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Ethyl Acrylate-Hydroxyethyl Acrylate and Hydroxyethyl Acrylate-Methacrylic Acid: Reactivity Ratio Estimation from Cross-linked Polymer Using High Resolution Magic Angle Spinning Spectroscopy

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Solution free radical copolymerizations of hydroxyethyl acrylate/methacrylic acid (HEA/MAA) and ethyl acrylate/hydroxyethyl acrylate (EA/HEA) have been conducted in m-xylene (60wt% solvent level) over the temperature range of 70–130°C using tert-butyl peroxybenzoate as initiator. High resolution magic angle spinning spectroscopy (HR-MAS) and 2D-NMR have been utilized to characterize the copolymer gel for copolymer composition. The reactivity ratio values have been determined from low conversion copolymer composition data using the computer software package RREVM, which is based on the error in variables model (EVM) method. Also, Arrhenius-type reactivity ratio expressions have been developed that describe how reactivity ratios vary with temperature.

Keywords copolymerization, ethyl acrylate, methacrylic acid, reactivity ratio estimation, solution polymerization, hydroxyethyl acrylate, high resolution magic angle spinning

Introduction

Ethyl acrylate (EA), hydroxyethyl acrylate (HEA), and methacrylic acid (MAA) monomers are of great importance in several commercial applications. Their polymerization products find applications in the fields of coatings (1, 2) and biomaterials (3). Also, they are widely used in multi-component polymerizations, with the final polymer products utilized as paintings, adhesives and hydrogels (4–6). Very limited work has been done on the copolymerization of EA/HEA in bulk, solution or emulsion, especially in estimating reactivity ratios. Catala et al. (7) calculated reactivity ratios for HEA (M_1) with methyl- ethyl- butyl- (acrylate) (M_2) at 60°C using AIBN as initiator and 2-methoxyethanol as solvent. The monomer reactivity ratios were calculated using the Fineman-Ross method. Their results showed that increasing the length of the ester group in the alkyl acrylate reduces its reactivity and favors the addition of HEA into

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the copolymer. Increasing the length of the ester group was found to have less of an effect on the reactivity ratio for HEA. McIsaac (8) studied the kinetics of EA/HEA bulk copolymer at different feed ratios, initiator concentrations and temperatures. The reactivity ratios were calculated using non-linear least squares and EVM. The monomer feed compositions were calculated according to the Tidwell and Mortimer design criterion using the reactivity values from Catala et al. (7) as initial estimates. The resulting reactivity ratios were $r_{EA} = 0.505$ and $r_{HEA} = 0.958$. However, she reported that these values were not satisfactory enough due to several experimental difficulties with the system. These are mainly due to extremely rapid reaction rates even at low temperature and initiator concentration levels. One of these difficulties was staying within a low conversion level region, and obtaining a product that could be dissolved for solution $^1\text{H-NMR}$ characterization. Another problem was running the experiments without the occurrence of non-isothermal behavior. Similar work was also conducted by Chen et al. (9). They measured the reactivity ratios of HEA and butyl acrylate at the temperature range of 60–140°C in bulk, and the product was characterized by NMR for copolymer composition. Reactivity ratios were calculated and Arrhenius type relationships for temperature dependent reactivity ratios were eventually developed.

A limited number of studies have been conducted in the area of polymer gels for these monomers. Yasunaga et al. (5) studied the structure and segmental motion of a crosslinked polymethacrylic acid in the gel phase and related them to the degree of swelling and cross-linking. Rault et al. (6) studied thermal transitions in hydrogels based on interpenetrating networks of poly(ethyl acrylate) and poly(hydroxyethyl acrylate).

Reactivity ratio estimation according to the Tidwell and Mortimer (10) D-optimal design method requires the determination of copolymer composition at two initial feed compositions via (usually four) replicates at each feed point. Using this method, polymerization of some monomers like HEA may lead to the formation of gel (crosslinked polymer that does not dissolve), and subsequent characterization of such a product is quite challenging if not impossible. A recent review by Power (11) summarizes the difficulties with analyzing polymer gel by solution NMR and points out the advantages of using high resolution magic angle spinning technology (HR MAS). The restricted motion of the polymer backbone retains some of the dipolar coupling between the protons, which causes dramatic line broadening and low resolution. Also, the existence of many interfaces between the polymer (solid) and solvent (solution) affects the magnetic susceptibility and leads to further broadening of the resulting NMR signal. Researchers have shown that by rotating the sample rapidly at the magic angle (where $3\cos^2(\theta) - 1 = 0$) at spinning rates from 2 to 5 kHz, the broadening sources can be successfully overcome (11). Because of this, the combination of magic angle spinning (MAS) and high resolution probe technology is now considered a powerful technique for obtaining solution-like $^1\text{H-NMR}$ spectra of gel samples. EA/HEA and HEA/MAA copolymers are expected to be crosslinked (swelling gel at high HEA content) due to the nature of the monomers and their polymerization in *m*-xylene.

The objectives of this work are to determine reactivity ratio values of the largely unstudied HEA/MAA and EA/HEA copolymer systems. Both systems are used as part of multi-component recipes, hence, it is important to know their reactive characteristics if one is interested in understanding and modeling terpolymer or tetrapolymer systems that contain HEA/MAA or EA/HEA. In order to obtain copolymer composition data via solution NMR spectroscopy, the copolymer should be soluble in the appropriate deuterated NMR solvent. If the copolymer forms a crosslinked gel (as is the case for instance, for HEA/MAA due to esterification reaction and polymerization in *m*-xylene), then it is

impossible to obtain copolymer composition information to be used further for reactivity ratio estimation.

New advanced technology has to be employed in such a case. This can be accomplished by combining high resolution techniques with magic angle spinning (HR-MAS). The technique can handle crosslinked (swellable) gels and characterizes them with respect to copolymer composition through obtaining solution-like $^1\text{H-NMR}$ or $^{13}\text{C-NMR}$ spectra for the gel samples.

This study will be relevant to researchers who are involved with systems that show crosslinking behavior and hence their dissolution becomes impossible. In all these cases, the technique we describe herein may open new avenue for research concerning copolymer gels.

