Study of Free-Radical Copolymerization of Acrylamide with 2-Acrylamido-2-methyl-1-propane Sulphonic Acid

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ABSTRACT: The free-radical initiated synthesis of acrylamide-*co*-2-acrylamido-2-methyl-1-propane sulphonic acid (AAm-*co*-AMPS) was studied at 60 and 25°C. The monomer reactivity ratios were evaluated using Fineman-Ross and Kelen-Tüdos methods, based on elemental analysis of the copolymers and ^{13}C-NMR experimental data. The detailed copolymer microstructure was derived from reactivity ratios using the conditional probability based on the terminal kinetic model for free-radical polymerization. The homopolymers and copolymers were characterized using ^{1}H- and ^{13}C-NMR, and Fourier transform infrared (FTIR) spectroscopic methods, and differential scanning calorimetry. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 75: 619–628, 2000

Key words: free-radical copolymerization; monomer reactivity ratio; copolymer microstructure

INTRODUCTION

The detailed microstructure and compositional heterogeneity of copolymers is of great importance in considering copolymer properties. Such knowledge is particularly important in designing sophisticated polymer materials for special purposes.

Polymers based on acrylamide are the most widely commercially used water-soluble products.[1] Their uses range from paper manufacture[2] and water treatment,[3] through oil recovery,[4] to soil modification[5] and medical applications.[6]

McCormick and his group have conducted extensive research on copolymerization of different water-soluble polymers, polyelectrolytes,[7] and ampholytic copolymers,[8] and their solution properties. They reported the synthesis and structural study of random copolymers of acrylamide (AAm) with some sulphonated comonomers,[7,9] one of them being sodium-2-acrylamido-2-methyl-1-propane sulphonate. However, they have not studied the copolymerization of AAm with the acid form of the above-mentioned monomer. Because our primary interest is environmentally sensitive polymer gels based on acrylamide and 2-acrylamido-2-methyl-1-propane sulphonic acid (AMPS),[10] we have made a detailed study of copolymerization of those two comonomers from the point of view of the monomer reactivity ratios and copolymer composition, and the macromolecular microstructure and structural heterogeneity. Of course, we are aware of the fact that the kinetics of the formation of the corresponding gel can be significantly different from the kinetic parameters for analogous linear copolymers, due to the presence of the third comonomer in the process of gel formation (crosslink agent), as well as the high conversion commonly found in gel system. However, the detailed microstructure of linear homologues of the copolymer gels can help to explain, to a certain extent, the gel behavior.

EXPERIMENTAL

Copolymer Synthesis

The free-radical copolymerization of acrylamide (Serva Feinbiochemica) and 2-acrylamido-2-

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methyl-1-propane sulphonic acid (Merck) was carried out in aqueous solution at 25 and 60°C. In the case of copolymerization at 60°C ammonium persulphate ($1\cdot10^{-3}$ mol dm^{-3}) was used as the initiator. The copolymerization at 25°C was initiated employing the ammonium persulphate–sodium bisulphite redox couple, the concentrations of both in monomer solution being $1 \cdot 10^{-3}$ mol dm^{-3}. The total monomer concentration was kept constant in all polymerizations at 0.850 mol dm^{-3}. The water used was Milli-Q purified, thoroughly purged with oxygen-free nitrogen prior to experiments. The monomer solutions were purged with nitrogen for another 10–15 min before the reaction was initiated. Copolymerization was conducted in a three-necked round-bottom flask, equipped with condenser and electro-driven PTFE stirrer. The reaction mixture was continuously flushed with nitrogen during the reaction. The copolymerization reaction was stopped after a short time, typically 2–3 min, i.e. at low conversion, by precipitating the copolymer in a large amount of acetone. The prepared copolymers were dissolved in distilled water, precipitated again in acetone and dried in vacuum at room temperature.

Compositional Analysis

The copolymer compositions were determined by elemental analysis of sulphur and nitrogen for the samples prepared by polymerization at 60°C, and by ^{13}C-NMR spectroscopy on selected samples polymerized at 60°C and 25°C.

Nuclear Magnetic Resonance Spectroscopy

^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker Avance DRX 400 MHz spectrometer at 298 K, using approximately 2–3 % (w/v) copolymer solutions in D_2O. The ^{13}C-NMR spectra were obtained by an overnight accumulation of at least 8000 scans, with a delay of 10 s. The nuclear Overhauser effect (NOE) was eliminated by gated decoupling.[11] The error in determination of the peak area in ^{13}C-NMR spectra was estimated to be 5%.

Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectra of the copolymers were recorded using a Bio-Rad infrared spectrophotometer, model FTS-60. The spectra were obtained on the solid samples using the photoacoustic (PAS) technique.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) scans of the copolymers were recorded using a Polymer Laboratories DSC, model 12000. The method employed for recording the scans was as follows: ramp from 25–200°C at 20°C/min; isotherm at 200°C for 1 min; ramp from 200–10°C at 30°C/min; isotherm at $10^{°C}$ for 2 min; ramp from 10–240°C at 10°C/min.

RESULTS AND DISCUSSION

The copolymerization reactions of AAm and AMPS were performed at 60°C, because most of the copolymer gel syntheses we have conducted have been done at either 60°C or 70°C.[10] Other synthesis parameters, such as initiator concentration and total monomer concentration, are also the same as in the corresponding gel preparations, and are described in the experimental section. A second series of copolymerizations was performed at 25°C, for selected monomer feed compositions, as we wished to compare compositions of the copolymers prepared at different temperatures, and determine if there is any temperature effect on copolymerization of AAm-AMPS.

Copolymer Composition

The copolymer composition data for the AAm-AMPS system copolymerized at 25 and 60°C are given in Table I. In all cases the conversion was kept low. In the case of copolymerization at 25°C the conversion was below 3.5%; at 60°C the copolymerization rate was higher, and the conversion values were somewhat higher, up to 10%. In Table I the composition data obtained from both the elemental analysis for sulphur and nitrogen, and ^{13}C-NMR peak integration on selected samples are given. The fraction of AMPS in the copolymer, *f*(AMPS), was calculated from the following equation[9]:

$$f(\mathrm{AMPS}) = \frac{14.0 \cdot S\%}{32.1 \cdot N\%} \qquad (1)$$

where S% and N% are the weight percentage of S and N obtained from elemental analyses.

The ^{13}C-NMR compositional analysis was done using the well resolved carbonyl peak because it has different chemical shifts for AAm and AMPS carbonyl. The data obtained by the two methods

Table I The Composition Data of Acrylamide (AAm)-2-acrylamido-2-methyl-1-propane Sulphonic Acid (AMPS) Copolymers

Mole Fraction in Feed		Copolymerization at 60°C				Copolymerization at 25°C
		Elemental Analysis				
AAm	AMPS	*S* (%)	*N* (%)	AMPS in Copolymer (mol %)[a]	^{13}C-NMR AMPS in Copolymer (mol %)	^{13}C-NMR AMPS in Copolymer (mol %)
0.9	0.1	3.28	15.21	9.37 ± 0.03		9.0 ± 0.5
		3.25	15.18			
0.8	0.2	5.13	12.90	17.57 ± 0.22		
		5.19	12.72			
0.7	0.3	6.43	11.48	24.31 ± 0.11		
		6.42	11.57			
0.6	0.4	8.13	10.65	33.43 ± 0.13		34.7 ± 1.7
		8.18	10.63			
0.5	0.5	6.98	7.38	41.14 ± 0.05	43.0 ± 2.1	43.0 ± 2.1
		6.99	7.42			
0.3	0.7	9.94	7.50	58.19 ± 0.39	60.0 ± 3.0	
		9.94	7.40			
0.2	0.8	11.59	7.32	69.01 ± 0.0		69.8 ± 3.5
		11.59	7.32			
0.1	0.9	11.83	6.53	79.81 ± 0.79		
		11.68	6.32			

[a] Error based on either two or three experimental determinations.

seem to be in good agreement, i.e. within the limits of experimental error, although the ^{13}C-NMR data are somewhat higher. Compositional data for copolymers prepared at 25°C are in good agreement with those copolymerized at 60°C. It can be concluded that there is no obvious temperature effect on composition of the AAm-AMPS copolymers.

The ^{1}H- and ^{13}C-NMR spectra of the copolymers are discussed later.

Reactivity Ratio Study

As the first step in elucidation of copolymer microstructure the monomer reactivity ratios for AAm (r_1) and AMPS (r_2) were determined. Two commonly used methods were employed in calculations. The graph for copolymerization of AAm-AMPS system at 60°C, according to the Finemann-Ross method[12] is shown in Figure 1 and according to the Kelen-Tüdos method[13] in Figure 2. The values for the monomer reactivity ratios, based on elemental analysis data and ^{13}C-NMR data for the copolymers prepared at 25 and 60°C, are listed in Table II. The Finemann-Ross and Kelen-Tüdos methods give slightly different results in both cases. The reactivity ratios (in particular r_2) for copolymerization at 25°C have higher values than for reaction at 60°C. According to Table I the difference can be attributed to the different methods for evaluation of the compositional data, rather than a true temperature effect.

