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Ibrahim Erol<sup>a</sup>

<sup>a</sup> Faculty of Science and Arts, Department of Chemistry, University of Afyon, Kocatepe Afyon, Turkey

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# Copolymers of 2-(3-(6-tetralino)-3-methyl-1-cyclobutyl)-2-Hydroxyethyl Methacrylate with Acrylonitrile and 4-Vinylpyridine: Synthesis, Characterization, and Monomer Reactivity Ratios

IBRAHIM EROL

*Faculty of Science and Arts, Department of Chemistry, University of Afyon, Kocatepe Afyon, Turkey*

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The copolymerization of 2-(3-(6-tetralino)-3-methyl-1-cyclobutyl)-2-hydroxyethyl methacrylate (TCHEMA), monomer with acrylonitrile and 4-vinylpyridine were carried out in 1,4-dioxane solution at 65°C using AIBN as an initiator. The copolymers were characterized by FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR spectroscopic techniques. Thermal properties of the polymers were also studied by thermogravimetric analysis and differential scanning calorimetry. The copolymer compositions were determined by elemental analysis. The monomer reactivity ratios were calculated by the Fineman-Ross and Kelen-Tüdös method. Also, the apparent thermal decomposition activation energies were calculated by the Ozawa method with a Shimadzu TGA 50 thermogravimetric analysis thermobalance.

**Keywords:** hydroxyethyl methacrylate; cyclobutane; copolymers; monomer reactivity ratios; activation energy

## 1 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 functional groups. 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 increasing interest. Functional groups give the polymer structure special character, substantially different from the inherent properties of the basic polymer chain (1).

Poly(hydroxyalkyl methacrylate)s have found a wide range of biomedical applications including hydrogel, hemodialysis, membranes, contact lenses, and a variety of other related and potential uses (2–4). The copolymers of these monomers with some other monomers are also used in applications as previously mentioned (5–7). Chemical modifications on the hydroxyl group of 2-hydroxyethyl methacrylate (HEMA) and poly(HEMA) and its copolymers are a synthetic route for the preparation of new functional methacrylate esters

(8–13). Moreover, polymers with the cyclobutane ring in their side or main chains, which show a positive type photoresist property, have been of interest to polymer chemists (14). Disubstituted cyclobutanes also show some biological activities (15–17). Polymers containing the cyclobutane ring, which is a small, strained carbon ring, are generally decomposed by irradiation with deep ultraviolet light (18, 19).

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 (20, 21). The calculation of the monomer reactivity ratios requires mathematical treatment of experimental data on the compositions of copolymers and monomer feed mixtures.

TCHEMA is a new methacrylate monomer having pendant aryl substituted cyclobutane ring and 2-hydroxyethyl groups. In a previous study (22), the synthesis, characterization, electrical and optical properties of the TCHEMA monomer are reported. In addition, the electrical conductivity of

Address correspondence to: Ibrahim Erol, Faculty of Science and Arts, Department of Chemistry, University of Afyon, Kocatepe Afyon, Turkey. Tel.: +90 0272 228 1312; Fax: +90 0272 228123; E-mail: iberol@hotmail.com or ierol@aku.edu.tr

TCHEMA-4VP copolymers are described (23). No studies on reactivity ratios in the copolymerization of 2-(3-(6-tetralino)-3-methyl-1-cyclobutyl)-2-hydroxyethyl methacrylate (TCHEMA), with any commercial monomer are found in the literature.

The present article investigates the synthesis, structural, and thermal characterization of copolymers of TCHEMA with acrylonitrile (AN) and 4-vinylpyridine (4VP) as well as the determination of reactivity ratios in the copolymerization. In addition, the activation energies of the copolymers were also obtained.

## 2 Experimental

### 2.1 Materials

1,4-Dioxane, chloroform, methanol, and ethanol (Merck) were used as received. TCHEMA was prepared as reported (22). AN (Aldrich) was freed from the inhibitor by distillation under reduced pressure, and 4-vinylpyridine was distilled from calcium hydride by under vacuum. 2,2-Azobisisobutyronitrile (AIBN) was recrystallized from a chloroform-methanol (1:1 V/V) mixture. All the solvents were purified by distillation prior to use.

### 2.2 Copolymerization of 2-(3-(6-tetralino)-3-methyl-1-cyclobutyl)-2-hydroxyethyl Methacrylate (TCHEMA), with Acrylonitrile and 4-Vinylpyridine

Copolymerizations of TCHEMA with AN and 4VP using different proportions of TCHEMA were carried out in glass ampoules under N<sub>2</sub> 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 three-fold freeze-thawing cycles and then immersed in a oil bath at 65 ± 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. After the desired time the copolymers were separated by precipitation in

ethanol and reprecipitated from CH<sub>2</sub>Cl<sub>2</sub> solution. To check for the possible formation of homopolymers, 4VP – TCHEMA and AN-TCHEMA copolymers were purified by Soxhlet extraction for 8 h in ethanol. The polymers were finally dried over vacuum at 45°C to constant weight. The amounts of monomeric units in the copolymers were determined by elemental analysis. The feed compositions and copolymer composition for the copolymerization of AN-co-TCHEMA and 4VP-co-TCHEMA are presented in Tables 1 and 2.

