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Observations on some copolymerisations involving *N*-isopropylacrylamide

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Abstract

Free radical copolymerisations of *N*-isopropylacrylamide (NIPA) with acrylic acid (AA), methacrylic acid (MAA) and 2-methyl-2-acrylamidopropane sulphonic acid (AMPS) have been conducted over a range of conversions in ethanol, ethanol and water respectively. It was necessary to devise special methods for isolating the copolymers, since the common device of precipitation into a non-solvent could not be adopted here. Experimental procedures necessary to overcome rapid attainment of high conversion, crosslinking and irreproducibility for the systems containing AA and MAA as comonomers are discussed. For all three systems compositions of linear copolymers were determined by conductometric titration vs. aq. NaOH. The monomer reactivity ratios (r) were calculated from the initial monomer feed composition, the fractional conversion and the copolymer composition, by means of the extended Kelen-Tüdős method. The 95% confidence ellipses were also computed. The results are: $r_1 = 14.0 \pm 1.9$ and $r_2 = 0.07 \pm 0.09$ for NIPA(1)/AA(2), $r_1 = 10.2 \pm 1.4$ and $r_2 = 0.01 \pm 0.03$ for NIPA(1)/MAA(2) and $r_1 = 2.4 \pm 0.8$ and $r_2 = 0.03 \pm 0.02$ for NIPA(1)/AMPS(2). Hence none of these systems undergoes azeotropic copolymerisation. The extent of compositional heterogeneity has been demonstrated by computed curves of instantaneous copolymer composition at different stages of conversion. Examination of the rather limited literature on linear copolymerisations involving NIPA discloses possible flaws and uncertainties in some of the procedures employed. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: *N*-isopropylacrylamide; Copolymerisation; Reactivity ratios

1. Introduction

N-isopropylacrylamide (NIPA) has been, and continues to be, the most widely used component of reversibly thermosensitive systems in water, viz. solutions of linear PNIPA and swollen hydrogels of crosslinked species [1–6]. The lower critical solution (or swelling) temperature (T_c) for phase separation or deswelling is ca. 33°C. This temperature can be altered by incorporation of a comonomer [4]. Although the overall composition of the linear or crosslinked copolymer is normally known from analysis, the compositional heterogeneity is not. This aspect is affected by the fractional conversion as well as the relevant monomer reactivity ratios. In chemically crosslinked systems these two factors should extend also to the multifunctional crosslinking agent. In the literature, information on reactivity ratios involving NIPA is very scant.

Previously we have examined the swelling behaviour and T_c of chemically crosslinked copolymers of NIPA with acrylic acid (AA), methacrylic acid (MAA) and 2-acrylamidopropane sulphonic acid (AMPS) in pure water [4] as well as in aq. media of different pH [5]. The sodium salts of AA and MAA were also used as comonomers [6]. The aims of the present study are threefold viz. (1) to conduct linear copolymerisations and thereby obtain reactivity ratios for the systems having AA, MAA and AMPS as comonomers. At this stage we have not yet attempted to derive reactivity ratios for the reaction between each monomer and the crosslinker (*N*,*N* methylene bis acrylamide). NIPA will be taken as monomer-1 (with subscript-1 appended to relevant quantities). Subscript-2 will be appended to the acidic comonomers. (2) To point out some experimental problems and their resolution and (3) to discuss other reports on copolymerisations involving NIPA.

2. Experimental

2.1. Materials

Ethanol, *n*-hexane, toluene (all from BDH), AMPS (Sigma Chemical Co.), ammonium persulphate (APS)

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Table 1
Solubility of monomers, homopolymers and copolymers at room temperature (✓ soluble; × insoluble)

	AA	NIPA	PAA	PNIPA	P(NIPA-*co*-AA)
Acetone	✓	✓	×	✓	✓[a] ×[b]
Dioxan	✓	✓	×[c]	×	×
Ethanol	✓	✓	✓	✓	✓
n-hexane	×	×	×	×	×
Iso-propanol	✓	✓	✓	✓	✓
Methanol	✓	✓	✓	✓	✓
Toluene	✓	✓	×	×	×
Toluene/*n*-hexane (27/73 w/w)	✓	✓	×	×	×
Water	✓	✓	✓	✓	✓

[a] When content of NIPA is high.
[b] When content of NIPA is low.
[c] θ—solvent at 30°C [8].