In the following elucidation of the copolymer microstructure the r values obtained by the

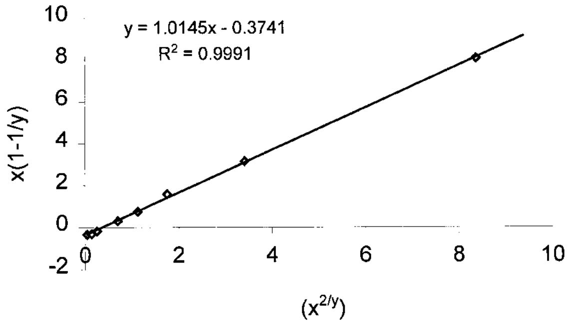

Figure 1 Fineman-Ross plot for AAm-*co*-AMPS system; polymerization at 60°C; x = [AAm]/[AMPS], y = d[AAm]/d[AMPS].

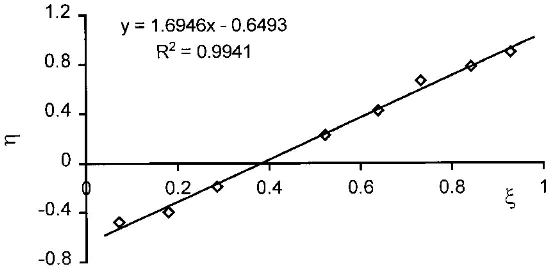

Figure 2 Kelen-Tüdos plot for AAm-*co*-AMPS system; polymerization at 60°C.

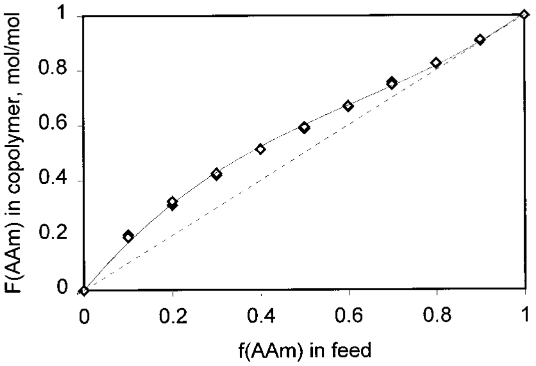

Figure 3 Copolymerization curve for AAm-*co*-AMPS system copolymerized at 60°C: experimental data (◆), calculated according to copolymer equation with experimental r_1, r_2 (solid line) and with $r_1 = r_2 = 1$ (dotted line).

Kelen-Tüdos method, as a more reliable method,[14] are used.

A comparison of the experimental data for the instantaneous copolymer composition with data calculated by means of copolymer composition equation[15] using $r_1 = 1.05$ and $r_2 = 0.42$, for copolymerization at 60°C, is shown in Figure 3. The straight line included in the graph represents copolymerization where $r_1 = r_2 = 1$, which refers to a truly random distribution of monomers and the copolymer composition the same as the feed composition. From Figure 3 one can conclude that the terminal kinetic model[15] can be successfully used to predict the composition of AAm-AMPS copolymers using the experimentally obtained r values. Also, the value of $r_1 \cdot r_2$ (0.44) suggests that AAm-AMPS copolymers have an alternating tendency.

Copolymer Microstructure

With the knowledge of free-radical copolymerization mechanism and experimentally obtained values of the kinetic parameters, r_1 and r_2, we can proceed to evaluate AAm-AMPS copolymer microstructure. According to Igarashi[16] and Pyun[17], several useful statistically evaluated structural parameters can be defined for the system, which characterize the copolymer microstructure.

Figure 4 shows the probability values for growing AAm-AMPS copolymer radical chain, i.e. probability that a growing radical chain with terminal AAm monomer unit will react with AAm, P(11), or with AMPS, P(12). The probabilities were calculated according to the following equations:

$$P(11) = r_1[\text{AAm}]/(r_1[\text{AAm}] + [\text{AMPS}]) = 1 - P(12) \quad (2)$$

and similarly for P(22) and P(21):

$$P(22) = r_2[\text{AMPS}]/(r_2[\text{AMPS}] + [\text{AAm}]) = 1 - P(21) \quad (3)$$

where [AAm] and [AMPS] are concentration of AAm and AMPS monomers in the feed solutions, respectively.