Experimental

Reagents

Technical grade monomers were employed without further treatment (hydroxyethyl acrylate was inhibited with 10–15 ppm 4-tert butyl catechol, methacrylic acid was inhibited with 200–250 ppm hydroquinine, ethyl acrylate was inhibited with 15–20 ppm methyl-ethyl hydroquinine). The initiator was tert-butyl peroxybenzoate. Solvents used over the course of the experiments and characterization of the copolymers (m-xylene, petroleum ether, deuterated dimethyl sulfoxide (DMSO- d_6), acetone, deuterated dimethyl formamide (DMF- d_7)) were used as packaged.

Characterization of Copolymers

The conversion of monomer to polymer was determined by gravimetry in all cases. Copolymer compositions were determined using solution and gel phase $^1\text{H-NMR}$ as follows:

HEA/MAA System. For experiments with high methacrylic acid feed content, the reaction mixture was heterogeneous even at low conversion. Copolymers prepared at 100 and 130°C dissolved in dimethyl sulfoxide (DMSO) satisfactorily, but copolymer prepared at 70°C was partially dissolvable in DMSO, and hence obtaining separate peaks for all samples was difficult. The copolymer was precipitated in petroleum ether and then filtered. The isolated copolymers were analyzed by solution $^1\text{H-NMR}$. The $^1\text{H-NMR}$ spectra were acquired with a 500 MHz Bruker Avance NMR spectrometer in deuterated dimethyl sulfoxide (DMSO- d_6) at room temperature. The operating conditions were as follows: temperature of the probe: 20°C, reference: DMSO- d_6 assigned at ≈ 2.46 ppm, spectral width: 4496.4–5000 Hz, pulse repetition time: 5 s, number of scans: 16–32. For experiments with high hydroxyethyl acrylate feed content, the reaction mixture was heterogeneous even at low conversion. The copolymer was precipitated in acetone and then filtered. The isolated copolymers were analyzed by gel $^1\text{H-NMR}$. $^1\text{H-NMR}$ spectra were acquired with a 500 MHz Bruker Avance NMR spectrometer with a Doty Scientific XC-4 HRMAS probe at room temperature. The operating conditions were as follows: temperature of the probe: 20°C, swelling solvent and internal reference: DMSO- d_6 assigned at ≈ 2.46 ppm, spectral width: 7500 Hz, 90° pulse width: 9 μs , pulse repetition time: 5 s, and number of scans: 64. Samples were prepared at room temperature by

transferring 1–2 mg of the copolymer to a 20 μ L Kel-F sealing cell placed within a 4 mm MAS silicon nitride rotor with Vespel caps.

EA/HEA System. For experiments with high ethyl acrylate feed content, the reaction mixture was found to be homogeneous at low conversion, the copolymers dissolved in chloroform and precipitated in petroleum ether. The isolated copolymers were analyzed by solution $^1\text{H-NMR}$. The $^1\text{H-NMR}$ spectra were acquired as above in deuterated chloroform (CDCl_3) at room temperature with reference (CDCl_3) assigned at ≈ 7.26 ppm. For experiments with high hydroxyethyl acrylate feed content, the reaction mixture was heterogeneous and the resulting copolymers were gels stuck on the interior surface of the ampoules. The copolymer products partially dissolved in dimethyl formamide (DMF) and precipitated in petroleum ether or deionized water. It was found that analyzing the sample with regular solution $^1\text{H-NMR}$ resulted in dramatic line broadening and low resolution, as will be discussed below. Because of that, the isolated copolymers were analyzed by gel-phase HR-MAS NMR using deuterated DMF.

Reactivity Ratio Estimation Experiments. The experiments carried out for reactivity ratio determination were designed based on the D-optimality criterion of Tidwell and Mortimer (10). This requires the use of the following equations for the initial monomer feed compositions (subscript 1 denotes hydroxyethyl acrylate in HEA/MAA and ethyl acrylate in EA/HEA):

$$f_1' = \frac{r_2}{2 + r_2} \quad (1)$$

and

$$f_1'' = \frac{2}{2 + r_1} \quad (2)$$

HEA/MAA System. The initial estimates required for reactivity ratios r_1 (hydroxyethyl acrylate) and r_2 (methacrylic acid) were obtained from the Q-e values (12), and were calculated to be $r_1 = 1.225$ and $r_2 = 0.294$. Based on these values, the initial monomer feed mixture compositions calculated from Equations (1) and (2) were $f_1' = 0.6202$ and $f_1'' = 0.1282$. Three or four replicate runs were conducted at the two monomer feed compositions and the resulting copolymers were analyzed for copolymer composition. The polymerizations were carried out at temperatures 70, 100, and 130°C. The reactivity ratio estimation experiments were conducted using m-xylene at a level of about 60 wt% of the total initial mixture at each reaction temperature with tert-butyl perbenzoate as initiator at about 0.00075 mol/L (in all cases, L refers to liter of monomer). The conversion level for each reactivity ratio experiment was maintained below 6%.

EA/HEA System. The initial estimates required for reactivity ratios r_1 (ethyl acrylate) and r_2 (hydroxyethyl acrylate) were obtained from the work of McIsaac (8) as $r_1 = 0.505$ and $r_2 = 0.958$. Based on these values, the initial monomer feed mixture compositions calculated from Equations (1) and (2) were $f_1' = 0.7984$ and $f_1'' = 0.3239$. Three or four replicate runs were conducted at the two monomer feed compositions, and the resulting copolymers were analyzed for copolymer composition. The polymerizations were carried out at temperatures 100 and 130°C. The reactivity ratio estimation experiments

were conducted using *m*-xylene at a level of about 60 wt% of the total initial mixture at each reaction temperature with *tert*-butyl perbenzoate as initiator at about 0.001 mol/L.