### 2.3 Measurements

Infra-red spectra were measured on a Mattson 1000 FT-IR spectrometer. The <sup>1</sup>H and <sup>13</sup>C-NMR Spectra of the monomer and copolymers were recorded in CDCl<sub>3</sub> with tetramethylsilane as the internal standard using a Varian Gemini 200 MHz spectrometer. Thermal data were obtained by using a TGA-50 thermo balance in N<sub>2</sub> atmosphere. The glass-transition temperatures (*T*<sub>g</sub>'s) of the copolymers were determined with a Shimadzu DSC-50 instrument at a heating rate of 10°C min<sup>-1</sup> in nitrogen 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.

## 3 Results and Discussion

### 3.1 Structural Characterization of the Copolymers

The formula of the copolymers is illustrated in Scheme 1.

The FTIR spectra of poly(AN-co-TCHEMA) are shown in Figure 1b. The FTIR spectra of the AN-TCHEMA copolymers shows characteristic bands at 2227 cm<sup>-1</sup> (-C≡N), 1738 cm<sup>-1</sup> (-C=O), 3485 cm<sup>-1</sup> (-OH, broad), 1510 cm<sup>-1</sup> (aromatic C=C stretching), 3100 cm<sup>-1</sup> (aromatic C-H stretching vibrations), and 1150 (-C-O). The <sup>1</sup>H-NMR

**Table 1.** Monomer composition in feed and in copolymer<sup>a</sup>

Sample	Feed composition in mole fraction		Conversion (%)	Elemental N%	Copolymer composition in mole fraction	
	AN ( <i>M</i> <sub>1</sub> )	TCHEMA ( <i>M</i> <sub>2</sub> )			AN ( <i>m</i> <sub>1</sub> )	TCHEMA ( <i>m</i> <sub>2</sub> )
1	0.20	0.80	10.0	1.54	0.28 (0.29 <sup>b</sup> )	0.72
2	0.30	0.70	10.0	2.42	0.41	0.59
3	0.40	0.60	5.0	3.48	0.48	0.52
4	0.50	0.50	7.0	3.69	0.50	0.50
5	0.60	0.40	9.0	4.84	0.58	0.42
6	0.70	0.30	7.0	5.97	0.64 (0.61 <sup>m</sup> <sup>b</sup> )	0.36
7	0.80	0.20	9.0	6.96	0.69	0.31

<sup>a</sup>Solvent: 1,4-dioxane; temperature: 65 ± 1°C; initiator: AIBN (1% weight of the monomers); non-solvent: ethanol.

<sup>b</sup>From the results of peak integration in <sup>1</sup>H-NMR.

**Table 2.** Monomer composition in feed and in copolymer<sup>a</sup>

Sample	Feed composition in mole fraction		Conversion (%)	Elemental N%	Copolymer composition in mole fraction	
	4VP ( $M_1$ )	TCHEMA ( $M_2$ )			4VP ( $m_1$ )	TCHEMA ( $m_2$ )
1	0.20	0.80	7.00	3.10	0.49	0.51
2	0.30	0.70	9.00	3.50	0.52(0.55 <sup>b</sup> )	0.48
3	0.40	0.60	10.00	4.40	0.60	0.40
4	0.50	0.50	8.00	5.59	0.70	0.30
5	0.60	0.40	8.00	6.32	0.74	0.26
6	0.70	0.30	7.00	7.55	0.80	0.20
7	0.80	0.20	9.00	8.83	0.86(0.87 <sup>b</sup> )	0.14

<sup>a</sup>Solvent: 1,4-dioxane; temperature:  $65 \pm 1^\circ\text{C}$ ; initiator: AIBN (1% weight of the monomers); non-solvent: ethanol.

<sup>b</sup>From the results of peak integration in <sup>1</sup>H-NMR.

