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RADICAL COPOLYMERIZATION OF ACRYLOYLMORPHOLINE WITH 2-HYDROXYETHYL METHACRYLATE: MONOMER REACTIVITY RATIOS AND THERMAL PROPERTIES

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ABSTRACT

Poly(acryloylmorpholine-co-2-hydroxyethyl methacrylate) were prepared by traditional free radical polymerization. Copolymerization with acryloylmorpholine (ACM) and 2-hydroxyethyl methacrylate (HEMA) monomers were carried out in tetrahydrofuran solution at 60ºC using 2,2'-azobisisobutyronitrile (AIBN) as initiator. The copolymers were characterized by FT-IR, ^{1}H and ^{13}C nuclear magnetic resonance (NMR). Monomer compositions of the copolymers were established by nitrogen results of elemental analysis. The reactivity ratios of monomers ACM (r_1) and HEMA (r_2) in the copolymer were calculated by various methods. According to these methods, r_1 was 1.73-2.01 and r_2 was 0.48-0.74. Thermogravimetric analysis was used to investigate the thermal properties of copolymers.

Keywords: Acryloylmorpholine, 2-hydroxyethyl methacrylate, Reactivity ratios

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1. INTRODUCTION

Polymers are generally used in a wide range of applications often for their low cost, light weight and good mechanical properties or for combination of these characteristics. Copolymerization, which is one of the superior methods of modifying polymer properties, is also widely used in the production of commercial polymers. Copolymers can be tailored depending on the desired properties by changing the monomers, monomer compositions, and techniques of copolymerization. It is very important to determine the relationship between the structure and property of polymers obtained by radical copolymerization of vinyl monomers. Hence, copolymers found extensive uses in various fields of applications in different ways. Detailed examination of copolymers, both microstructure and composition heterogeneity, is of great importance in evaluating the properties of complex polymer materials planned for specific purposes [1,2].

Copolymers obtained at different ratios resulting in the incorporation of two different monomers lead to the construction of new materials which are very important for the scientific and commercial field. The monomer content of the copolymers, the relative activities of the monomers relative to one another determine the resulting degree of incorporation. The knowledge of the copolymer composition, which depends on the reactivity ratio, is an important step in the evaluation of this polymer. The monomer reactivity ratios, which play an important role in the elucidation of the copolymer structure, are an important factor in the prediction of the copolymer structure property relationship in clarifying the copolymerization kinetics [3,4].

The copolymer composition can be analyzed with methods, such as nuclear magnetic resonance [5-7] or elemental analysis [8-10]. Later, reactivity ratios of the monomers in the copolymer can be found by different methods such as; the Finemann-Ross (F-R), inverted Finemann-Ross (inverted F-R), Yezrielev-Brokhina-Roskin (Y-B-R), Kelen-Tudos (K-T) and extended Kelen-Tudos (extended K-T) methods [11-14].

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Acryloylmorpholine (ACM) is a cyclic acrylamide that has excellent properties such as good solubility in water and organic solvents, good biocompatibility for human body, and superabsorbent material in special application areas. But, amazingly has remained unstudied as its polymer. Poly(acryloylmorpholine) is a well known hydrophilic polymer and it has like properties ACM. The same manner as hydrophilic 2-hydroxyethyl methacrylate (HEMA) is toxic to living cells but its polymer poly(2-hydroxyethyl methacrylate) is extremely biocompatible, chemically and thermally stable. Therefore, these special monomers, their homopolymers and copolymers are of great interest in the academic, medicine and industrial fields [15-18].

The copolymerization of ACM with HEMA for the preparation of particular materials has not been reported until now. The present study aims to the poly(ACM-co-HEMA)s copolymers were synthesized by radical-initiated solution copolymerization and the monomer reactivity ratios and thermal properties of their were analyzed for stimulate new excitement in related fields.