Polymerization experiments were carried out in borosilicate glass ampoules of about 10 ml capacity. The monomers, solvent and initiator were weighed, and approximately 5 mL aliquots were pipetted into the ampoules. The ampoules were degassed by several vacuum-freeze-thaw cycles until no air bubbles were observed to rise. The ampoules were then flame-sealed using a gas-oxygen torch, and stored in liquid nitrogen until ready for use. The reaction was carried out by placing the ampoules in a temperature shaker-oil bath at the desirable temperature. The ampoules were removed after the appropriate reaction time and then submerged in liquid nitrogen to stop the reaction. We observed that the reaction mixture for HEA/MAA at both feeds was heterogeneous and the reaction mixture for EA/HEA was only heterogeneous at high HEA feed content. In both cases, the removed ampoules were weighed, scorched, broken and the content precipitated into a 30-fold excess of petroleum ether and/or acetone, and subsequently filtered. Any remaining polymerization mixture in the ampoules was removed by continuous washing with acetone or petroleum ether. The copolymers were dried in a vacuum oven (55–80°C) until a constant weight was reached.

The resulting copolymer composition data from NMR were analyzed for reactivity ratio determination using the RREVM computer program (13) which accounts for errors in all variables (error in measuring the feed composition f_1 , and copolymer composition F_1). The error was estimated to be 0.5% in the initial monomer feed composition in all cases. The error in copolymer composition for HEA/MAA was estimated to be 10% at 70°C, 8% at 100°C, and 12% at 130°C. In EA/HEA, the copolymer composition error was 8% at 100 and 130°C and 11% at 70°C. All samples for gel phase NMR were run at the same spinning rate, in order to increase the reproducibility of our results to the extent possible, and hence minimize integration difficulties due to sample preparation, shimming and spinning rate.

Results and Discussion

Figure 1 shows typical solution $^1\text{H-NMR}$ spectra of low conversion HEA/MAA copolymer with high MAA feed content dissolved in DMSO-d_6 . The $^1\text{H-NMR}$ spectra

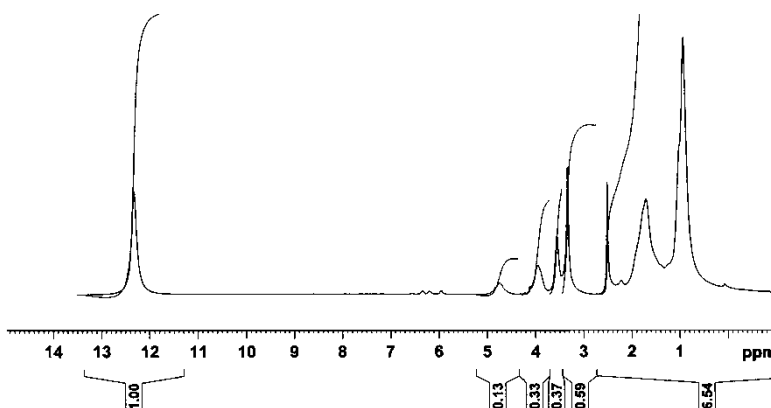


Figure 1. Typical solution $^1\text{H-NMR}$ spectra of hydroxyethyl acrylate/methacrylic acid copolymer in DMSO-d_6 .

are assigned respectively as: 0.8–1.4 ppm for methyl protons of methacrylic acid, 1.4–2.2 ppm for all methine protons of the hydroxyethyl acrylate and methacrylic acid units, and methylene protons of the hydroxyethyl acrylate units in the copolymer chain, 3.3 ppm for water in DMSO- d_6 and 12.0–12.6 ppm for the proton of the carboxyl group of MAA units. The HEA/MAA copolymer units resonances of the region 3.4–5.0 ppm were assigned to ($-OCH_2CH_2OH$) of HEA units and were resolved by employing 2D- 1H - ^{13}C heteronuclear multiple quantum coherence (HMQC) (see Figure 2). Figure 2 shows the chemical shifts as follows: 4.5–5.0 ppm for $-OH$ of the HEA units, 3.7–4.2 ppm for $-OCH_2$ units and 3.4–3.7 ppm for $-CH_2$ units of the HEA.

Similarly, Figure 3 shows a typical solution 2D- 1H - ^{13}C -HMQC spectrum of low conversion EA/HEA solution copolymer with high EA feed content dissolved in $CDCl_3$. By studying this spectrum we find that there are two contours at 60 ppm in ^{13}C spectrum belong to two different functional groups and appear at chemical shift of 3.7 and 4.1 ppm in 1H spectrum. Also, another two contours appear at 4.1 ppm in 1H spectrum and appear at 60 and 66 ppm in ^{13}C spectrum. No correlated for the peak located at 3.5 ppm in 1H spectrum, because of that, this peak is assigned for proton in hydroxyl group of HEA, the hydroxyl group location are also checked with the addition of deuterated water, D_2O , (D_2O affects chemical shift location, and later causes the disappearance of the $-OH$ signal due to ions exchange), the peak at 3.7 ppm assigned for protons in methine group connected to $-OH$ in HEA, and the peak at 4.1 ppm is assigned for protons in $-OCH_2$ of HEA and EA.

For HEA/MAA copolymer samples with high HEA content, the products were highly crosslinked and found to swell (not dissolve as in high MAA content) in DMSO. The products were characterized for copolymer composition by utilizing 1H -MAS-NMR spectroscopy. Typical 1H -MAS-NMR spectra of HEA/MAA copolymer gels are

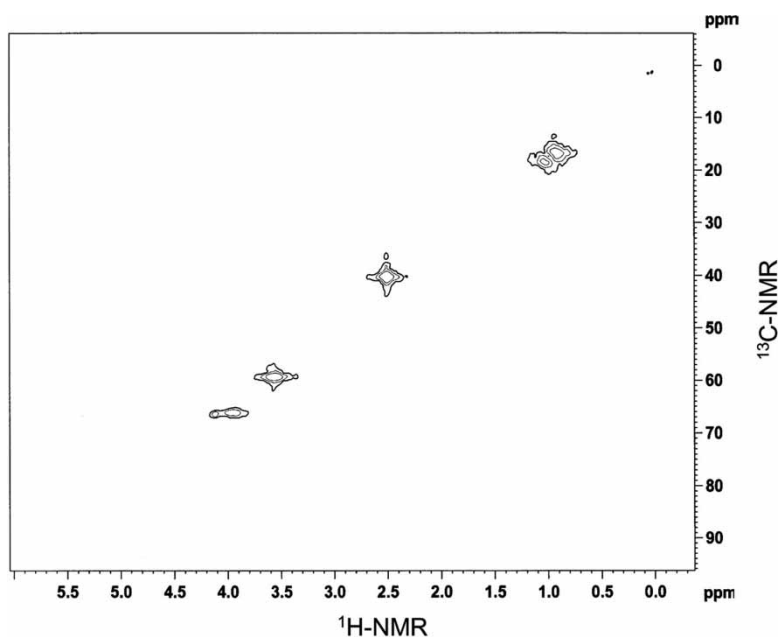


Figure 2. Typical 2D- 1H - ^{13}C -HMQC spectra of hydroxyethyl acrylate/methacrylic acid copolymer in DMSO- d_6 .