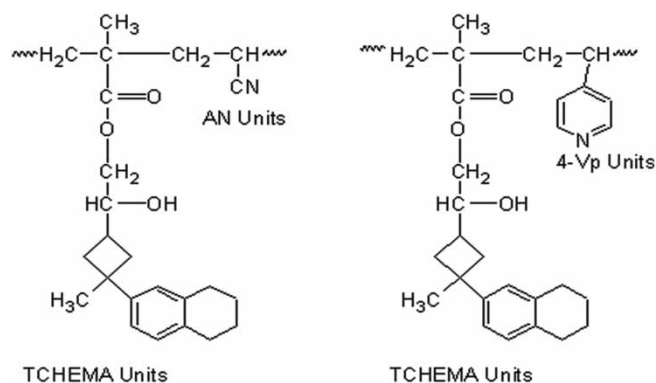
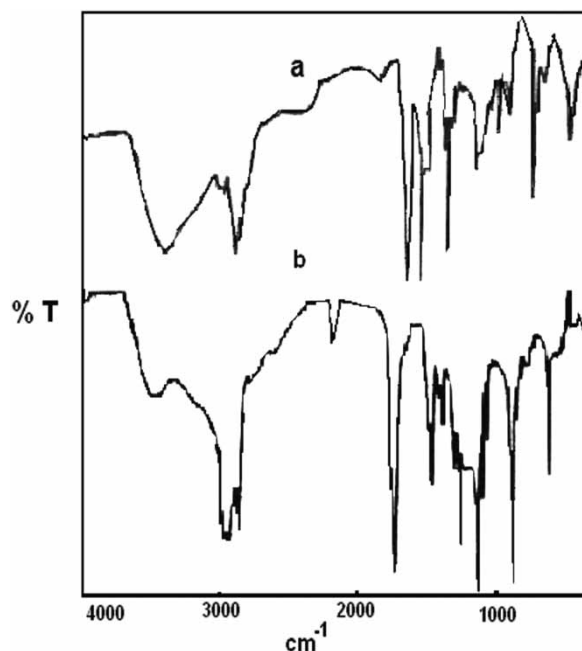
spectrum of poly(AN-co-TCHEMA) are shown in Figure 2. <sup>1</sup>H-NMR ( $\delta$  ppm): 7.0–7.33 (ArH), 3.1–4.2 (-OCH<sub>2</sub>CH-OH), 2.2–3.1 (cyclobutane ring protons), 1.4–1.7 (-CH<sub>3</sub> on the cyclobutane ring and CH<sub>2</sub> protons on the AN units), 0.8–1.2 (methylene protons in the polymer backbone, and methyl protons on the polymer backbone). <sup>13</sup>C-NMR peak assignments of the copolymers ( $\delta$  ppm): 167 (ester carbonyl), 132–150 (Ar C in polymer backbone), 78 (OCH<sub>2</sub>), 81 (-C≡N), 72 (CH (OH) 42.5–38.9 (carbons in cyclobutane ring)), 28.6 (CH<sub>3</sub> in cyclobutane ring), 20.1–22.0 (CH<sub>3</sub> and CH<sub>2</sub> on polymer backbone).

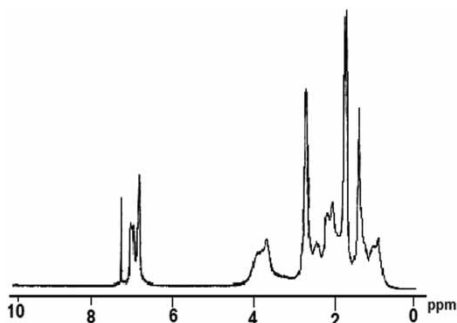
Although the IR spectra of the 4VP-TCHEMA (Fig. 1a) copolymers show characteristic bands at 1740 cm<sup>-1</sup> (C=O), 3100–3000 cm<sup>-1</sup>, 1590 cm<sup>-1</sup> (aromatic C-H), 1160 cm<sup>-1</sup> (C-O). The <sup>1</sup>H-NMR spectra of the copolymers show broad peaks at 6.9–7.5 ppm (ArH), 3.2–4.3 ppm (OCH<sub>2</sub>CH-OH), 2.3–3.3 ppm (cyclobutane ring protons), 1.3–1.7 (-CH<sub>3</sub> on the cyclobutane ring and CH<sub>2</sub> protons on the 4-VP units), 0.9–1.5 ppm (other aliphatic protons including those in the backbone). The <sup>13</sup>C-NMR spectrum of poly(4VP-co-TCHEMA) is shown in Figure 3. <sup>13</sup>C-NMR peak assignments of this copolymer ( $\delta$  ppm): 169 (ester carbonyl), 121–154 (Ar C in polymer backbone), 75 (OCH<sub>2</sub>), 72 (CH (OH) 44.5–38.5 (carbons in cyclobutane

ring)), 28.5 (CH<sub>3</sub> in cyclobutane ring), 19.1–22.0 (CH<sub>3</sub> and CH<sub>2</sub> on polymer backbone).

### 3.2 Molecular Weights of the Polymers

The molecular weights of the polymers were determined by GPC with polystyrene and tetrahydrofuran as the standard solvent, respectively. The  $M_w$  and  $M_n$  values and polydispersity indices ( $M_w/M_n$ ) of the polymer samples are presented in Table 3. The polydispersity index of the polymers ranges from 1.55 to 1.74. The theoretical values of  $M_w/M_n$  for the polymers produced via radical recombination and disproportionation are 1.5 and 2.0, respectively (24). In the homopolymerization of TCHEMA, the growing chains terminate by disproportionation. The polydispersity indices of

**Sch. 1.** Structure of the copolymers.**Fig. 1.** FTIR spectrum of poly(4VP-co-TCHEMA) (a)  $m_1:m_2$ : [60:40] and poly(AN-co-TCHEMA) (b)  $m_1:m_2$ : [50:50].