2. EXPERIMENTAL

2.1. Materials

To remove the inhibitor, acryloylmorpholine (ACM) (Aldrich), which was passed through a column filled with basic aluminum, was then distilled under reduced pressure prior to use. 2-Hydroxyethyl methacrylate (HEMA) (Merck) was washed with dilute NaOH and distilled water to liberate it from the inhibitor. Then, the diethylether was evaporated with the aid of an evaporator. And finally dried in a vacuum oven. To purify 2,2'-azobisisobutyronitrile (AIBN) (Sigma) was recrystallized three times in methanol. To remove water from tetrahydrofuran (THF) (Aldrich), it was dried using anhydrous $MgSO_4$ and distilled before use. Toluene and hexane (Aldrich) were purchased and used without any treatment.

2.2. Synthesis of Copolymers

Seven copolymers were obtained due to monomers taken at different molar ratios. Appropriate amounts of ACM and HEMA with THF and AIBN (0.2% of total weight of monomers) were placed in a polymerization tube. The copolymerization mixtures were purged with argon for deoxygenation. The polymerization tubes were sealed by heating and immerse in an oil bath at 60°C. The yields of the copolymers were kept below 15%. All the copolymerization mixtures were poured dropwise into a mixture of toluene and hexane (1:1). Dissolving and precipitating were repeated for purification. The copolymers were finally dried in vacuum oven at 50°C for two days.

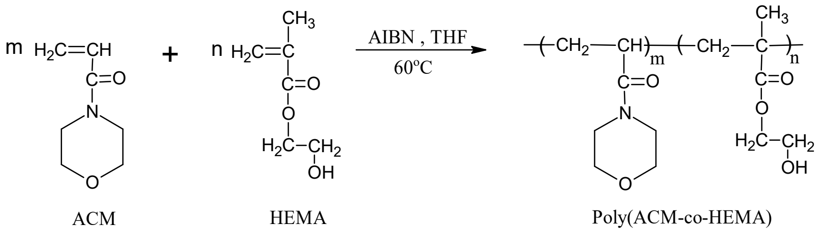
2.3. Characterization of the Copolymers

^{1}H and ^{13}C NMR spectra were taken using a Jeol FX-90Q spectrometer with d-chloroform as solvent. IR spectra of solid samples of KBr pellet shape were taken using a Mattson 1000 FTIR spectrophotometer. Elemental analysis results were obtained using a Leco 935 CHNS instrument. Thermal analysis data were obtained using a Shimadzu TA-50 thermal analyzer.

3. RESULTS AND DISCUSSION

3.1. Structural Characterization of Poly(ACM-co-HEMA) Copolymers

The copolymers were obtained via free radical polymerization with the ACM and the HEMA. The copolymers of seven different compositions were obtained as a result of all the operations performed. The synthesis of the copolymers is shown in Scheme 1.



Scheme 1. Synthesis of the copolymers

Elemental analysis (N%) results of the copolymers, mole fraction of ACM monomer in feed (M_1) and mole fraction of ACM in the copolymers (m_1) are shown in Table 1.

Table 1. Elemental analysis, mole fraction of monomer in feed and in the copolymers

The Copolymers	Elemental Analysis N (wt %)	Mole fraction of ACM monomer in feed M_1	Mole fraction of ACM monomer in the copolymers m_1^*
A	9.18	0.85	0.92
B	7.94	0.70	0.79
C	7.23	0.60	0.71
D	6.38	0.50	0.62
E	5.51	0.40	0.53
F	4.53	0.30	0.44
G	2.96	0.15	0.28

*Calculated from nitrogen results in the copolymers

The Fourier transform infrared spectra of seven copolymers are given in Figure 1 for comparison with the copolymers. The characteristic peaks of the copolymers are seen at 1730 (for carbonyl of ester in the HEMA units) and 1639 cm^{-1} (for carbonyl of amide in the ACM units). The relative intensities of these characteristic peaks vary depending on the percentage of monomer in the copolymer. In addition, it is seen that the O-H broad peak at 3450 cm^{-1} is directly proportional to the HEMA unit in the copolymer.