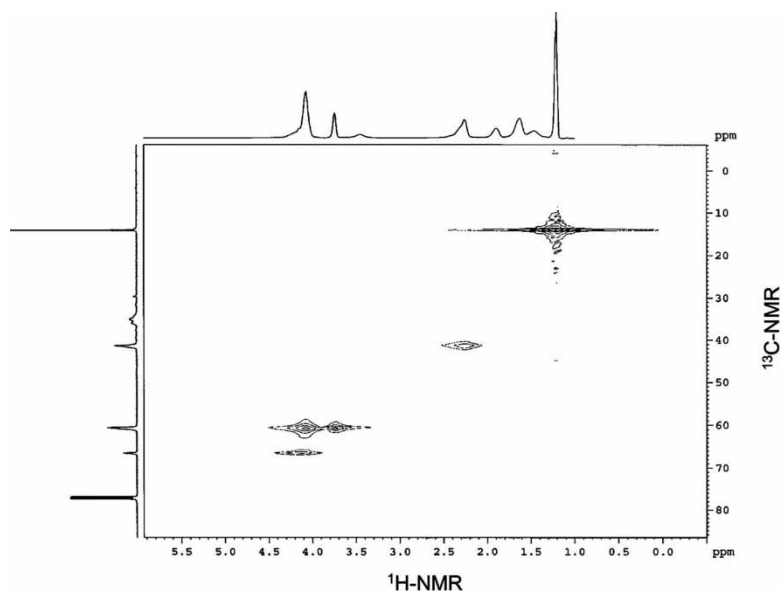


Figure 3. Typical solution 2D- ^1H - ^{13}C -HMQC spectra for HEA/EA copolymer in CDCl_3 .

shown in Figure 4. Applying gel phase (MAS) spectroscopy was successful in obtaining a solution-like ^1H -NMR spectrum for all gel samples. However, obtaining a good phasing and integration for the spectrum was difficult unless we run the sample under the same spinning rate. There was no need to conduct further investigation for peaks specifications especially since the chemical shift for the functional groups of interest appears in the same

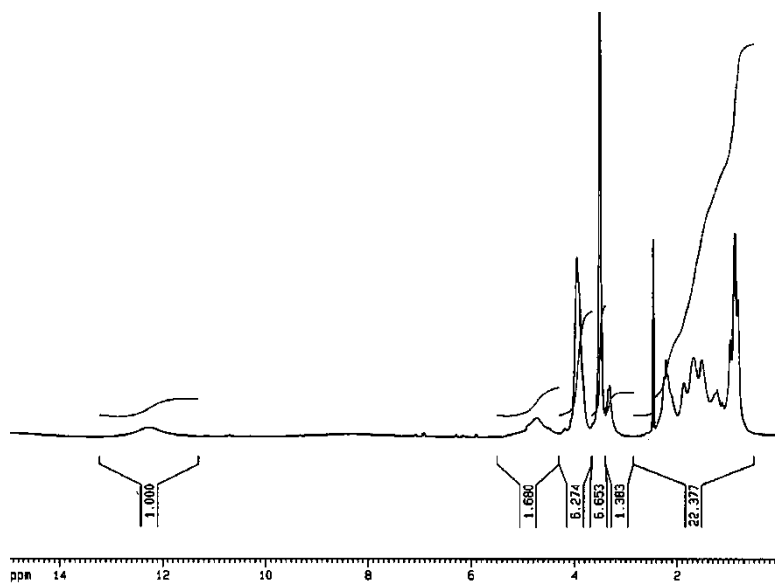


Figure 4. Typical gel ^1H -NMR spectrum for the hydroxyethyl acrylate/methacrylic acid copolymer in DMSO-d_6 .

regions as the solution part. The only difference was that the methine, ($-\text{CH}_2$)OH, peak in HEA units slightly overlapped with water from DMSO- d_6 which is usual due to broadening in gel phase NMR and very close chemical shift between water and methine units which cause overlapping.

It is essential to consider what causes the crosslinked chains especially if the cross-linking reaction is significant and highly likely to occur. In our case, the most dominant reason is the esterification reaction between carbonyl group in MAA units and hydroxyl group in HEA units, which is highly probable at elevated temperatures. The assumption has been made so that the expected microstructures of the polymeric chains are a combination between schematic (a) and (b) as shown in Figure 5. In reaction -a-, monomers may react with each other and appear in the polymer chain without any further reactions that change the structure of the monomeric unit. In reaction -b-, the ester formation reaction between the two monomers is highly expected especially at elevated temperature. When reaction -b- occurs, then high ($-\text{OCH}_2$) peak intensity is expected to form than if reaction -b- did not exist. Because of the high possibility that reaction -b- is taking place, the calculation of copolymer compositions was conducted by splitting the integrated area under the ($-\text{OCH}_2$) peak into two parts, one part consists of ($-\text{OCH}_2$) which forms due to esterification reaction, and the other part consists of ($-\text{OCH}_2$) presents in HEA units from the monomer basic structure. The former was calculated as follow, for ester linkage to form, there is a loss of one proton in ($-\text{COOH}$) unit and one proton from ($-\text{OH}$) unit and a formation of one ($-\text{OCH}_2$) group. The amount of proton of ($-\text{OCH}_2$) presents in HEA monomer structure is double the amount of proton of ($-\text{OH}$) shown in the spectrum. The difference between the total amount of ($-\text{OCH}_2$) presents in the sample and the amount present in HEA is considered the amount of ($-\text{OCH}_2$) group formed due to esterification reaction. Then, the amount of proton of ($-\text{OH}$) and ($-\text{COOH}$) lost due to ester linkages were half the amount of ($-\text{OCH}_2$) formed due to esterification reaction. The amount of protons considered in our calculations are the sum of the protons of ($-\text{OH}$) from the two sources. A similar procedure was applied for ($-\text{COOH}$). The relative amount of monomers incorporated into the copolymer was estimated from the corrected integrated areas of $-\text{COOH}$ of MAA and $-\text{OCH}_2$ of HEA.

