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# Study of Free-Radical Copolymerization of *N*-Isopropylacrylamide with 2-Acrylamido-2-methyl-1-propanesulphonic Acid

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**ABSTRACT:** The free-radical copolymerization of *N*-isopropylacrylamide and 2-acrylamido-2-methyl-1-propanesulphonic acid at varying comonomer mole ratios was studied at 70°C. The extent of conversion was determined as a function of time and comonomer mixture composition, and copolymer compositions were determined using elemental analysis and <sup>13</sup>C NMR spectroscopy. Monomer reactivity

ratios were evaluated for low conversions using Kelen-Tüdös and Fineman-Ross methods. The copolymers were characterized using <sup>13</sup>C and <sup>1</sup>H NMR spectra, FTIR spectroscopy, and differential scanning calorimetry. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2563–2569, 2003

**Key words:** NMR; reactivity ratios; copolymerization

## INTRODUCTION

The microstructure and composition of copolymers are important factors in copolymer properties. For the design of new copolymer materials, prediction of microstructure and composition from copolymerization kinetics, via monomer reactivity ratios, is of primary importance.

The homopolymer of *N*-isopropyl acrylamide (NIPA) is water-soluble and thermoresponsive in a readily accessible temperature range, by virtue of a lower critical solution temperature (LCST) of the order 32°C,<sup>1,2</sup> which can be modified by copolymerization<sup>3,4</sup> and grafting<sup>5,6</sup> with other monomers. It has been reported that the LCST of polyNIPA can be increased or decreased by incorporating hydrophilic or hydrophobic units into the polymer chain.<sup>7</sup> Moreover, pH-sensitive units have been incorporated into polyNIPA chains<sup>8</sup> so that the resulting copolymer exhibits an LCST above the reaction temperature at the reaction pH, but will convert to an LCST below the reaction temperature by changing the pH. This copolymer can be used in enzyme separation, recovery and recycling.<sup>8</sup>

2-Acrylamido-2-methyl-1-propanesulphonic acid (AMPS) is a relatively strong acid<sup>9</sup> that has had a wide variety of applications (as the acid or its salts or as a comonomer) including packaging films,<sup>10</sup> foam stabilizers,<sup>11</sup> photographic materials,<sup>12–22</sup> and water absorbents.<sup>23,24</sup> Copolymers of AMPS with

ethylene dimethacrylate have been used to make contact lenses,<sup>25</sup> and poly(AMPS-graft-styrene) gives self-reinforced hydrogels.<sup>26</sup> There had been few studies of copolymerization of NIPA and AMPS,<sup>27,28</sup> until the recent report of Xue and co-workers<sup>29</sup> of monomer reactivity ratios for copolymers of NIPA and AMPS (and other comonomers).

The objective of the present investigation was to determine monomer reactivity ratios for the NIPA/AMPS comonomer system and to characterize NIPA/AMPS copolymers, as part of a broader study of poly(NIPA-co-AMPS) hydrogels. In a number of reports on determination of monomer reactivity ratios, little attention has been paid to the variation of overall copolymerization rate with comonomer mixture composition. In the present work, we have determined conversion as a function of reaction time for a range of copolymer compositions, and evaluated reactivity ratios at controlled, constant conversion.

## EXPERIMENTAL

Free-radical copolymerization of NIPA (supplied by Acros Organics in 99% purity) and AMPS (Merck, 99%) at constant total monomer concentration (2.0 mol L<sup>-1</sup>) in milli-Q water, was carried out in sealed glass bottles with polyethylene stoppers at 70°C, using 0.05 mol L<sup>-1</sup> ammonium persulphate as initiator. The water was purged with nitrogen for about 10 min, and the reaction mixtures were purged again for several minutes prior to heating.