**Fig. 2.**  $^1\text{H-NMR}$  spectrum of poly(AN-co-TCHEMA)  $m_1:m_2$ :[48:52].

poly(TCHEMA), poly(AN) and poly(4-VP) suggest that in both cases chain termination by disproportionation outweighs coupling, and the tendency for termination by disproportionation is greater for TCHEMA than for AN and 4-VP. The values of  $M_w/M_n$  in copolymerization are also known to depend on chain termination in the same way as in homopolymerization (25).

### 3.3 Copolymer Compositions and Monomer Reactivity Ratios

The monomer reactivity ratios for the copolymerization of TCHEMA with AN and 4VP were determined from the monomer feed ratios and the copolymer composition. The Fineman–Ross (FR) (26) and Kelen–Tudos (KT) (27) methods were used to determine the monomer reactivity ratios. The significance of parameters of FR and KT equations are presented in Tables 4 and 5. According to the FR method, the monomer reactivity ratios can be obtained as follows:

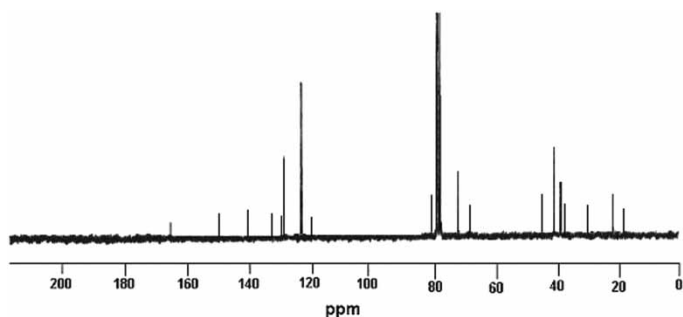
$$G = Hr_1 - r_2 \quad (1)$$

where  $r_1$  and  $r_2$  correspond to the AN or 4VP and TCHEMA monomers, respectively. The parameters  $G$  and  $H$  are defined as follows:

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

with

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



**Fig. 3.**  $^{13}\text{C-NMR}$  spectrum of poly(TCHEMA-co-4VP)  $m_1:m_2$ :[49:51].

**Table 3.** The GPC result of the copolymers

Poly(AN-co-TCHEMA)	$M_w$	$M_n$	$M_w/M_n$
28/72	41,200	26,500	1,55
50/50	44,400	27,280	1,63
69/31	38,900	25,850	1,50
Poly(4VP-co-TCHEMA)			
49/51	39,700	22,800	1,74
70/30	39,500	24,250	1,63
86/14	35,760	23,100	1,55

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

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

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

where  $\eta$  and  $\xi$  are functions of the parameters  $G$  and  $H$

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

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

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

The graphical plots concerning the methods previously reported are given for poly(AN-co-TCHEMA) in Figures 4 and 5, whereas the reactivity ratios are summarized in Table 6. In all cases, and for all graphical methods, the plots are linear, and this indicates that these copolymerizations follow conventional copolymerization kinetics and that the reactivity of a polymer radical is determined only by the terminal monomer unit.

The monomer reactivity ratios ( $r_1$  and  $r_2$ ) of poly(AN-co-TCHEMA) are less than 1. This indicates that the system copolymerizes statistically. Comparing TCHEMA to AN, it should be stated that two monomers show similar copolymerization behavior. The reactivities of these monomers are close together. 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.

For TCHEMA and 4VP systems the  $r_1$  values are higher than the  $r_2$ . The reactivity of growing radicals with 4VP unit, as measured by  $1/r_2$  seems to be higher toward TCHEMA monomer than its own monomer. The  $r_1$  and  $r_2$  values strongly suggest that the copolymer chain contains a greater number of 4VP units and less TCHEMA units than in the feed. The result from the F-R and K-T methods agrees. Although the copolymerization of TCHEMA with 4-VP an alternating tendency shows, and the copolymer



**Table 4.** F-R and K-T parameters for poly(AN-co-TCHEMA) systems

Sample no.	$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f - 1)/f$	$H = F^2/f$	$\eta = G/(\alpha + H)$	$\varepsilon = H/(\alpha + H)$
1	0.25	0.38	-0.410	0.17	-0.320	0.130
2	0.43	0.62	-0.260	0.30	-0.190	0.210
3	0.67	0.94	-0.040	0.47	-0.030	0.301
4	1.00	1.00	0.004	0.99	0.002	0.482
5	1.50	1.38	0.416	1.63	0.153	0.591
6	2.33	1.80	1.038	3.02	0.252	0.740
7	4.00	2.21	2.189	7.24	0.263	0.871

$$\alpha = (H_{\max} \cdot H_{\min})^{1/2} = 0.67.$$

**Table 5.** F-R and K-T parameters for poly(4VP-co-TCHEMA) systems

Sample no.	$F = M_1/M_2$	$f = m_1/m_2$	$G = F(f - 1)/f$	$H = F^2/f$	$\eta = G/(\alpha + H)$	$\varepsilon = H/(\alpha + H)$
1	0.25	0.94	-0.015	0.066	-0.031	0.137
2	0.43	1.07	0.027	0.173	0.464	0.293
3	0.67	1.53	0.232	0.293	0.330	0.413
4	1.00	2.25	0.562	0.444	0.650	0.520
5	1.50	2.81	0.972	0.801	0.792	0.660
6	2.33	4.07	1.762	1.339	1.002	0.763
7	4.00	6.10	3.341	2.620	1.097	0.863