For EA/HEA copolymer samples with high HEA content, the products were found to be partially dissolved in DMF. A regular solution $^1\text{H-NMR}$ for these samples results in extreme line broadening and very low resolution as shown in Figure 6(a). The products were further characterized for copolymer composition by utilizing $^1\text{H-MAS-NMR}$ spectroscopy (see Figure 6(b)). One can notice that we have been successful in applying gel-phase (MAS) spectroscopy and in obtaining a typical solution-like $^1\text{H-NMR}$ spectrum for all gel samples. In order to assign chemical shifts for the functional groups in the copolymer, further investigations for peak specifications were conducted by studying the chemical shift of each monomer in DMF- d_7 . $^1\text{H-NMR}$ Spectrum for

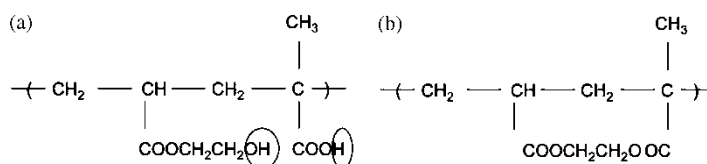


Figure 5. Schematic description of the resulting chemical structure in the copolymer due to esterification reaction.

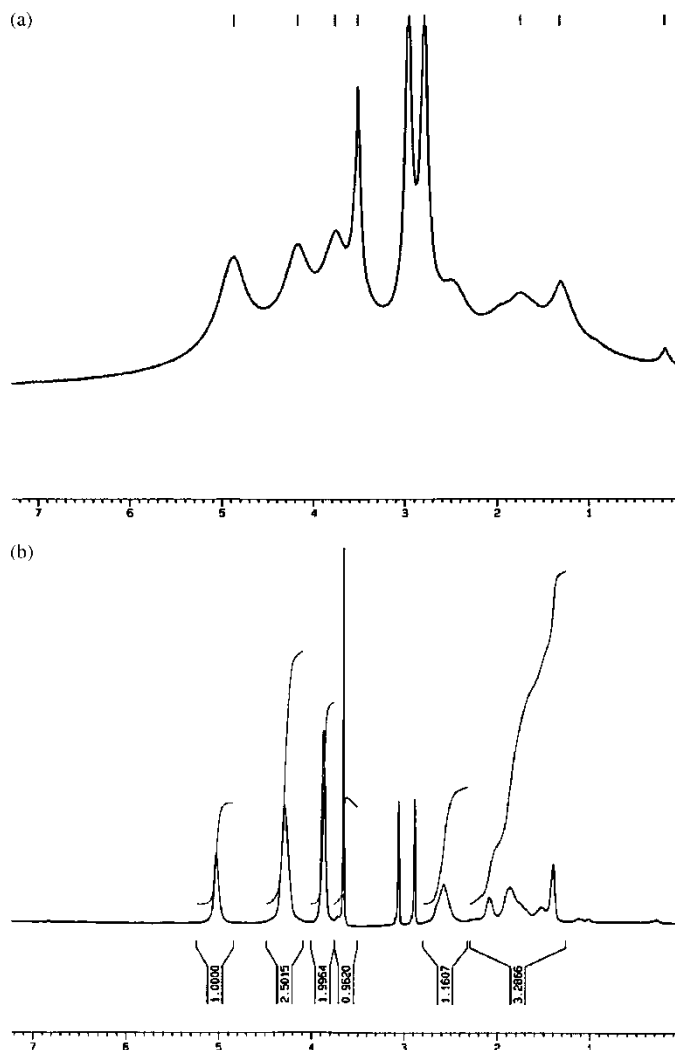


Figure 6. a) Typical solution $^1\text{H-NMR}$ spectrum for HEA/EA in DMF-d_6 , b) Typical $^1\text{H-MAS-NMR}$ spectroscopy for the same sample in DMF-d_6 .

EA monomer in DMF-d_7 , and $2\text{D-}^1\text{H-}^{13}\text{C-HMQC}$ spectra for HEA monomer in the same solvent are shown in Figures 7 and 8, respectively. According to the results in Figures 7 and 8, peaks shown in Figure 6(b) were classified as follows: the peak located at 5.0 ppm was assigned to the proton in $-\text{OH}$ of HEA. The peak located at 4.3 ppm was assigned to the protons in $-\text{OCH}_2$ of HEA. Finally, the peak located at 3.9 ppm was assigned to the methine protons in $-(\text{CH}_2)\text{OH}$ of HEA.

For this particular system, the polymer produced was an extremely soft gel (partially soluble) in DMF. The most probable reason for crosslinkage formation is the self esterification of HEA monomer because of high temperature. For every two losses in $(-\text{OH})$ functional groups, there is a formation of two $(-\text{OCH}_2)$ and a loss of two $(-\text{CH}_2)$ functional groups. Analysis for the corrected amount of protons is not possible at this time because the amount of methine in $(-\text{CH}_2\text{OH})$ in HEA overlaps with the water peak

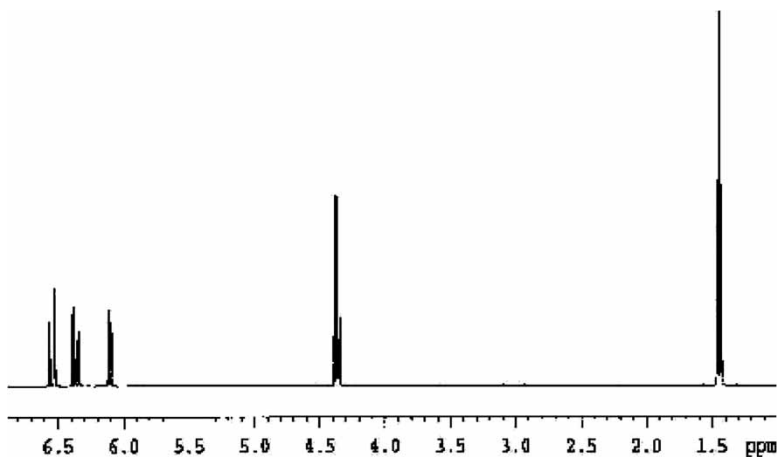


Figure 7. Typical solution $^1\text{H-NMR}$ for ethyl acrylate monomer in DMF-d_7 .