Copolymerization was allowed to take place for times of the order of a few minutes, depending on the

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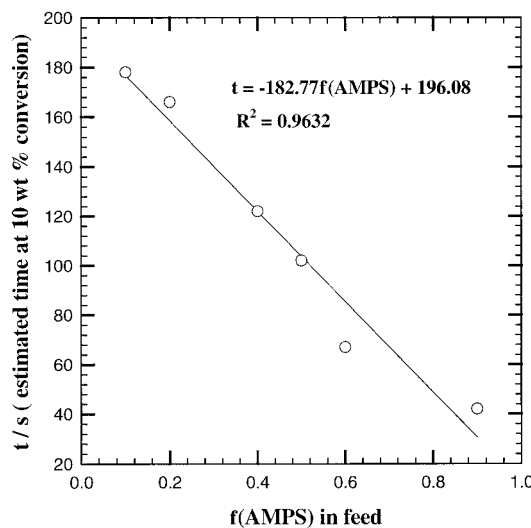
comonomer compositions. Polymerization was terminated by precipitating the reaction mixtures in a large volume of acetonitrile or (for copolymers with a high proportion of NIPA) acetonitrile/diethyl ether mixtures (1 : 1 by volume) at room temperature. The precipitated copolymers were purified by redissolving in small amount of milli-Q water, then reprecipitating. The purification procedure was carried out at least twice to ensure complete removal of unreacted monomers. Finally, the copolymers were dried in vacuum at 60°C for about 4 days.

Copolymer compositions were determined by elemental analysis for sulphur and nitrogen, and by  $^{13}\text{C}$  NMR<sup>30,31</sup> for selected samples. The advantage of using  $^{13}\text{C}$  rather than  $^1\text{H}$  NMR for the analysis is that the variation in carbon chemical shifts in neutral organic compounds is approximately 20-fold greater than that of protons: the total range of  $^{13}\text{C}$  shifts is more than 600 ppm and the positions of individual spectral bands can readily be measured with precision better than 0.1 ppm.

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded with a Bruker Avance DRX 400 MHz spectrometer at 300 K, using approximately 30 mg of dried copolymer dissolved in 0.5 mL  $\text{D}_2\text{O}$ . The  $^{13}\text{C}$  NMR spectra were run using inverse gated decoupling with a pulse angle of 55° for copolymers and 35° for homopolymers, and the spectra were obtained by accumulation of about 5000 scans, with a delay of 10 s (AMPS/NIPA copolymers) or 15 s (AMPS and NIPA homopolymers).

FTIR spectra of NIPA and AMPS homopolymers and NIPA/AMPS copolymers incorporated into KBr discs were obtained using a Bio-Rad model FTS-60 spectrophotometer.

DSC scans were recorded using a Polymer Laboratories model 12000 instrument. Glass transition temperatures ( $T_g$ ) were obtained as the average values from two to four repeated heating scans, with scan rate 10°C min<sup>-1</sup> in the temperature range -80 to 150°C to avoid decomposition of the copolymers.



**Figure 1** Reaction time for 10% conversion in copolymerization of AMPS and NIPA at 70°C as a function of comonomer mixture composition.

## RESULTS AND DISCUSSION

The variation of reaction time for 10% conversion with comonomer mixture composition is shown in Figure 1. The significant result is the reaction time increases more than fourfold as the mol fraction of NIPA in the comonomer mixture increases from 0.1 to 0.9.

Copolymers obtained from comonomer mixtures polymerized to  $3 \pm 1\%$  conversion were subjected to elemental analysis for sulphur and nitrogen, and copolymer compositions evaluated from eq. (1)

$$F_1 = x/(x + y) = 14.0.\text{S}\%/32.1.\text{N}\% \quad (1)$$

where  $F_1$  is the mol fraction of AMPS, and S% and N% are weight % of S and N, respectively, in the copolymer. The data set is given in Table I, which includes copolymer compositions determined for a few copolymers from NMR spectra, and literature data.<sup>28</sup>

**TABLE I**  
Comonomer Mixture and Copolymer Composition Data for Copolymerization of 2-Acrylamido-2-methyl-1-propanesulphonic Acid (AMPS) and *N*-Isopropylacrylamide (NIPA) at 70°C