(from Wilkinson Vickers Ltd.) were used as received. Azo-bis-isobutyronitrile (AIBN) (from Fluka Chemical Co.) was recrystallised from ethanol. AA, MAA and NIPA (Aldrich Chemical Co.) were purified as described previously [4]. Deionised water from a Millipore Milli-U10 water purification system was used where appropriate.

2.2. Copolymerisation

2.2.1. NIPA/AA

Of the three systems the first one examined, NIPA/AA, gave rise to unprecedented difficulties and expenditure of time despite our extensive experience in conducting copolymerisations (e.g. Ref. [7]). With water as solvent and APS as initiator reactions at 60–65°C were vitiated by almost immediate, very high conversion and/or products containing crosslinked species. These problems could not be reliably and consistently overcome even after attention to changing the temperature, reaction time, concentration of initiator and total concentration of monomers. Results of solubility tests summarised in Table 1 show that acetone is a suitable water miscible precipitant. However, it suffers from the disadvantage of acting as a solvent for copolymers having a high content of NIPA. Dioxan as solvent with AIBN as initiator at 50–60°C gave rise to irreproducibility, the fractional conversion being sometimes zero, medium or extremely high. Moreover, the product was sometimes linear and on other occasions it contained some crosslinked species. From our work on related hydrogels it emerged that the copolymerisations could be slowed down by using aq. dioxan in place of water [9]. Hence dioxan/water (50/50 w/w) with APS was tried at 50–60°C, but the problems were similar to those encountered with dioxan. Precipitation into diethyl ether with dioxan or ethanol (see later) as solvent yielded a turbid product from which it was exceedingly difficult to isolate a solid precipitate.

With appropriate precautions ethanol as solvent with AIBN proved the best medium. Temperatures varying between 50 and 55°C were used. The concentrations of initiator and of total monomers were 5×10^{-3} and $0.5\ \text{mol dm}^{-3}$, respectively. Feed mixtures of different mole fractions of NIPA (f_1^0) were flushed with oxygen free nitrogen for 10 min (as was done for all experiments) and the reaction vessel sealed and placed in a thermostated bath. Due to the problems in controlling the extent of reaction and linearity of product neither a fixed time of reaction nor a single fixed temperature could be adopted. However, the following guideline was obtained: increasing the mole fraction of NIPA in the monomer feed required the temperature and time of copolymerisation to be reduced. In addition it was necessary to stir the feed continuously throughout the copolymerisation in order to avoid crosslinking. Hence, the copolymerisation was carried out in a round-bottomed flask. No ideal solvent/precipitant system could be found (see Table 1). The device adopted finally was to allow the ethanol to evaporate off at ambient temperature. The residue (copolymer plus unreacted monomers) was washed with large portions of toluene/*n*-hexane (27/73 w/w) mixture and left to dry at ambient temperature for 24 h prior to drying to constant weight in a vacuum oven at 47°C. Conversions were obtained gravimetrically. It had been found that the mixture of the composition quoted was a good solvent for the monomers but a non-solvent for copolymers of all compositions (Table 1). By weighing the dry copolymer after each washing, it was confirmed that a minimum of three washings was sufficient to ensure complete removal of unreacted monomer.

2.2.2. NIPA/MAA

The problems associated with the system NIPA/AA applied to a lesser extent in the copolymerisation of NIPA/MAA. Since the former were eventually resolved (NIPA/AA), the same suitable conditions for preparation and isolation of copolymer were applied to NIPA//MAA.

2.2.3. NIPA/AMPS

The NIPA/AMPS copolymerisation was conducted in aqueous solution due to the insolubility of AMPS in non-aqueous media. APS was used as initiator and the temperature employed was 50°C. The concentrations of total

Table 2
Mole fraction of NIPA in feed (f_1^0) and copolymer (F_1) at different fractional conversions (θ), with AA, MAA and AMPS as comonomers