from the solvent. Knowing this amount is essential to separate the amount of $(-\text{OCH}_2)$ from HEA from that of EA in order to calculate the corrected peak intensities. It is also essential to know the peak intensity of $-\text{CH}_3$ of EA. However, because the polymer formed is partially soluble in the solvent, we assumed that the crosslinking reaction is not that significant and we proceeded with the standard calculation. The relative amount of monomeric units incorporated into the copolymer was estimated from the integrated area under the peak intensities of $-\text{OH}$ of HEA and $-\text{OCH}_2$ of HEA and EA.

The monomer feed composition mole fraction, f_1 , the copolymer composition mole fraction, F_1 , and the corresponding conversion at all temperatures are presented in Tables 1 to 3 for HEA/MAA and Tables 4 to 6 for EA/HEA. One can notice that the

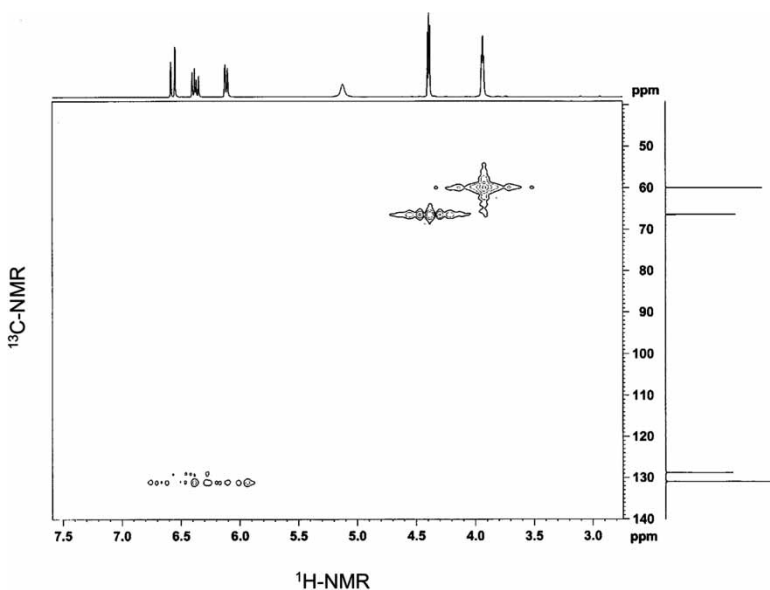


Figure 8. Typical $^2\text{D-}^1\text{H-}^{13}\text{C-HMQC}$ spectra for hydroxyethyl acrylate monomer in DMF-d_7 .

Table 1
HEA/MAA^a reactivity ratio estimation data: 70°C

f_1	F_1	Conversion %
0.64	0.54	~0.5
0.64	0.49	~0.1
0.64	0.50	~0.1
0.14	0.17	1.99
0.14	0.15	5.46
0.14	0.17	1.99
0.14	0.15	5.46

^a1 = HEA, 2 = MAA for Tables 1 to 3.

Table 2
HEA/MAA reactivity ratio estimation data: 100°C

f_1	F_1	Conversion %
0.68	0.58	<1
0.68	0.55	0.43
0.68	0.52	<1
0.68	0.57	0.64
0.14	0.19	0.73
0.14	0.18	0.84
0.14	0.18	1.13
0.14	0.18	0.94

experiments were successfully controlled and achieved the required low conversion levels. It was found that the copolymerization rates in solution for both reaction feed mixtures were extremely high despite the use of high solvent concentration, thus a very low initiator concentration was utilized. Results from RREVM reactivity ratio estimation for HEA/MAA (point values for r_1 and r_2) are presented in Table 7, along with those

Table 3
HEA/MAA reactivity ratio estimation data: 130°C

f_1	F_1	Conversion %
0.68	0.52	0.43
0.68	0.56	0.85
0.68	0.57	0.34
0.14	0.18	<1
0.14	0.18	0.78
0.14	0.19	0.97
0.14	0.20	0.96

Table 4
EA/HEA^a reactivity ratio estimation data: 70°C

f_1	F_1	Conversion %
0.3027	0.1679	1.8513
0.3027	0.1621	0.6377
0.3027	0.2005	0.2261
0.3095	0.1746	0.4057
0.7579 ^b	0.6143	0.5164
0.7579 ^b	0.6098	< 1
0.7579 ^b	0.6237	0.5712
0.7579 ^b	0.6190	0.6207

^a1 = EA, 2 = HEA for Tables 4 to 6.

^bExperiment conducted with p-xylene.

Table 5
EA/HEA reactivity ratio estimation data: 100°C

f_1	F_1	Conversion %
0.79	0.71	3.81
0.79	0.69	3.55
0.79	0.69	1.81
0.79	0.71	2.20
0.31	0.19	0.39
0.31	0.18	~0.7
0.31	0.17	0.62

obtained from Q-e values. Similarly, results from RREVM reactivity ratio estimation for EA/HEA are presented in Table 8. No data were available in the open literature for comparison for both systems. According to the values listed in Tables 7 and 8, both reactivity ratios are, apparently, changed with polymerization temperatures. To determine if the

Table 6
EA/HEA reactivity ratio estimation data: 130°C

f_1	F_1	Conversion %
0.79	0.70	3.50
0.79	0.71	21.48
0.80	0.73	7.17
0.80	0.73	11.55
0.31	0.25	2.44
0.31	0.23	2.53
0.31	0.23	4.41

Table 7
HEA/MAA reactivity ratio values

r_1 (HEA)	r_2 (MAA)	Condition	Reference
1.225	0.2940	Calculated using Q-e values	Brandrup and Immergut (12)
0.2661	0.7381	70°C, 60 wt% m-xylene	This work
0.2888	0.5971	100°C, 60 wt% m-xylene	This work
0.2592	0.5680	130°C, 60 wt% m-xylene	This work

observed differences in reactivity ratios are significant, 95% joint confidence contours are graphically presented in Figures 9 and 12 for both systems, respectively.