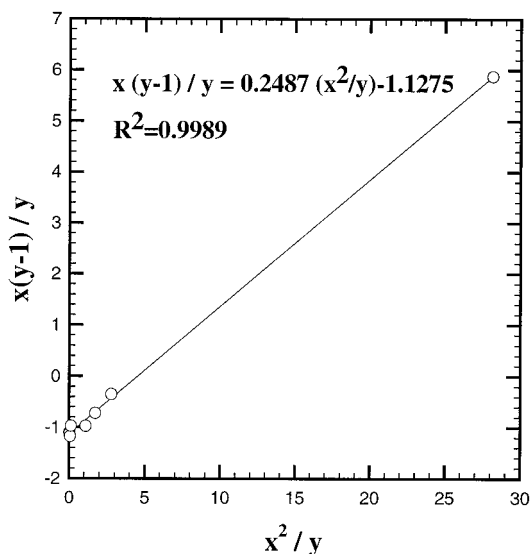
$f_1^a$	S%	N%	$F_1^b$	$F_1^c$
0.90	$13.32 \pm 0.08$	$7.82 \pm 0.01$	$74.21 \pm 0.08$	$87 \pm 14$
0.60	$9.48 \pm 0.28$	$9.55 \pm 0.39$	$44.70 \pm 1.4$	$57 \pm 5$
0.50	$7.77 \pm 0.10$	$9.24 \pm 0.11$	$36.69 \pm 1.1$	$43 \pm 4$
0.40	$6.38 \pm 0.04$	$9.64 \pm 0.07$	$28.86 \pm 0.01$	
0.10	$2.41 \pm 0.14$	$11.34 \pm 0.19$	$9.28 \pm 1.1$	
0.05	$1.13^d$		$4.1^d$	
0.03	$0.71^d$		$2.6^d$	
0.01	$0.26^d$		$0.9^d$	

<sup>a</sup> Mol fraction of AMPS in the comonomer mixture.

<sup>b</sup> Evaluated from elemental analysis data.

<sup>c</sup> Evaluated from NMR spectra.

<sup>d</sup> Raw data from ref.<sup>28</sup>



**Figure 2** Finemann-Ross plot for copolymerization of AMPS-NIPA.

The  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR spectral assignments for the homopolymers and one copolymer are given in Tables II–IV.  $^1\text{H}$  NMR spectra and spectral assignments for *N*-isopropylacrylamide monomer dissolved in the  $\text{CDCl}_3$  have been reported elsewhere.<sup>32</sup>

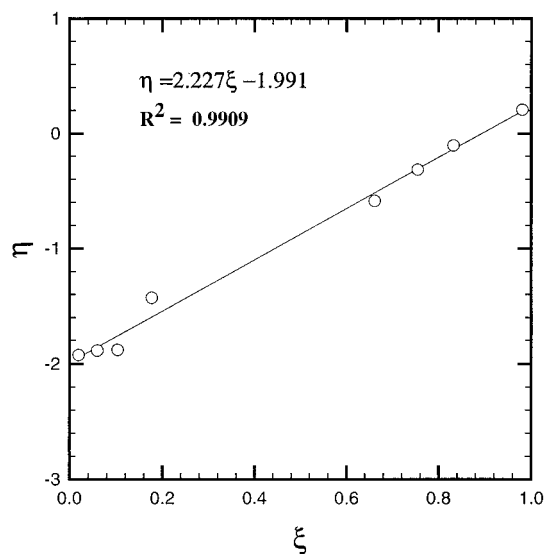
The copolymer compositions determined by elemental analysis were used to evaluate monomer reactivity ratios of AMPS (1) and NIPA (2), using the Kelen-Tüdös (K-T)<sup>33</sup> and Finemann-Ross (F-R)<sup>34</sup> methods. The K-T method is more widely used because of its simplicity and reliability.<sup>35</sup>