From Figure 4 one can see that to have the same probability of adding the AMPS and AAm monomer units to the growing radical chain with terminal AMPS unit, i.e. P(22) = P(21), the molar fraction of AAm in feed should be approximately 0.3, which requires the feed composition to be shifted to a high fraction of AMPS.

Table II Monomer Reactivity Ratios for Copolymerization of AAm (1)–AMPS (2) at 25°C and 60°C

	T = 60°C Elemental Analysis		T = 25°C ^{13}C-NMR	
Method	r_1	r_2	r_1	r_2
Fineman-Ross	1.01 ± 0.01	0.37 ± 0.04	1.07 ± 0.01	0.54 ± 0.03
Kelen-Tüdos	1.05 ± 0.06	0.42 ± 0.03	1.05 ± 0.06	0.51 ± 0.03

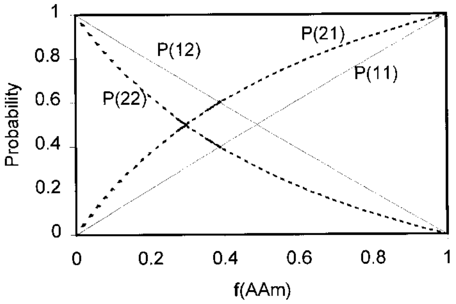

Figure 4 Probabilities for growing radical chain in AAm-AMPS copolymerization.

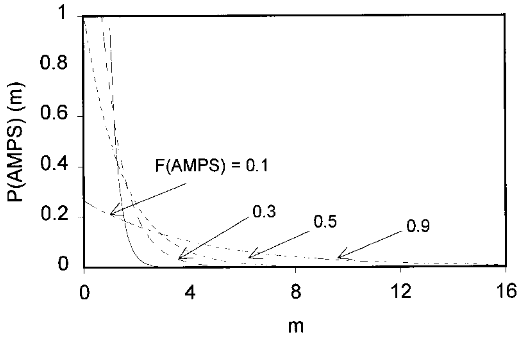

Figure 6 Probability of forming a sequence of m units of AMPS for chosen fractions of AMPS in feed.

From such statistical considerations it is further possible to evaluate the probability of forming a sequence of exactly m monomer units of AAm and AMPS in copolymer chain, $P_{\mathrm{AAm}}(m)$ and $P_{\mathrm{AMPS}}(m)$:

$$P_{\mathrm{AAm}}(m) = P(11)^{m-1}P(12) \quad (4)$$

$$P_{\mathrm{AMPS}}(m) = P(22)^{m-1}P(21) \quad (5)$$

Figure 5 and 6 present probability functions calculated according to eqs. 4 and 5, for several feed compositions. Figure 5 shows that for higher fraction of AAm in the feed the distribution function becomes more uniform. On increasing the fraction of AMPS monomer in the feed, the probability function of forming a sequence of m AAm units becomes narrower with regard to m. For low AAm content in the feed (< 30 mol %), the probability of forming a sequence of $m > 5$ AAm units is negligible.

The probability of forming a sequence of m AMPS monomer units gives slightly narrower distribution functions than for AAm. For a feed composition with 10 mol % of AMPS the probability of forming a sequence of m (AMPS) > 3 is negligible.

Similar conclusions can be drawn from consideration of the average sequence length, m, of AAm and AMPS units in the copolymer, shown in Figure 7. The m values were calculated according to[8]

$$\bar{m}(\mathrm{AAm}) = 1 + (r_1[\mathrm{AAm}]/[\mathrm{AMPS}]) \quad (6)$$

$$\bar{m}(\mathrm{AMPS}) = 1 + (r_2[\mathrm{AMPS}]/[\mathrm{AAm}]) \quad (7)$$

In Table III are listed m values for selected feed compositions. In general, the higher the proportion of the monomer in the feed, the larger its average sequence length. From Figure 7 and Table III one can see that AAm monomer forms sequences of a longer length, m. The same average length of AAm and AMPS monomer sequences is attained when the fraction of AAm in feed is 38.7 mol %, and $m(\mathrm{AAm}) = m(\mathrm{AMPS}) \cong 1.66$.