HEA/MAA. Figure 9 clearly shows that the reactivity ratio joint confidence contours for 100 and 130°C do overlap. This means that operating at elevated temperature has no significant effect on HEA/MAA reactivity ratios. However, the reactivity ratio of MAA with increasing temperature from 70 to 130°C is, apparently, more sensitive to temperature changes than that associated with HEA, which leads to more incorporation of MAA units in the copolymer chains with increasing temperature. These findings may have an impact on copolymer composition and sequence length characteristics. This observation can also be confirmed via Figure 10. Figure 10 shows the instantaneous copolymer composition of HEA as a function of HEA content in the initial monomer feed mixture. We can see that, at high HEA content, the copolymerization of this monomer pair in solution generates polymer chains enriched in MAA units compared to HEA units with increasing temperature. Also, one can notice that, at very low HEA content, the curves at 100 and 130°C almost coincide and hence temperature seems to have a negligible effect on copolymer composition.

The azeotropic point can be calculated by:

$$f_{1,az} = \frac{1 - r_1}{2 - r_1 - r_2} \quad (3)$$

and is $f_{1,az} = 0.263$ at 70°C, $f_{1,az} = 0.362$ at 100°C, and $f_{1,az} = 0.368$ at 130°C. Also, it is clear that, after the azeotropic point, more MAA units will be incorporated in the copolymer chains with decreasing temperature.

Table 8
EA/HEA reactivity ratio values

r_1 (EA)	r_2 (HEA)	Condition	Reference
0.5 ± 0.05	0.88 ± 0.09	60°C, AIBN, Bulk	Catala et al. (7)
0.5050	0.9580	50°C, AIBN, Bulk	McIsaac (8)
0.5387	2.0992	70°C, 60 wt% m-xylene	This work
0.7498	2.2361	100°C, 60 wt% m-xylene	This work
0.6517	1.4214	130°C, 60 wt% m-xylene	This work

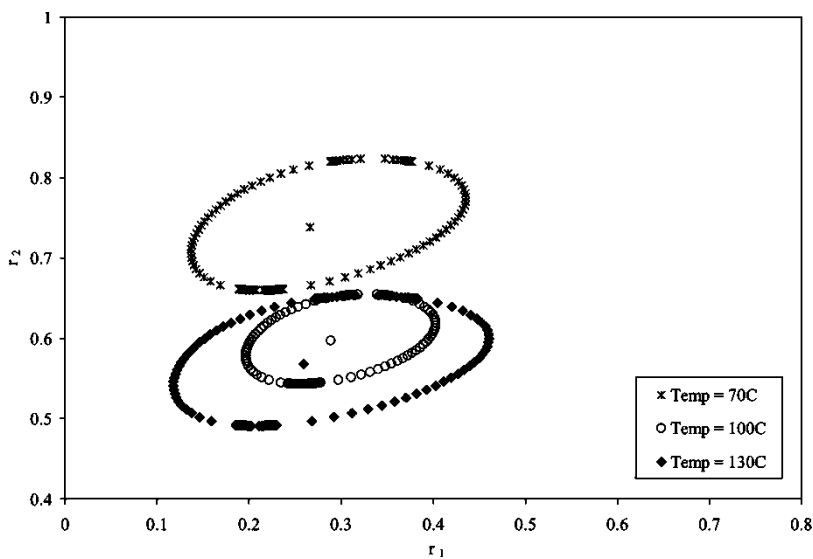


Figure 9. 95% joint confidence contours with point estimates for reactivity ratio determination of HEA/MAA at 70, 100 and 130°C in solution (1 = HEA, 2 = MAA).

Figure 11 shows results on the temperature dependence of reactivity ratios (Arrhenius plots for r_1 and r_2 vs. inverse temperature, presented as $\ln r$ vs. $(1/T)$). The following expressions can be derived for the HEA/MAA copolymer system in m-xylene:

$$\ln r_1 = -1.4365 + 48.7/T \quad (4)$$

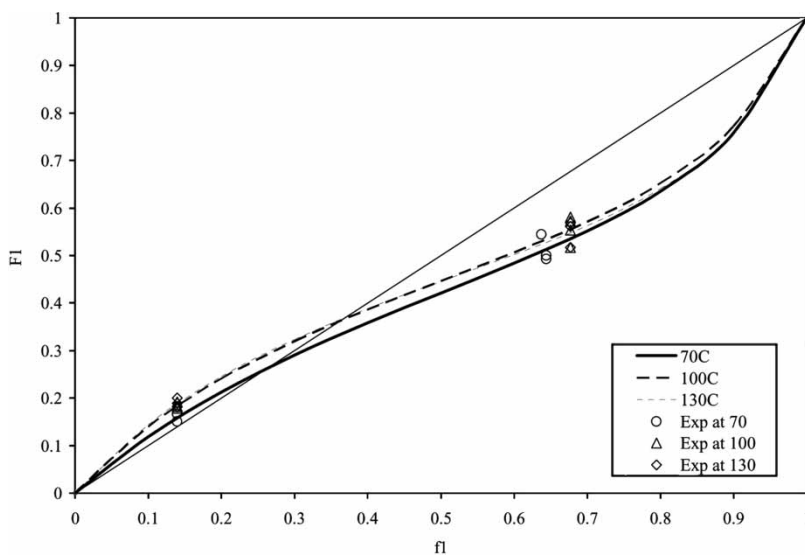


Figure 10. HEA/MAA copolymer composition using Mayo-Lewis model (1 = HEA).