According to the terminal model for copolymerization, the copolymer composition at low conversion is given by

$$d[M_1]/d[M_2] = ([M_1]/[M_2])\{(r_1[M_1] + [M_2])/(r_2[M_2] + [M_1])\} \quad (2)$$

**TABLE II**  
Chemical Shifts and Assignments for the AMPS Homopolymer

$\delta/\text{ppm}$	Assignment
$^{13}\text{C}$ NMR	
(23.03)	( $-\text{CH}_3$ , residue solvent, acetonitrile)
29.08	$-\text{CH}_3$
37.9–39.8	$-\text{CH}_2$ ( $-\text{CH}_2-\text{CH}-$ ) broad
44.96–46.06	$-\text{CH}$ ( $-\text{CH}_2-\text{CH}-$ ) broad
55.22	$-\text{C}-$ ( $-\text{C}(\text{CH}_3)_2$ )
60.72	$-\text{CH}_2-\text{SO}_3^-$ (AMPS)
(121.77)	( $-\text{CN}$ , residue solvent, acetonitrile)
178.58–179.29	$-\text{C}=\text{O}$
$^1\text{H}$ NMR	
1.3047, 1.639, 1.657	$-\text{CH}_2(\text{CH}_2\text{CH})$
1.460	$-\text{CH}_3$
1.946–2.149	$-\text{CH}(-\text{CH}_2\text{CH}-)$ broad
3.18–3.34	$-\text{CH}_2$ (AMPS, $-\text{CH}_2-\text{SO}_3^-$ )



**Figure 3** Kelen-Tüdös plot for copolymerization of AMPS-NIPA.

where  $[M_1]$  and  $[M_2]$  are the concentrations of monomer 1 and monomer 2, respectively, and  $r_1$  and  $r_2$  are the monomer reactivity ratios. With the substitutions  $y = d[M_1]/d[M_2]$ ,  $x = [M_1]/[M_2]$ , the F-R method gives the equation

$$x(y-1)/y = r_1(x^2/y) - r_2 \quad (3)$$

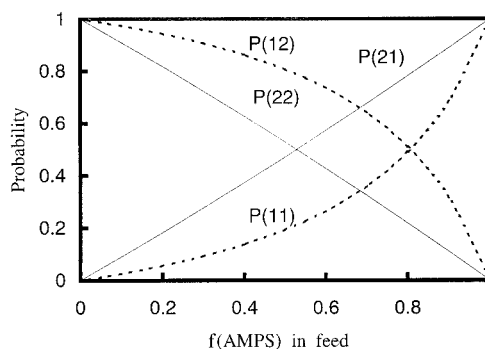
The graph of  $x(y-1)/y$  is shown in Figure 2, and the reactivity ratios obtained by linear regression are listed in Table V.

The K-T method utilizes the transformed variables  $G = x(y-1)/y$  and  $F = x^2/y$  and an arbitrary constant  $\alpha$  ( $\alpha > 1$ ) to give the equation

$$G/(\alpha + F) = \{r_1 + (r_2/\alpha)\}F/(\alpha + F) - (r_2/\alpha) \quad (4)$$

With the substitutions  $\eta = G/(\alpha + F)$ ,  $\xi = F/(\alpha + F)$ , eq. (4) takes the form

$$\eta = \{r_1 + (r_2/\alpha)\}\xi - (r_2/\alpha) \quad (5)$$



**Figure 4** Probabilities for growing AMPS-NIPA copolymer radical chain without penultimate effects.

**TABLE III**  
Chemical Shifts and Assignments  
for the NIPA Homopolymer

$\delta/\text{ppm}$	Assignment
<sup>13</sup> C NMR	
24.28	—CH <sub>3</sub>
37.42	—CH <sub>2</sub> (—CH <sub>2</sub> —CH—) broad
44.49–45.74	—CH (—CH <sub>2</sub> —CH—, —CH(CH <sub>3</sub> ) <sub>2</sub> ) overlapping
177.95	—C—O
<sup>1</sup> H NMR	
1.128	—CH <sub>3</sub>
1.425–1.699	—CH <sub>2</sub> (—CH <sub>2</sub> —CH—)
1.975–2.203	—CH (—CH <sub>2</sub> CH—)
3.873	—CH (—CH(CH <sub>3</sub> ) <sub>2</sub> )