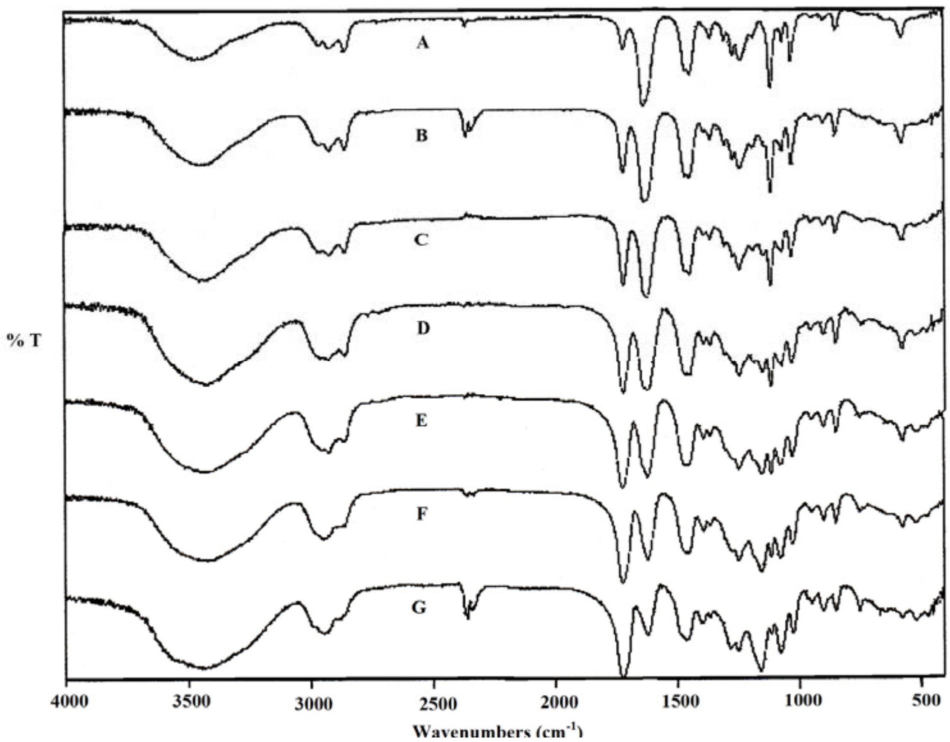


Figure 1. FT-IR spectra of the copolymers

The ^{1}H-NMR spectrum of poly(ACM62-co-HEMA) or the copolymer D shows characteristic signals at 4.6-3.5 (ring protons in the ACM and protons of carbons adjacent to oxygen in the HEMA units), 3.2 (O-H proton in the HEMA units), and 1.0-2.5 ppm [the main chain protons of both the ACM and the HEMA units, and the methyl protons connected to the main chain; Figure 2(a)].

The ^{13}C-NMR spectrum of the copolymer D demonstrates characteristic peaks at 176 (carbonyl carbon in the HEMA units), 173 (carbonyl carbon in the ACM units), 66 (carbons adjacent to oxygen in the ACM rings), 60 (carbon bonded to OH in the HEMA units), 44 (carbons adjacent to oxygen in the HEMA units), 42 (carbons adjacent to nitrogen in the ACM rings), 34-25 (the main chain carbons of both the ACM and the HEMA units), and 18 ppm [the methyl carbons connected to the main chain; Figure 2(b)].