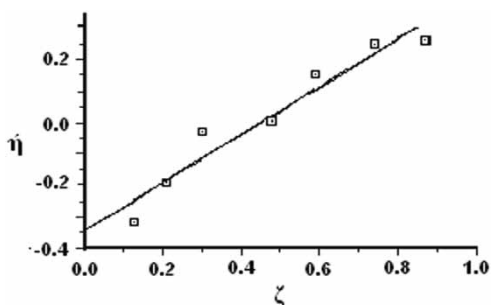
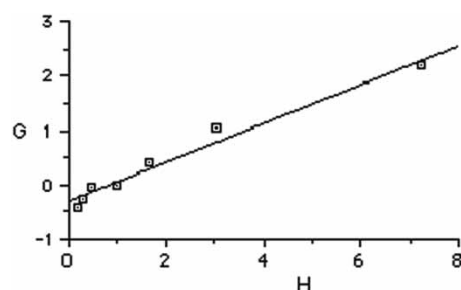
$$\alpha = (H_{\max} \cdot H_{\min})^{1/2} = 0.42.$$

sequence will be statistical in structure with more 4VP. The relationships between mole fractions of 4VP in copolymer and 4VP in feed are shown in Figure 6.

### 3.4 Glass Transition Temperatures

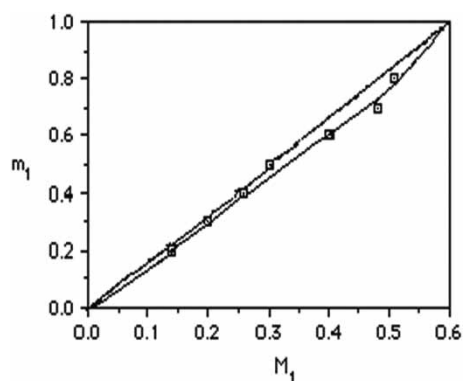
From DSC measurements  $T_g$  was taken as the midpoint of the transition region. The  $T_g$  values of poly(TCHEMA), poly(AN), and poly(4VP) obtained under the same conditions with the copolymers were found 117°C, 85°C, and 150°C, respectively. The glass transition temperature of poly(4VP) is considerably higher than the other polymers. The  $T_g$  value of poly(TCHEMA) is higher than the other methacrylate polymers. Apparently the bulky tetralino and hydroxyl side group decreases the flexibility of the chain and the free volume, thereby increasing  $T_g$ . The  $T_g$  of the copolymers ranged between the values of the two homopolymers.

Among the many strategies available for increasing the  $T_g$  of methacrylate polymers, the most promising 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(cyclohexyl methacrylate) (28) to 194°C for poly(bornyl methacrylate) and 200°C for poly(isobornyl methacrylate) (29). 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) (30).  $T_g$  values for 4VP-TCHEMA copolymers ranged between the values of the two homopolymers. Introduction of TCHEMA units into 4VP units led to a decrease in the  $T_g$  of poly(4VP-co-TCHEMA). A decrease in  $T_g$  of 4VP-TCHEMA copolymers may be due to the introduction of comonomer, TCHEMA, into 4VP, which reduces the

**Fig. 4.** K-T plot for poly(AN-co-TCHEMA) system.**Fig. 5.** F-R plot for poly(AN-co-TCHEMA) system.

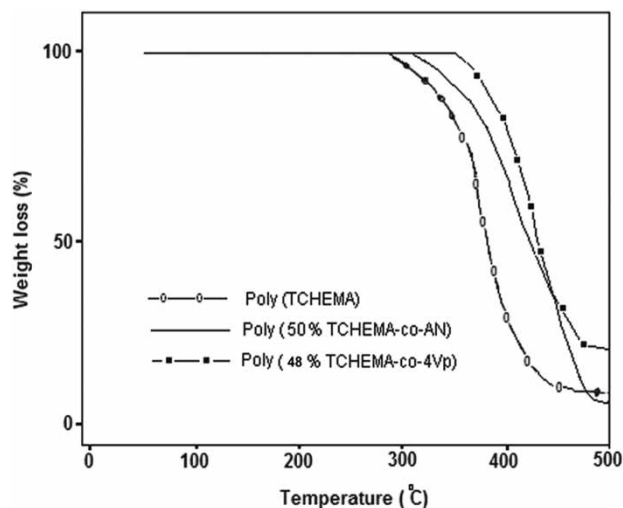
**Table 6.** Comparison of reactivity ratios by various methods

System	Methods	$r_1$	$r_2$	$r_1 r_2$	$1/r_1$	$1/r_2$
Poly(AN-co-TCHEMA)	F-R	0.36	0.29	0.10	2.78	3.45
	K-T	0.42	0.38	0.16	2.38	2.63
	Average	0.39	0.34	0.13	2.56	2.94
Poly(4VP-co-TCHEMA)	F-R	1.32	0.06	0.08	0.76	16.67
	K-T	1.34	0.12	0.16	0.75	8.33
	Average	1.33	0.09	0.12	0.75	11.11

**Fig. 6.** Plots of mole fraction of 4VP in copolymers ( $m_1$ ) measured by elemental analysis vs. mole fraction of 4VP in feeds ( $M_2$ ).

intermolecular interactions between the molecular chains due to structure loosening.