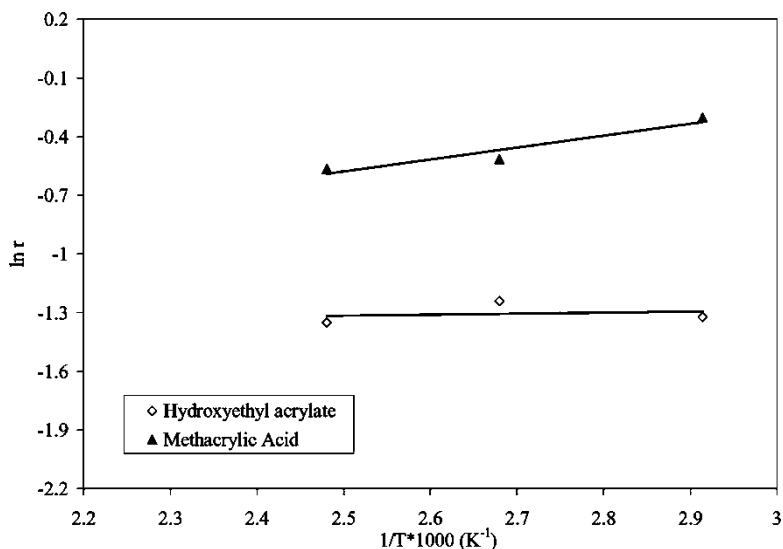


Figure 11. Temperature dependence of reactivity ratios for HEA/MAA.

and

$$\ln r_2 = -2.1107 + 612.7/T \quad (5)$$

where T is in degrees Kelvin.

EA/HEA. Figure 12 suggests that the reactivity ratios for 130°C belong to different populations than the populations of reactivity ratios obtained at 70°C and 100°C. The

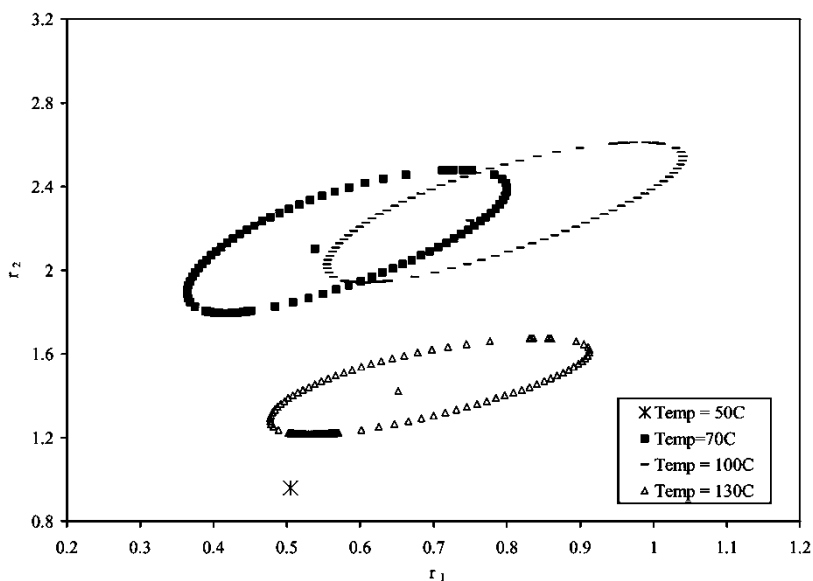


Figure 12. 95% joint confidence contours with point estimates for reactivity ratio determination of EA/HEA at 70, 100 and 130°C in solution (1 = EA, 2 = HEA).

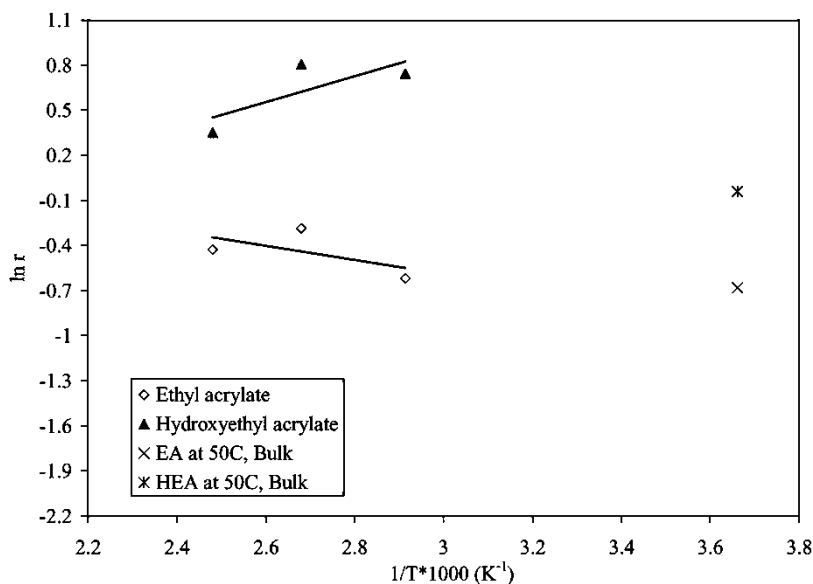


Figure 13. Temperature dependence of reactivity ratios for EA/HEA.

positioning of the contour at 130°C seems rather puzzling and it could be due to experimental difficulties with the system at the specific temperature (very fast rates and gel formation).

Finally, results on the temperature dependence of reactivity ratios (Arrhenius plots for r_1 and r_2 vs. inverse temperature, presented as $\ln r$ vs. $(1/T)$) are shown in Figure 13. The points for HEA are suspect due to the aforementioned experimental uncertainties. The following expressions can be derived for EA/HEA copolymer system in *m*-xylene:

$$\ln r_1 = 0.8124 - 467.1/T \quad (6)$$

and

$$\ln r_2 = -1.6962 + 865.3/T \quad (7)$$

where T is in degrees Kelvin.

No similar work has been found in the open literature for these particular systems, to the best of our knowledge.

Conclusions

The reactivity ratios of HEA/MAA and EA/HEA copolymers have been estimated by applying high resolution magic angle spinning (HR MAS-NMR) spectroscopy to analyze the resultant copolymer gels of hydroxyethyl acrylate/methacrylic acid and ethyl acrylate/hydroxyethyl acrylate. The copolymers were synthesized using free radical copolymerizations in *m*-xylene at 70, 100 and 130°C. Gel phase NMR seems a promising technique for the analysis of such difficult copolymer systems.

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