where  $0 \leq \xi \leq 1$ . Using the value of given by<sup>33</sup>  $\alpha = (F_m F_M)^{1/2}$ , where  $F_m$  and  $F_M$  are the smallest and largest values, respectively, of  $F$ , the graph of  $\eta$  vs.  $\xi$  is shown in Figure 6, and the values of  $r_1$  and  $r_2$  obtained by linear regression are given in Table V.

Although the reactivity ratio values determined using the K-T and F-R methods are in good agreement, on the grounds that the K-T method is more reliable we adopt the values  $r_1 = 0.24$ ,  $r_2 = 1.12$ . These values are in approximate agreement with published data.<sup>29</sup>

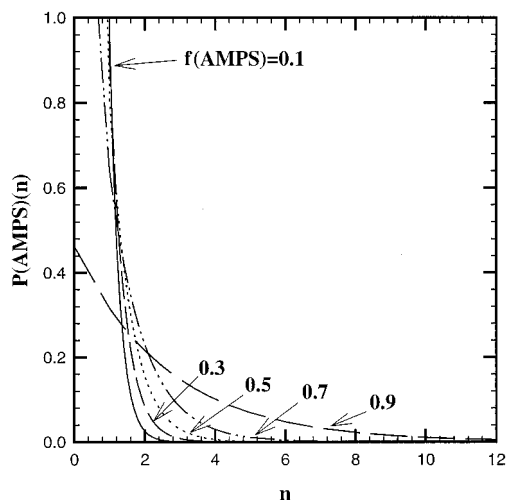
The probabilities of a growing chain that terminates with an AMPS radical adding AMPS,  $P(11)$  or NIPA,  $P(12)$ , are given by<sup>35,36</sup>

$$P(11) = r_1[\text{AMPS}]/(r_1[\text{AMPS}] + [\text{NIPA}]) = r_1x/(r_1x + 1) = 1 - P(12) \quad (6)$$

Similarly, the probabilities of a growing chain with a terminal NIPA radical adding NIPA,  $P(22)$ , or AMPS,  $P(21)$ , are

**TABLE IV**  
Chemical Shifts and Assignments  
for the AMPS-NIPA Copolymers

$\delta/\text{ppm}$	Assignment
<sup>13</sup> C NMR	
24.31	—CH <sub>3</sub> (NIPA)
29.24	—CH <sub>3</sub> (AMPS)
37.8–39.54	—CH <sub>2</sub> (AMPS-NIPA, —CH <sub>2</sub> —CH—) broad
44.53–46.06	—CH (NIPA(—CH <sub>2</sub> —CH—) + AMPS(—CH(CH <sub>3</sub> ) <sub>2</sub> ) overlapping
54.97	—C— (AMPS)
60.43	—CH <sub>2</sub> —SO <sub>3</sub> <sup>−</sup> (AMPS)
178.29	—C = O (AMPS-NIPA, —NHCO)
<sup>1</sup> H NMR	
1.098	—CH <sub>3</sub> (NIPA)
1.439	—CH <sub>3</sub> (AMPS)
1.648	—CH <sub>2</sub> (NIPA, AMPS, —CH <sub>2</sub> CH—) overlapping
2.032	—CH (NIPA, AMPS, —CH <sub>2</sub> CH—) overlapping
3.311–3.365	—CH <sub>2</sub> (AMPS, —CH <sub>2</sub> —SO <sub>3</sub> <sup>−</sup> )
3.834	—CH (NIPA, —CH(CH <sub>3</sub> ) <sub>2</sub> )



**Figure 5** Probabilities of forming a sequence of  $n$  units of AMPS for selected mol fractions of AMPS in feed.

$$P(22) = r_2[\text{NIPA}]/(r_2[\text{NIPA}] + [\text{AMPS}]) = r_2/(r_2 + x) = 1 - P(21) \quad (7)$$

Figure 4 shows that for equal probability of adding AMPS and NIPA units to a growing chain with terminal AMPS radical, the required proportion of AMPS in the comonomer mixture is around 80 mol %. The corresponding composition for NIPA-terminated chains is approximately 50 mol % AMPS.