Two additional structural parameters for the AAm-AMPS copolymer system are presented in

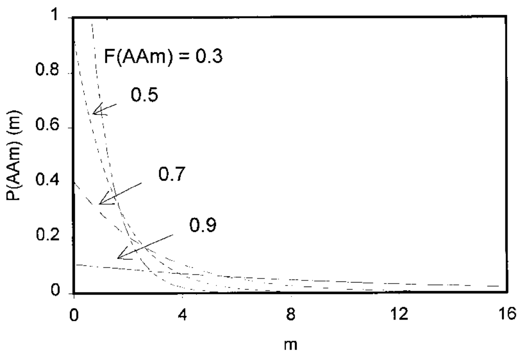

Figure 5 Probability of forming a sequence of m units of AAm for chosen fractions of AAm in feed.

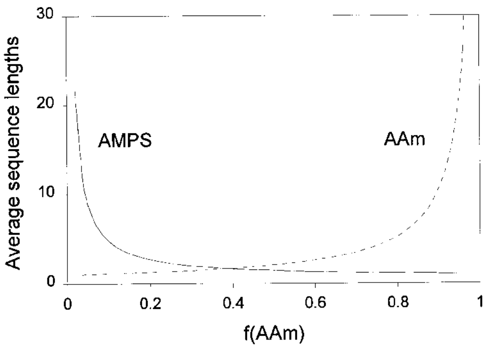

Figure 7 Dependence of average sequence length of AAm and AMPS units on fraction of AAm in feed.

Table III Average Sequence Length $\bar{m}$, of AAm and AMPS Units in the AAm-AMPS Copolymer

f(AAm)	$\bar{m}$(Aam)	$\bar{m}$(AMPS)
0.9	10.45	1.05
0.8	5.20	1.11
0.7	3.45	1.18
0.6	2.58	1.28
0.5	2.05	1.42
0.4	1.70	1.63
0.3	1.45	1.98
0.2	1.26	2.68
0.1	1.12	4.78

Figures 8(a,b). The run number, R, is defined as the fraction of AAm and AMPS sequences (runs) occurring in the polymer chain. The parameter χ is a measure of the departure from randomness. Both parameters have similar dependence on monomer feed ratio, [AAm]/[AMPS]. The AAm-AMPS copolymer system shows a slight alternating tendency ($2 > \chi > 1$) in a broad range of monomer feed ratios, and approaches the completely random microstructure at very high fraction of either AAm or AMPS. The run number and χ have a maximum at the same monomer feed ratio value, [AAm]/[AMPS] $\cong$ 0.63. At this feed composition the copolymer has the same average monomer sequence length for AAm and AMPS, and has the greatest alternating tendency.

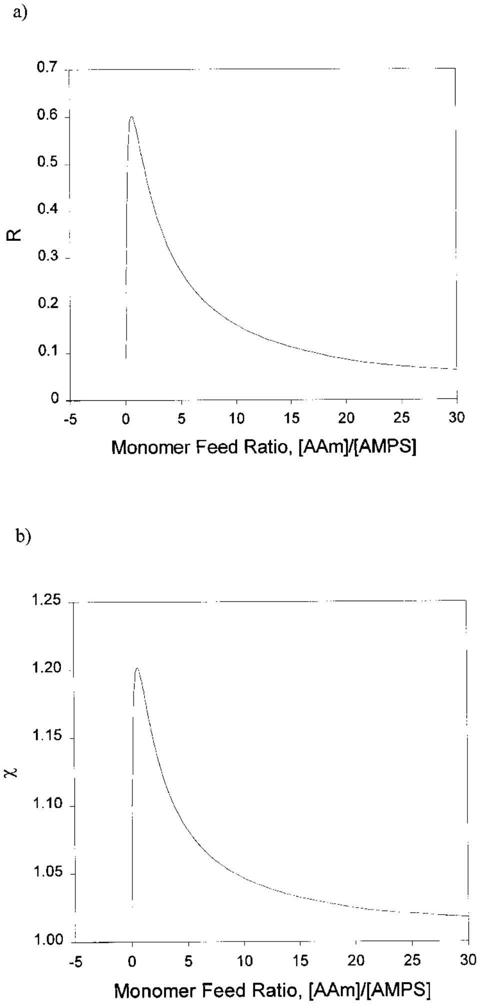

Figure 8 (a) Run number for AAm-AMPS copolymer; (b) χ-parameter of AAm-AMPS copolymer.