The Tg of the AN-TCHEMA copolymers ranged between the values of the two homopolymers. The high Tg value of 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 TCHEMA units in the copolymer. These values are indicated in Table 7.

**Fig. 7.** TGA curves of the polymers (heating rate 10°C/min under a nitrogen atmosphere).

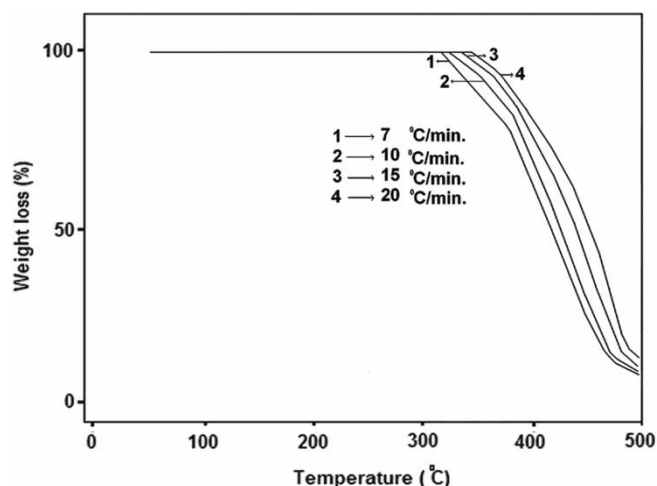
### 3.5 Decomposition Kinetics

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. In Figure 7, the TGA thermograms of polymers are shown. Some degradation characteristics of

**Table 7.** Some TGA results and Tg values of the copolymers

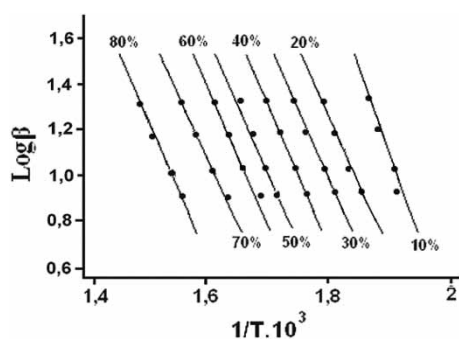
Polymer	IDT <sup>a</sup>	The temperature (°C) for a weight loss of			The Residue (%) at 450°C	
		20	50	70	Tg	
Poly(TCHEMA)	280	352	378	397	17	117
Poly(AN)	320	370	490	—	40	85
Poly (AN-co-TCHEMA)						
28/72	297	375	418	474	21	113
50/50	305	390	425	485	29	101
69/31	314	402	433	497	36	93
Poly(4-VP)	380	398	412	430	3	150
Poly(4VP-co-TCHEMA)						
49/51	332	384	422	442	11	120
60/40	350	400	430	455	8	135
86/14	372	413	439	467	5	141

<sup>a</sup>Initial decomposition temperature.



**Fig. 8.** Thermal degradation curves of poly(4VP-co-TCHEMA) (0.60:0.40) at different heating rates.

the copolymers are given in Table 7 by comparison with those of the homopolymers. It is clear that two degradation stages are observed for poly(TCHEMA). The initial decomposition temperatures of poly(TCHEMA) are around 280°C, and independent of the side-chain structures. This result shows that



**Fig. 9.** Ozawa plots of the logarithm of the heating rate ( $\log \beta$ ) vs. the reciprocal of the temperature ( $1/T$ ) at different conversions for poly(4VP-co-TCHEMA) (0.60:0.40).

main-chain scission is an important reaction in the degradation of polymers, at least in the beginning. The degradation of poly(TCHEMA) occurred in two stages. The first stage was observed 275–375°C. The second stage decomposition commenced at 380–450°C. The parent homopolymers have typically decomposed maximum points at 320°C for poly(AN) and 350°C for poly(4VP) under nitrogen atmosphere, respectively. The thermal stabilities of two copolymers are between those of the corresponding homopolymers. The copolymers samples showed also two 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 increases with an increase in AN and 4VP monomers concentration. Thermal degradation of poly-*n*-alkyl methacrylates typically produces the monomer as a result of depolymerizations (31, 32). The formation of cyclic anhydride-type structures by intramolecular cyclisation is another main process in degradation of these polymers (33). Some methacrylic esters with hydrophilic side chains, such as 2-hydroxyethyl, behave differently from most of poly-*n*-alkyl methacrylates. It was reported that the thermal degradation of poly 2-hydroxyethyl methacrylate and its derivative produced some monomers but not the anhydride structure (34, 35). For the study of the kinetics of the thermal degradation of polymers, we can select isothermal thermogravimetry (ITG) or thermogravimetry (TG) at various heating rates (36). ITG is superior for obtaining an accurate activation energy for thermal degradation, although it is time-consuming. For the thermal degradation of polymers, in which depolymerization is competing with cyclization or crosslinking due to the side groups, TG at various heating rates is much more convenient than ITG for the investigation of thermal degradation kinetics. Therefore, in this work, TG curves at various heating rates were obtained, and the activation energies ( $\Delta E_d$ ) for the thermal degradation of the polymers were calculated with Ozawa plots, which are widely used. Degradations were performed in the scanning mode, from 35 to 500°C, under a nitrogen flow (20 mL min<sup>-1</sup>), at various heating rates (7.0, 10.0,