According to Vollmert,<sup>36</sup> the probabilities of forming a closed sequence with exact  $n$  AMPS units,  $P(\text{AMPS})(n)$ , and  $n$  NIPA units,  $P(\text{NIPA})(n)$ , are given by

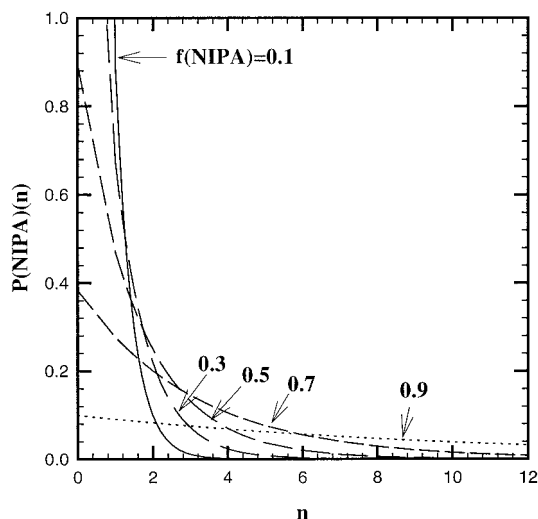
$$P(\text{AMPS})(n) = P(11)^{n-1}P(12) \quad (8)$$

$$P(\text{NIPA})(n) = P(22)^{n-1}P(21) \quad (9)$$

Figures 5 and 6 present probability functions calculated according to eqs. (8) and (9) for selected comonomer mixture compositions. As the proportion of AMPS in the comonomer mixture decreases to 10 mol %, the probability of forming a sequence of more than two AMPS units becomes negligibly small. The probability functions for NIPA units (Fig. 6) are somewhat broader than for AMPS, but the probability of forming NIPA sequences of significant is still small except in comonomer mixtures containing a high proportion of NIPA.

**TABLE V**  
Monomer Reactivity Ratios for Copolymerization of  
AMPS (1) and NIPA (2) at 70°C

Method	$r_1$	$r_2$
K-T	$0.24 \pm 0.06$	$1.12 \pm 0.04$
F-R	$0.25 \pm 0.03$	$1.13 \pm 0.22$



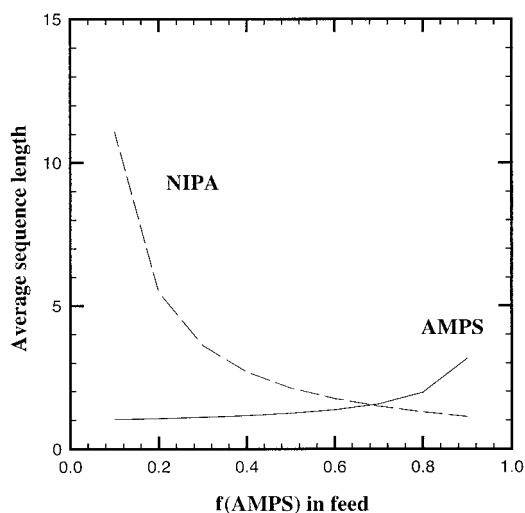
**Figure 6** Probabilities of forming a sequence of  $n$  units of NIPA for chosen mol fractions of NIPA in feed.