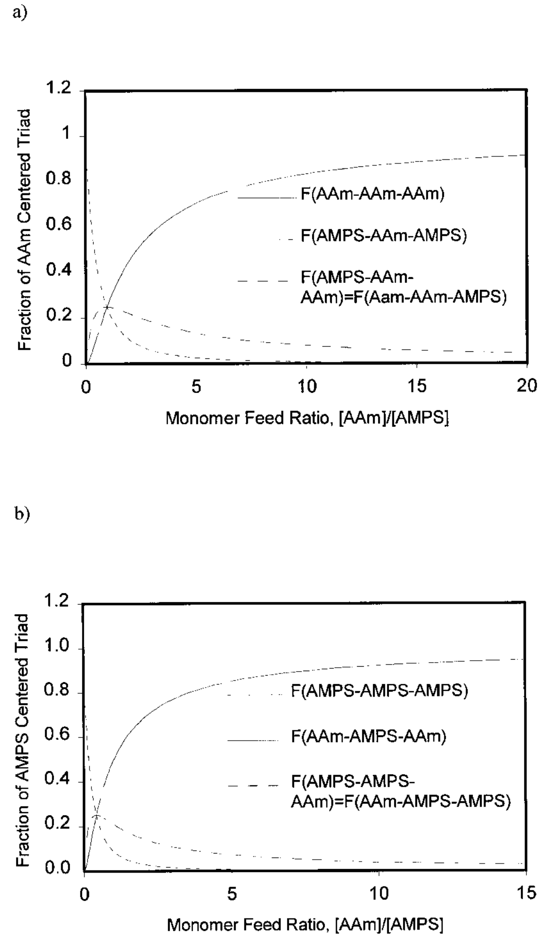

Figure 9 Fraction of AAm (a) and AMPS (b) centered triads in AAm-AMPS copolymer as a function of monomer feed ratio.

Higher order sequence distribution functions, in terms of conditional probability of AAm and AMPS centered triads, are calculated on the basis of monomer reactivity ratios,[19,20] and are shown in Figure 9(a,b). As expected, increasing the ratio [AAm]/[AMPS] increases the fraction of AAm