**Table 8.** The apparent activation energies of investigated copolymers under thermal degradation in N<sub>2</sub>

Sample	Activation energy (kJ/mol)/Conversion (%)								
	10	20	30	40	50	60	70	80	90
Poly(TCHEMA)	142.8	162.6	156.7	160.5	167.2	165.8	164.3	162.7	161.9
Poly(TCHEMA31%-co-AN)	111.4	97.9	118.2	99.0	115.8	115.8	119.0	93.3	102.1
Poly(TCHEMA42%-co-AN)	119.4	111.6	129.1	118.2	134.5	124.2	128.8	103.0	118.1
Poly(TCHEMA50%-co-AN)	133.6	118.0	129.2	118.4	139.9	132.8	138.7	115.9	124.4
Poly(TCHEMA52%-co-AN)	129.8	135.9	128.0	123.2	141.9	145.7	141.1	127.4	126.8
Poly(TCHEMA14%-co-4VP)	137.6	150.2	133.8	139.9	161.8	157.4	159.8	139.8	138.5
Poly(TCHEMA26%-co-4VP)	138.4	153.9	139.3	137.6	167.8	139.4	141.0	135.9	149.9
Poly(TCHEMA40%-co-4VP)	143.3	151.3	149.4	159.7	169.6	164.7	149.5	141.6	149.0
Poly(TCHEMA51%-co-4VP)	150.4	155.6	159.4	148.9	164.0	167.8	155.7	156.8	155.0



15.0, and 20.0°C min<sup>-1</sup>). In Figure 8, the TGA thermograms of poly(4VP-co-THEMA) (0.60:0.40) are shown. Samples (5–8 mg) held in alumina open crucibles were used, and their weights were measured as a function of the temperature and stored in a list of data of the appropriate built-in program of the processor. The TGA curves were immediately printed at the end of each experiment, and the weights of the sample were then transferred to a personal computer at various temperatures.

According to the method of Ozawa (37), the apparent thermal decomposition activation energy ( $E_d$ ) can be determined from the TGA thermograms at various heating rates, such as those in Figure 8, and with the following equation:

$$E_d = -\frac{R}{b} \left[ \frac{d \log \beta}{d(1/T)} \right] \quad (7)$$

Where  $R$  is the gas constant;  $b$  is a constant (0.4567); and  $\beta$  is the heating rate (°C/min). According to Equation (7), the activation energy of degradation can be determined from the slope of the linear relationship between  $\log \beta$  and the reciprocal of the temperature, as shown in Figure 9; the  $\Delta E_d$  values for the polymers are given in Table 8.  $\Delta E_d$  calculated from the Ozawa method is superior to other methods for complex degradation because it does not use the reaction order in the calculation of the decomposition activation energy (38). Therefore;  $\Delta E_d$  calculated from the Ozawa method is superior to the former methods for complex degradation.

#### 4 Conclusions

Copolymers of THEMA with AN and 4VP have been prepared by free radical polymerization in 1,4-dioxane at 65°C. The reactivity ratios of the copolymers were estimated using linear graphical methods. The glass transition temperatures of the THEMA with AN and 4VP copolymers were obtained and compared. The TGA studies concluded that the thermal stability of the copolymers increases with an increase of AN and 4VP in the copolymer chain. The activation energy of the decomposition of the investigated polymers was calculated by the Ozawa method with the TGA data.