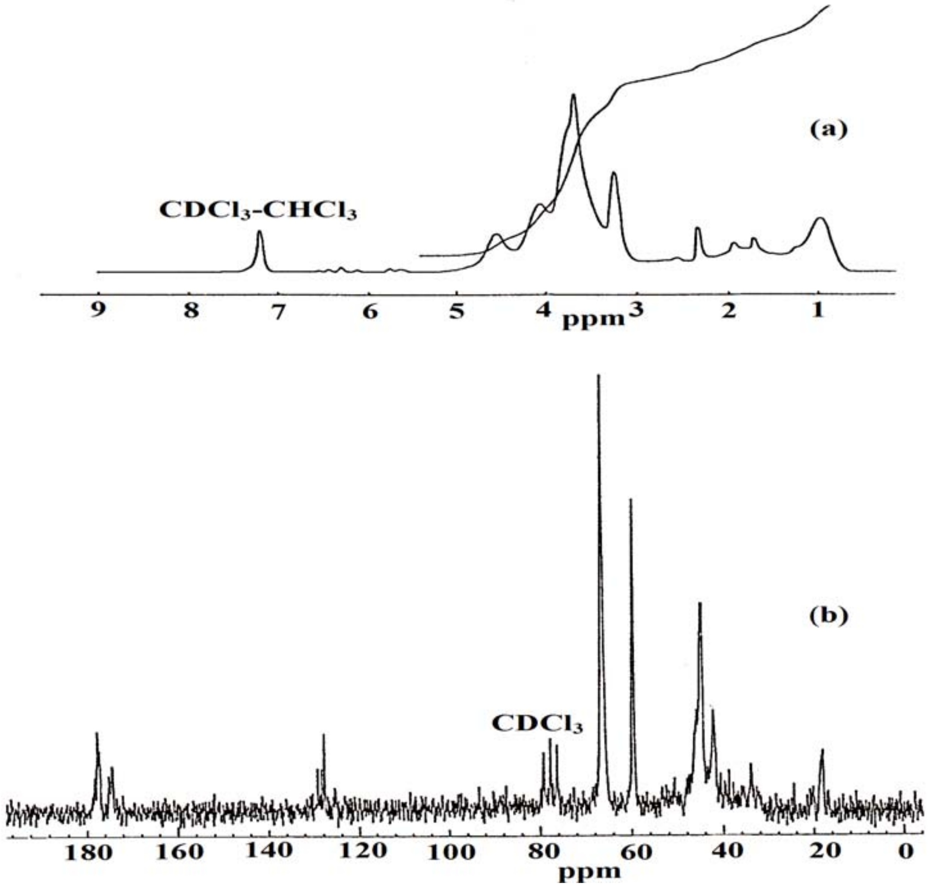


Figure 2. (a) ^{1}H and (b) ^{13}C NMR spectra of the copolymer D

3.2. Thermal Properties of The Copolymers

The thermogravimetric analysis (TGA) curves of the copolymers are represent in Figure 3

