temperature (°C)			Residue (%) at 450 °C	T_g
		20	50	70		
Poly(TKEMA)	250	330	375	410	8	85
Poly(AN)	320	370	490	—	40	97
Poly(TKEMA–AN)						
71/29	260	330	375	425	23	86
51/49	280	350	380	430	27	90
26/74	308	360	402	443	34	94
Poly(ST)	325	380	400	450	2	105
Poly(TKEMA–ST)						
60/40	277	330	390	413	6	91
45/55	283	350	400	419	5	98
18/82	302	362	405	427	3	103

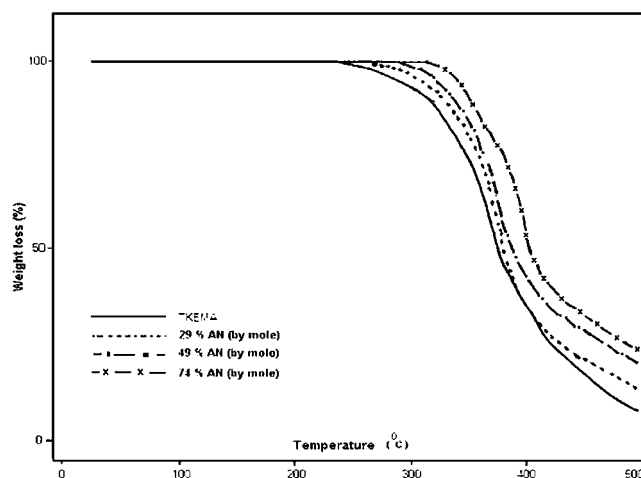IDT, initial decomposition temperature.

Figure 11 TGA curves of copoly(TKEMA–AN) (heating rate = 10°C/min under a nitrogen atmosphere).

atmosphere. In Figures 11 and 12, the TGA thermograms of the polymers are shown. Two degradation stages can be observed for poly(TKEMA) The initial decomposition temperature of poly(TKEMA) is around 250°C and independent of the side-chain structures. This result shows that main-chain scission is an important reaction in the degradation of the polymers, at least in the beginning. The degradation of poly(TKEMA) occurs in two stages. The first stage can be observed 245–250°C. The second stage of decomposition commences at 380–425°C.[22] Some degradation characteristics of the copolymers are given in Table VII and compared with those of the homopolymers. The thermal stabilities of the two copolymers are between those of the corresponding homopolymers. The copolymer samples also show two decomposition steps. The actual decomposition temperature range depends on the composition of the constitutional monomeric units in the copolymer. The initial decomposition temperature and thermal stability of the copolymers increase with an increase
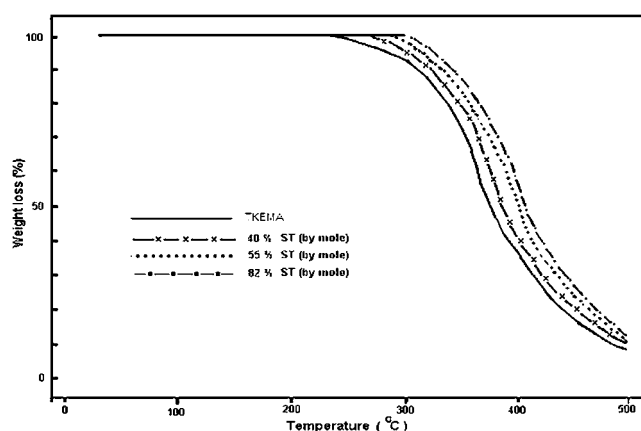
in the AN and ST monomer concentrations. My results are in agreement in the literature.[23,24]

CONCLUSIONS

Copolymers of TKEMA with AN and ST have been prepared by free-radical polymerization in 1,4-dioxane at 65°C. The reactivity ratios of the copolymers have been estimated with linear graphical methods. The r_1 values are higher than the corresponding r_2 values in all cases, and this means that a kinetic preference exists for the incorporation of TKEMA into the copolymer structure. The T_g values of TKEMA copolymers with AN and ST have been obtained and compared. The TGA studies show that the thermal stability of the copolymers increases with increases in AN and ST in the copolymer chain.

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Figure 12 TGA curves of copoly(TKEMA-*co*-ST) (heating rate = 10°C/min under a nitrogen atmosphere).