The copolymer microstructure can be evaluated by average sequence length,  $\lambda$ , of AMPS and NIPA units in the copolymer chain. The  $\lambda$  values were calculated from the following equations:<sup>36</sup>

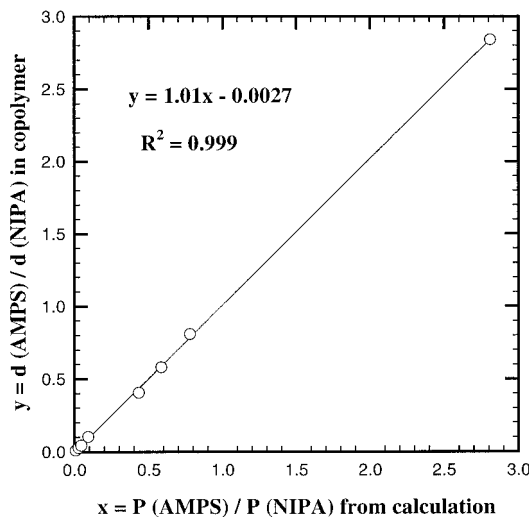
$$\lambda(\text{AMPS}) = r_1\{[\text{AMPS}]/[\text{NIPA}]\} + 1 \\ = r_1\{f(\text{AMPS})/(1 - f(\text{AMPS}))\} + 1 \quad (10)$$

$$\lambda(\text{NIPA}) = r_2\{[\text{NIPA}]/[\text{AMPS}]\} + 1 \\ = r_2\{(1 - f(\text{AMPS}))/f(\text{AMPS})\} + 1 \quad (11)$$

where  $f(\text{AMPS})$  is the mol fraction of AMPS in the comonomer mixture. The average sequence lengths are shown as a function of comonomer mixture composition in Figure 7.



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



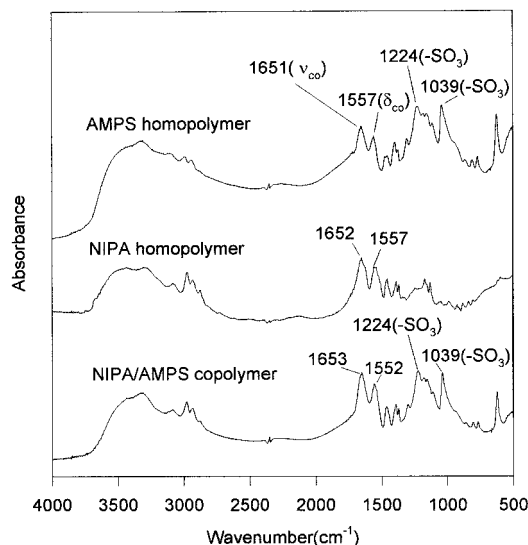
**Figure 8** Relationship between experimentally measured ratio of  $d[\text{AMPS}]/d[\text{NIPA}]$  and calculated ratio of probability of AMPS to probability of NIPA in copolymer chains.

The difference between the two monomers is that over most of the comonomer mixture composition range; the average sequence length of NIPA in the corresponding copolymer is greater than for AMPS.

Theoretically, for first-order Markovian statistics that corresponds to the terminal-effects-only case,<sup>37</sup> the following equation is valid.

$$y = \{P(\text{AMPS})/P(\text{NIPA})\} = (1 + r_1)/(r_2 + x) \quad (12)$$

where  $x = [\text{AMPS}]/[\text{NIPA}]$ ,  $y = d(\text{AMPS})/d(\text{NIPA})$ , and  $P(\text{AMPS})$  and  $P(\text{NIPA})$  are the conditional probabilities of AMPS and NIPA units, respectively, in the copolymer chains. Using  $r_1 = 0.24$  and  $r_2 = 1.12$ , the



**Figure 9** FTIR spectra for AMPS homopolymer (top), NIPA homopolymer (middle), and AMPS-NIPA copolymer with 50 mol % of AMPS in feed (bottom).