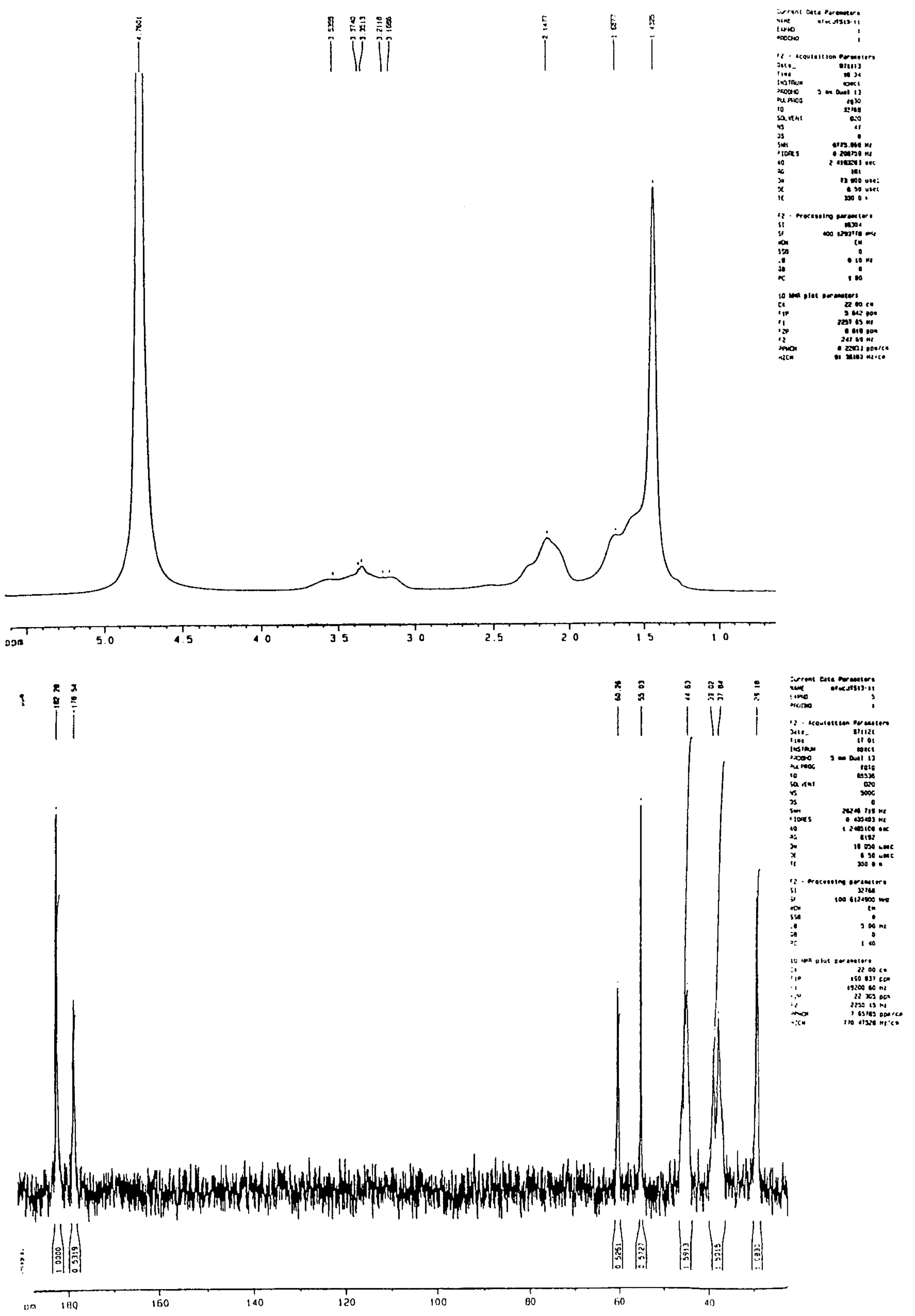

Figure 10 ^{1}H-NMR and ^{13}C-NMR spectra of AAm-AMPS copolymer with 40 mol % of AMPS in feed.

Table IV Chemical Shifts and Peak Assignments for AAm-AMPS Copolymers

Chemical Shift, ppm	Assignment
^{1}H-NMR	
1.42–1.7	—CH$_2$—(AAm + AMPS)—CH$_3$ (AMPS) overlapping
2.0–2.3	—CH— (AAm + AMPS)
3.1–3.6	—CH$_2$—SO$_3^-$ (AMPS)
^{13}C-NMR	
29.2	—CH$_3$ (AMPS)
32.98–38.7	—CH$_2$— (AAm + AMPS)
44.4–46.12	—CH— (AAm + AMPS)
55.1	$\overset{\vert}{\underset{\vert}{-C-}}$ (AMPS)
60.1–60.6	—CH$_2$— SO$_3^-$ (AMPS)
178.5–178.6	C=O (AMPS)
182.2	C=O (AAm)

dominant triads. The fraction of triads with two AAm or two AMPS monomer units exhibit a maximum at a particular [AAm]/[AMPS] value.

Copolymer Characterization

Nuclear Magnetic Resonance

Typical ^{1}H-NMR and ^{13}C-NMR spectra of AAm-AMPS copolymers are presented in Figure 10. The peak assignments are listed in Table IV. Comparison of the ^{1}H-NMR and ^{13}C-NMR spectra of the AAm and AMPS homopolymers with the spectra obtained for the corresponding copolymers show that there are no new peaks in the copolymer spectra. The reason is the similarity of AAm and AMPS monomer structures. Consequently average sequence lengths or the triad sequence distribution for the AAm-AMPS system cannot be directly measured by NMR spectroscopy. So, conclusions relating to the validity of the terminal model to describe the AAm-AMPS system can be judged only on the basis of the compositional data shown in Figure 3.

Fourier Transform Infrared Spectroscopy

FTIR spectra for AAm and AMPS homopolymers, together with a typical copolymer spectrum, are presented in Figure 11. The spectra show typical absorption bands as follows[21, 22] : N-H broad peak at approximately 3200–3300 cm^{-1}, N-H stretching at 2940–2980 cm^{-1}, amide I at 1657–1670 cm^{-1}, amide II at 1530–1560 m^{-1}, asymmetric CH$_3$ bending at 1460 cm^{-1}, and S=O stretching at ~1050 cm^{-1}. It has been shown[9] that IR spectroscopy can be useful in quantitative determination of copolymer composition, but that was not attempted here.

Differential Scanning Calorimetry

Thermal analysis of AAm-AMPS copolymers by DSC was performed to obtain glass transition temperature, T_g, as an important parameter characterizing the mechanical and thermal behavior of the copolymers. T_g values obtained from DSC scans for homopolymers of AAm and AMPS, and for their copolymers are given in Table V. P(AAm), P(AMPS) and the copolymers are amorphous polymers, with T_g in the range from approximately150°C for polyacrylamide homopolymer to 175°C for poly(2-acrylamido-2-methyl-1-propane sulphonic acid) homopolymer. It should be noted that P(AAm) and P(AMPS) and their copolymers, show a quite broad glass transition region, and it is hard to obtain repeatable and accurate T_gs. The reason probably lies in the fact that copolymerization reactions were stopped at low and different conversions, which gave a broad range of molar masses and molar mass distributions. In addition, high hydrophilicity of the homopolymers and copolymers possibly influenced the DSC data. Low reproducibility could be caused by the possibility of taking the sample portions from different stages of precipitation for DSC measurements. However, the general trend in the T_g dependence on copolymer composition is clearly seen.