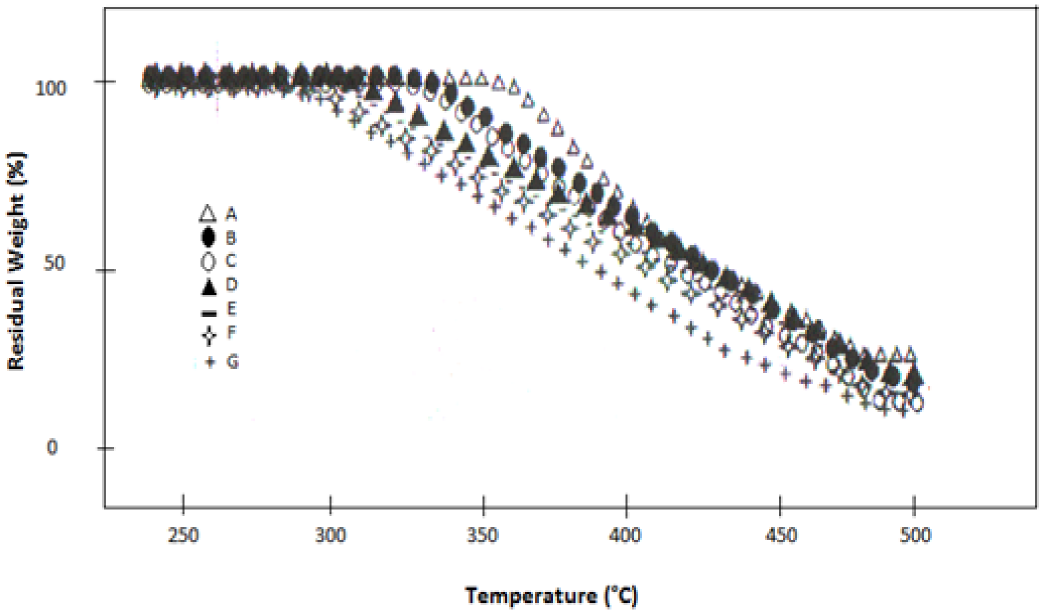


Figure 3. TGA curves of the copolymers

According to the decomposition temperature values obtained from the TGA curves in Table 2, the initial decomposition temperatures of the copolymers vary regularly from 295 to 358°C. It was seen that the residual amount increased, as the ACM units increased in the copolymers. It was estimated that there may be cross-linking between the tertiary carbon on the main chain of the ACM unit and the tertiary carbon of another chain [8].

Table 2. Decomposition temperatures of the copolymers

The Copolymers	Initial Decomposition Temperature T_i (°C)	Temperature of 50% mass loss $T_{50\%}$ (°C)	Residue at 500 °C (%)
A	358	441	29.7
B	342	432	28.6
C	335	422	27.2
D	324	413	24.6
E	321	410	22.1
F	297	400	19.2
G	295	395	17.2

3.3. Determination of Reactivity Ratios of The Copolymers

According to the elemental analysis results of the nitrogen given in Table 1, mole fraction of ACM in the copolymers (m_1) was calculated from the following equation:

$m_1.14 / [m_1.M_{ACM}+M_{HEMA}(1-m_1)]$ = elemental analysis gave the value of nitrogen (N%) / 100
The Finemann-Ross(F-R) equation [11] is given by the following equation:

$$G = Hr_1 - r_2$$

where M_1 and m_1 are the mole fractions of ACM in the feed and in the copolymers and $G = F(f-1)/f$, $H = F^2/f$, $F = M_1/M_2$, $f = m_1/m_2$, respectively. The interception and slope of G versus H give r_2 and r_1, respectively

The F-R equation is revised and thus, the intersection gives r_1 while giving the slope r_2.

$$G / H = -r_2 / H + r_1$$

On the other hand, Yezrielev-Brokhina-Roskin (Y-B-R) method [12] is expressed by the following relation

$$G = H^{3/2} r_1 - r_2$$

The Kelen-Tudos (K-T) [13] equation is an equation that contains different terms as shown below.

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

where η equals to $G / (\alpha + H)$, $\xi = H / (\alpha + H)$, and α equals to $(H_{max} H_{min})^{1/2}$. H_{max} and H_{min} are the highest and lowest values for H, respectively.

The parameters obtained from F-R, inverted F-R, Y-B-R and K-T graphs were given in Table 3 and are shown in Figure 4(a-d).

Table 3. Parameters for F-R, inverted F-R, Y-B-R, K-T methods

The Copolymers	$F=\frac{M_1}{M_2}$	$f=\frac{m_1}{m_2}$	$G=\frac{F(f-1)}{f}$	$H=\frac{F^2}{f}$	$\eta=\frac{G}{\alpha+H}$	$\xi=\frac{H}{\alpha+H}$	$\frac{G}{H}$	$\frac{1}{H}$	$H^{3/2}$
A	5.667	11.500	5.174	2.793	1.584	0.855	1.852	0.358	4.668
B	2.333	3.762	1.713	1.447	0.892	0.754	1.184	0.691	1.741
C	1.500	2.448	0.887	0.919	0.637	0.660	0.965	1.088	0.881
D	1.000	1.632	0.387	0.613	0.356	0.564	0.631	1.631	0.480
E	0.667	1.128	0.076	0.394	0.088	0.454	0.193	2.538	0.274
F	0.429	0.786	-0.117	0.234	-0.165	0.331	-0.500	4.274	0.113
G	0.176	0.389	-0.276	0.080	-0.499	0.145	-3.450	12.500	0.023