TABLE VI  
Dependence of the Glass Transition Temperature  
on the Copolymer Composition

$F_1^a$	$w_1^b$	$T_g(\text{Fox})^c/^\circ\text{C}$	$T_g(\text{expt})^d/^\circ\text{C}$
1	1	124.2	$124.2 \pm 2.2$
$0.7421 \pm 0.0008$	0.9428	124.7	$125.7 \pm 10$
$0.4470 \pm 0.0014$	0.7331	126.5	$124.9 \pm 2.2$
$0.3669 \pm 0.0011$	0.6468	127.2	$126.3 \pm 2.6$
$0.2886 \pm 0.0001$	0.5497	128.1	$126.6 \pm 3.3$
$0.0928 \pm 0.0011$	0.1691	131.6	$130.4 \pm 5.8$
0	0.000	133.2	$133.2 \pm 6.3$

<sup>a</sup> Mol fraction of AMPS in the copolymer.

<sup>b</sup> Weight fraction of AMPS in the copolymer.

<sup>c</sup> Calculated from eq. (13).

<sup>d</sup> Mean of at least four determinations.

values of P(AMPS)/P(NIPA) and the experimental values of  $y$  are compared in Figure 8. The linearity of the plot and the near-zero intercept confirm the applicability of the terminal model to copolymerization of this pair of monomers.

FTIR spectra for AMPS and NIPA homopolymers, together with a typical copolymer (from an equimolar comonomer mixture) spectrum, are presented in Figure 9. The  $1651\text{ cm}^{-1}$  ( $\nu_{\text{co}}$ ) and  $1557\text{ cm}^{-1}$  ( $\delta_{\text{co}}$ ) bands characteristic of amide carbonyl appear at 1652 and  $1557\text{ cm}^{-1}$  in NIPA homopolymer, and at 1653 and  $1552\text{ cm}^{-1}$  in the copolymer. The 1224 and  $1039\text{ cm}^{-1}$  bands of the sulfonic group of AMPS homopolymer appear at the same positions in the copolymer spectrum.

Glass transition temperatures, determined using differential scanning calorimetry, are given in Table VI. The value of  $T_g$  for NIPA homopolymer found in this work ( $133.2 \pm 6^\circ\text{C}$ ) is in accordance with the previously reported values  $135^\circ\text{C}^{38}$  and  $128\text{--}132^\circ\text{C}$  (depending on molecular weight).<sup>39</sup> A higher value of  $T_g$  for PNIPA ( $145.1^\circ\text{C}$ ) has also been reported.<sup>32</sup>

No melting or recrystallization peaks were found in the DSC scans of AMPS and NIPA homopolymers or their copolymers.

The glass transition temperature of amorphous polymers can vary widely with the chemical structure of the polymer. According to the semiempirical Fox<sup>40</sup> equation,  $T_g$  for a random copolymer is given by

$$1/T_g = (w_1/T_{g,1}) + (w_2/T_{g,2}) \quad (13)$$

where  $w_1$ , and  $w_2$  are the mass fraction of monomer 1 and monomer 2 in the copolymer, respectively, and  $T_{g,1}$  and  $T_{g,2}$  are the glass transition temperatures of the two corresponding homopolymers. Another commonly used empirical relationship is<sup>41</sup>

$$\ln T_g = (w_1/\ln T_{g,1}) + (w_2/\ln T_{g,2}) \quad (14)$$

In this case eqs. (13) and (14) give the same values of  $T_g$ . Experimental values of  $T_g$  are compared with values calculated using eq. (13) in Table VI. The Fox equation gives values of  $T_g$  that are systematically larger than the experimental values, but the differences are within experimental uncertainty.

## CONCLUSIONS

The rate of conversion of AMPS/NIPA comonomer mixtures to copolymer is strongly dependent on comonomer composition, and increases with the proportion of AMPS. Analysis of copolymer microstructure on the basis of the terminal model shows that the AMPS/NIPA comonomer pair has a tendency toward alternating microstructure, with relatively short monomer sequence lengths for comonomer mixtures with more than about 25 mol % AMPS.

The experimentally determined glass transition temperatures can be represented, to within experimental uncertainty, by the Fox equation.

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