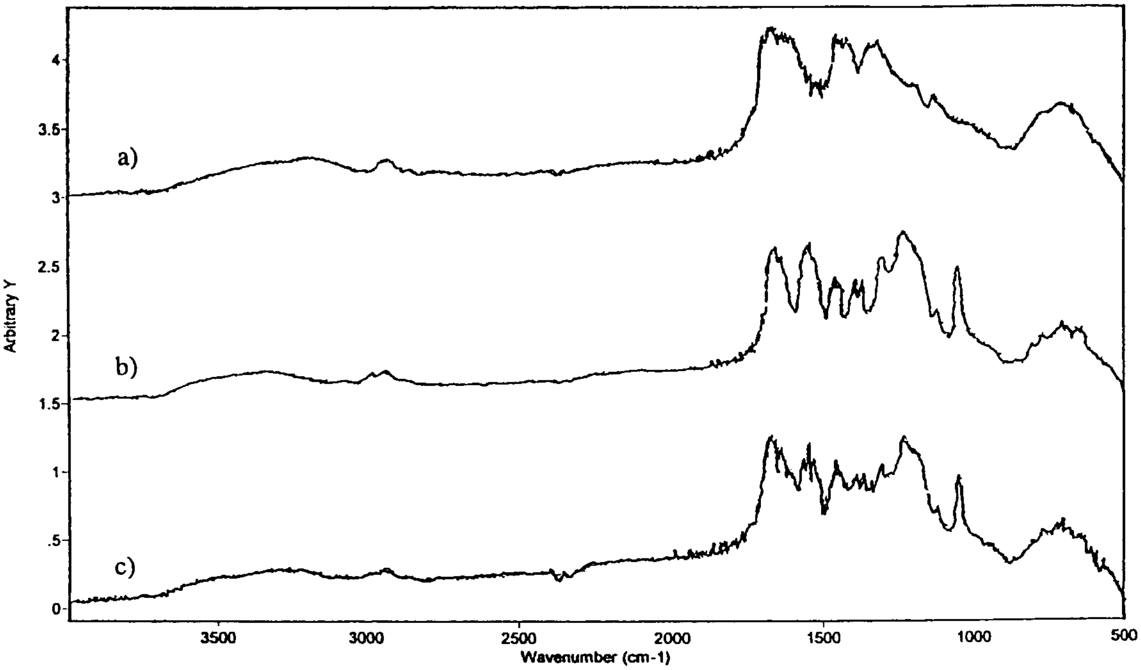

Figure 11 FTIR spectra for AAm (a) and AMPS (b) homopolymers, and AAm-AMPS copolymer with 60 mol % of AMPS in feed (c).

CONCLUSIONS

The AAm-AMPS copolymer system was studied in sense of AAm and AMPS reactivity ratios, copolymer microstructure, and copolymer characterization. The reactivity ratios for AAm and AMPS were determined by Fineman-Ross and Kelen-Tüdos methods, and the values obtained agree within the experimental error.

Using the conditional probability based on the terminal model for free-radical polymerization it was revealed that more AAm than AMPS is incorporated in the copolymer, and consequently, AAm monomer forms sequences of longer length. The AAm-AMPS copolymers show alternating tendency, with the greatest alternacy at monomer feed ratio of [AAm]/[AMPS] = 0.63. The completely random microstructure can be approached by using a very high fraction of either AAm or AMPS in feed.

^{1}H- and ^{13}C-NMR, and FTIR spectroscopic methods were used to characterize the AAm-AMPS copolymers. DSC shows that AAm-AMPS copolymers are amorphous with glass transition temperature, T_g, in the range from 150–175°C.

Table V Glass Transition Temperatures[a] for AAm-AMPS Homopolymers and Copolymers Obtained From DSC Measurements

AMPS in Feed (mol fraction)	T_g (°C)
1.0	175.6 ± 2.0
0.9	171.6 ± 2.2
0.5	163.4 ± 4.1
0.4	162.2 ± 9.1
0.1	157.3 ± 1.9
0.0	154.3 ± 4.7

[a] T_g was evaluated as the midpoint temperature of the glass transition region.

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