$\alpha = (H_{max} H_{min})^{1/2} = 0.473$

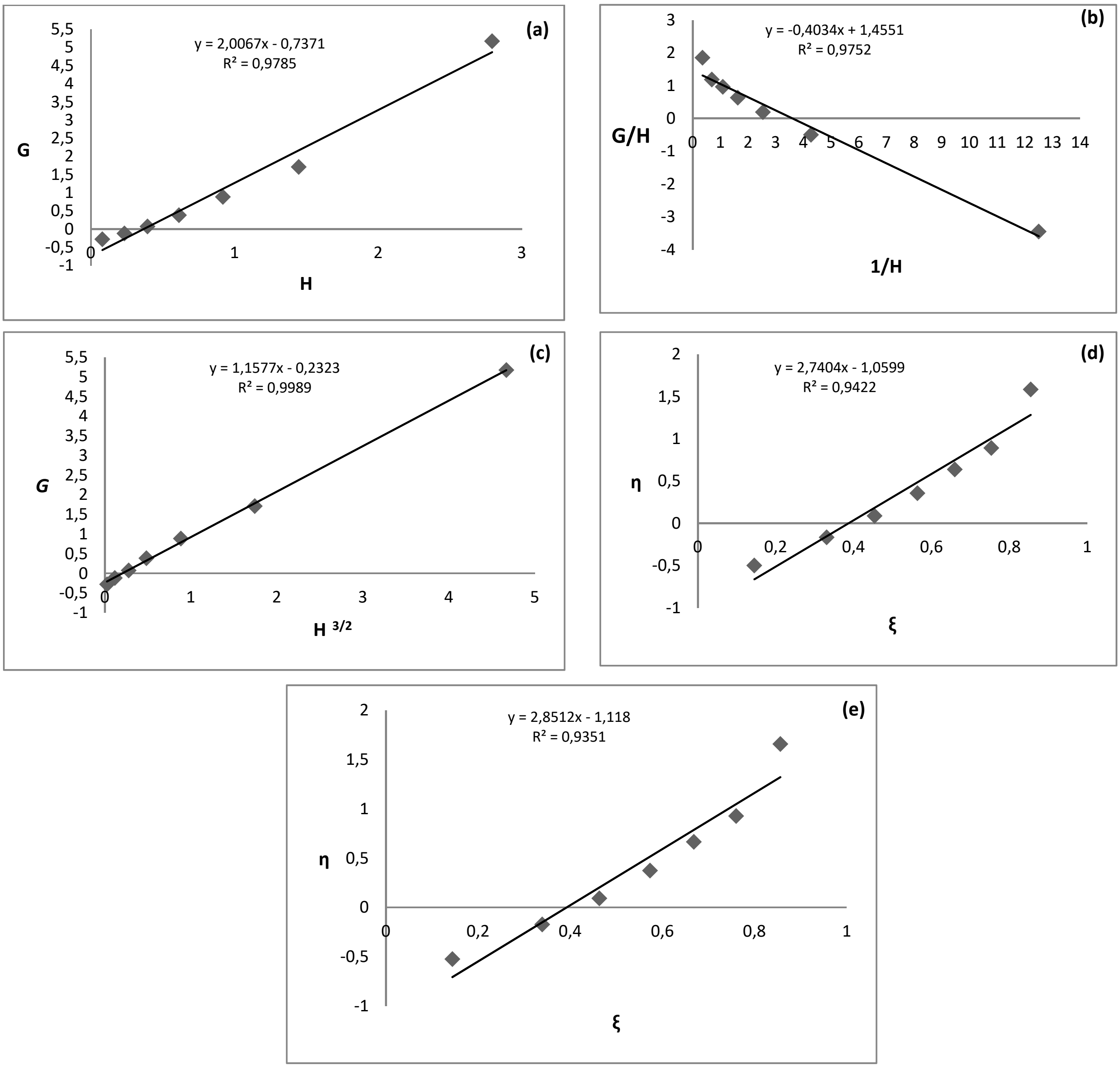


Figure 4. (a) F-R graph, (b) inverted F-R graph, (c) Y-B-R graph, (d) K-T graph, (e) extended K-T graph