#### 5 References

- Xiao, S., Huang, R.Y.M. and Feng, X.S. (2007) *Polymer*, **48**(18), 5355.
- Ivirico, J.L.E., Martinez, E.C., Sanchez, M.S., Criado, I.M., Ribelles, J.L.G. and Pradas, M.M.J. (2007) *Biomed. Mat. Res. Part B-App. Biomat.*, **83b**(1), 266.
- Pal, K., Banthia, A.K. and Majumdar, D.K. (2006) *Biomedical Materials*, **1**(2), 85.
- Pla-Roca, M., Fernandez, J.G., Mills, C.A., Martinez, E. and Samitier, J. (2007) *Langmuir*, **23**(16), 8614.
- Zhu, X.Z., Yin, Q.M., Zhao, J.R., Yin, J.H., Feng, Y. and Wang, Y.L. (2007) *Acta Polym. Sin.*, **(2)**, 172.
- Goel, N.K., Kumar, V., Bhardwaj, Y.K., Biswal, J. and Sabharwal, S. (2006) *J. Mac. Sci., Part A-Pure and Appl. Chem.*, **43**(8), 1151.
- Sanli, O. and Unal, H.I. (2002) *J. Mac. Sci., Part A-Pure and Appl. Chem.*, **39**(5), 447.
- Mohapatra, R., Swain, A.K., Mohapatra, R., Rana, P.K. and Sahoo, P.K. (2005) *Polym. & Polym. Comp.*, **13**(8), 807.
- Reyntjens, W., Jonckheere, L., Goethals, E. and DuPrez, F. (2001) *Macromol. Symp.*, **164**, 293.
- Boesel, L.F., Cachinho, S.C.P., Fernandes, M.H.V. and Reis, R.L. (2007) *Acta Biomaterialia*, **3**(2), 175.
- Bodas, D.S. and Khan-Malek, C. (2007) *Sen. Act. B-Chem.*, **120**(2), 719.
- Jang, S.C., Yi, S.C., Kim, Y.B. and Hong, J.W. (2005) *Polym. Adv. Tech.*, **16**(6), 484.
- Erol, I., Soykan, C. and Ahmedzade, M. (2002) *J. Polym. Sci. Part. A: Polym. Chem.*, **40**, 1756.
- Li, S., Li, H.Q., Meng, W.D. and Qing, F.L. (2007) *Acta Polym. Sinica*, **(2)**, 114.
- Tsotinis, A., Eleutheriades, A., Hough, K.A., Davidson, K. and Sugden, D. (2007) *Bio. Chem.*, **35**(2), 189.
- Warnecke, A., Fichtner, I., Garmann, D., Jaehde, U. and Kratz, F. (2004) *Bioconjugate Chemistry*, **1**(6), 1349.
- Seguin, E., Elomri, A., Magiatis, P., Skaltsounis, A.L., Chao, L.R. and Tillequin, F. (2002) *Natural Product Let.*, **16**(3), 187.
- Tsai, C.J. and Chen, Y. (2006) *React. Funct. Polym.*, **66**(11), 1327.
- Zharnikov, M., Ouchi, Y., Hasegawa, M. and Scholl, A. (2004) *J. Phys. Chem. B.*, **108**(3), 859.
- Arshady, R., Kenner, G.W. and Ledwith, A. (1981) *Macromol. Chem. Phys.*, **182**(1), 41–46.
- Ham, G. *Copolymerization High Polymers*; Interscience: New York, 1964; Vol. 18.
- Yakuphanoglu, F., Erol, I., Aydogdu, Y. and Ahmedzade, M. (2002) *Material Lett.*, **57**, 229.
- Aydogdu, Y., Erol, I., Yakuphanoglu, F., Aydogdu, A. and Ahmedzade, M. (2003) *Synthetic Met.*, **139**, 327.
- Vijayanand, P.S., Kato, S., Satokawa, S. and Kojima, T. *European Polymer Journal*, **43**(5), 2046.
- Bevington, J.C., Melville, H.W. and Taylor, R.P. (1954) *J. Polym. Sci.*, **12**, 449.
- Finemann, M. and Ross, S.D. (1950) *J. Polym. Sci.*, **5**, 259.
- Kelen, T. and Tüdös, F. (1981) *J. Macromol. Sci. Chem.*, **A16**(7), 1283–1297.
- Jang, F.H. and Woo, E.M. (1999) *Polymer*, **40**(9), 2231.
- Dogan, F., Kaya, I. and Yurekli, M. (2007) *Catalysis Let.*, **114**(1–2), 49.
- Pizzirani, G., Magagnini, P.J. and Giusti, P. (1971) *J. Polym. Sci. Part A-2: Polym. Phys.*, **9**(6), 1133.
- Zuev, V.V., Bertini, F. and Audisio, G. (2006) *Polym. Deg. Stab.*, **91**, 512.
- Bertini, F., Audisio, G. and Zuev, V.V. (2005) *Polym. Deg. Stab.*, **89**(2), 233.
- Gentilhomme, A., Cochez, M., Ferriol, M., Oget, N. and Miłoszynski, J.L. (2005) *Polym. Deg. Stab.*, **88**(1), 92.
- Martinez, G., Sánchez-Chaves, M., Marco Rocha, C. and Ellis, G. (2002) *Polym. Deg. Stab.*, **76**(2), 205.
- Demirelli, K., Coskun, M. and Kaya, E. (2001) *Polym. Deg. Stab.*, **72**(1), 75.
- Wallis, M. and Bhatia, K.S. (2006) *Polym. Deg. Stab.*, **91**(7), 1476.
- Ozawa, T. (1965) *Bull. Chem. Soc. Jpn.*, **38**, 1881.
- Regnier, N. and Guibe, C. (1997) *Polym. Degrad. Stab.*, **55**, 165.