Kelen and Tudos developed their own methods a little more than they had before [14]. This method, known as Extended K-T, is based on the effect of conversion on the copolymer and monomers compositions. The H and G parameters, which used to calculate η and ξ, are again defined as follows:

$H = f / Z^2$, and $G = (f - 1) / Z$;

where $Z = \log (1 - \zeta_1) / \log (1 - \zeta_2)$. The partial molar conversions of ACM and HEMA have been described as shown $\zeta_1 = \zeta_2 (f / F)$, and $\zeta_2 = w (\mu + F) / (\mu + f)$, $\zeta_1 = \zeta_2 (f / F)$, respectively; w refers to the yield of copolymerization, and μ indicates the ratio of the molecular weight of HEMA to the molecular weight of ACM. The extended K-T graph obtained using the data in Table 4 are shown in Figure 4(e). The r_1 and r_2 values calculated by different methods are given in Table 5. The results obtained from various methods are in agreement with each other. However, the values obtained by the F-R method differ from the values obtained by the other four methods [8]. The best value in R^2 (R: regression) values belongs to Y-B-R method with 0.999 and whereas, this value is higher than that of the values of other methods. The r_1 and r_2 values obtained from Y-B-R method were found to be 1.158 and 0.232, respectively.

Table 4. Parameters for extended K-T method

The Copolymers	Conversion w (wt%)	$\zeta_2 = \frac{w(\mu + F)}{(\mu + f)}$	$\zeta_1 = \zeta_2 \frac{f}{F}$	$Z = \frac{\log(1-\zeta 1)}{\log(1-\zeta 2)}$	$H = \frac{f}{Z^2}$	$G = \frac{f-1}{Z}$	$\eta = \frac{G}{\alpha + H}$	$\xi = \frac{H}{\alpha + H}$
A	0.144	0.076	0.154	2.210	2.559	4.953	1.658	0.856
B	0.137	0.095	0.153	1.664	1.359	1.660	0.928	0.760
C	0.121	0.087	0.142	1.683	0.864	0.860	0.665	0.668
D	0.113	0.085	0.139	1.685	0.575	0.375	0.374	0.573
E	0.109	0.084	0.142	1.746	0.370	0.073	0.091	0.463
F	0.095	0.075	0.137	1.890	0.220	-0.113	-0.174	0.339
G	0.084	0.070	0.155	2.321	0.072	-0.263	-0.525	0.144

$\alpha = (H_{max} H_{min})^{1/2} = 0.429$, $\mu = Mw_{HEMA}/Mw_{ACM} = 0.922$

The r_1 value obtained in all methods is approximately three times greater than the r_2 value. Thus, it can be said that the growing ACM radical would prefer to bind its own monomer much more than HEMA monomer. The copolymerization increases the ACM units in chains of copolymers. This confirms the presence of ACM blocks in the copolymers.

Table 5. Monomer reactivity ratios calculated with various methods

The Methods	$r_{1(ACM)}$	$r_{2(HEMA)}$
F-R	2.008	0.737
Inverted F-R	1.455	0.403
Y-B-R	1.158	0.232
K-T	1.681	0.501
Extended K-T	1.733	0.480

4. CONCLUSIONS

The thermal properties and monomer reactivity ratios of the synthesized copolymers were investigated. The initial decomposition temperatures, temperatures of 50% mass loss and residue at 500°C values were obtained for the copolymers. These thermal data indicate that the thermal stability of the copolymer increases, as the ACM unit increases in the copolymers. The reactivity ratios of ACM and HEMA in the copolymerization were found r_1: 1.158-2.008 and r_2: 0.232-0.737, respectively. According to the Y-B-R method, which stands out among the regression (R) values of the methods, the r_1 value was found 1.158 for the ACM and the r_2 value for HEMA was found 0.232 for the HEMA. These results show that the copolymer preferentially grows on the radical of the ACM monomer, rather than the HEMA monomer.

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