NIPA(1)/AA(2)			NIPA(1)/MAA(2)			NIPA(1)/AMPS(2)		
f_1^0	F_1	θ	f_1^0	F_1	θ	f_1^0	F_1	θ
0.714	0.972	0.165	0.900	0.989	0.107	0.909	0.955	0.200
0.714	0.965	0.254	0.800	0.973	0.140	0.667	0.807	0.352
0.714	0.966	0.134	0.667	0.955	0.115	0.500	0.631	0.731
0.714	0.973	0.110	0.500	0.920	0.109	0.333	0.677	0.199
0.667	0.962	0.117	0.333	0.818	0.221	0.200	0.528	0.243
0.667	0.959	0.143	0.300	0.854	0.298	0.020	0.149	0.120
0.667	0.968	0.153	0.250	0.770	0.322	0.010	0.142	0.010
0.625	0.947	0.276	0.111	0.612	0.220			
0.513	0.922	0.360	0.053	0.536	0.131			
0.333	0.833	0.301	0.020	0.559	0.122			
0.333	0.801	0.344						
0.143	0.421	0.164						

monomers and APS were 0.5 and 5×10^{-3} mol dm^{-3}, respectively. Reaction was carried out in a glass vial (25 ml capacity). The feed mixture was flushed with oxygen-free nitrogen for 10 min after which the vial was sealed and maintained at 50°C. After 20 min, a period established as suitable by preliminary tests, the reaction mixture was transferred to visking tubing and dialysed against water for one week, the water being changed daily. After this period the absence of monomer in the final sample of water was confirmed by conductometric analysis, the conductivity of the sample being equal to that of pure water. Following dialysis, the dialysed solution was transferred to a beaker, the water was removed over one week by evaporation at ambient temperature and the residue was dried to constant weight in a vacuum oven at 47°C. The conversions were obtained gravimetrically.

2.3. Analysis of copolymer composition

Copolymer composition was determined by conductometric acid–base titration, thereby affording directly the mole fraction of acidic monomer. A known mass of copolymer (0.1 g) was dissolved in water (40 ml) in a glass tube, which was then placed in a thermostated water bath. The conductivity of the copolymer solution after each incremental addition of titrant was monitored with a CMD 40 conductivity meter (WPA Scientific Instruments) (accurate to 1 μS). To ensure that titres were not too large, i.e. that the overall volume did not exceed 40 ml to any great extent, the appropriate concentrations of titrant (aq. NaOH) were 0.03 M for P(NIPA-*co*-AA) and P(NIPA-*co*-MAA) and 0.1 M for P(NIPA-*co*-AMPS). For the last of these systems it was also necessary to shake the solution due to its rather high viscosity.

3. Results

The composition of feed and copolymer as well as values of fractional conversion for the three-copolymer systems are given in Table 2. None of the values of the fractional conversion θ is <0.10; most are medium and one very high. The Fineman–Ross (F–R) [10] and Kelen–Tüdős (K–T) [11] procedures are generally unsuitable unless the conversion is low. For medium–high conversion, the iterative procedure of Mao and Huglin [12,13] and the extended Kelen–Tüdős method (Ex. K–T) [14] both of which involve the use of the value of θ, are preferable and have been shown to yield similar values for the reactivity ratios. In addition to the failure of the K–T and F–R methods to allow for effect of conversion on composition of residual feed mixture, the F–R procedure is also known to be affected by interchange of subscripts relating to the two monomers. In probably the most comprehensive listing of reactivity ratios [15], the compiler has, wherever possible, recalculated values of r_1, r_2 by means of the Ex. K–T method, using compositions and conversions quoted in the original papers. Accordingly, here we have adopted the Ex. K–T procedure, which is based on the terminal model, viz. the Mayo–Lewis equation [16]. It utilises Eq. (1)

$$\eta = r_1\xi - \frac{r_2}{\alpha}(1 - \xi) \tag{1}$$

where

$$\eta = \frac{G}{\alpha + H}, \quad \xi = \frac{H}{\alpha + H}, \quad \alpha = \sqrt{H_{\text{minimum}} \times H_{\text{maximum}}} \tag{2}$$

$$G = \frac{F - 1}{z}, \quad H = \frac{F}{z^2}, \quad z = \frac{\log(1 - \tau_1)}{\log(1 - \tau_2)} \tag{3}$$

$$\tau_2 = \left(\frac{\mu + f}{\mu + F}\right)\theta \quad \tau_1 = \tau_2\frac{F}{f} \tag{4}$$

θ is the fractional conversion of total monomers and

$$\mu = \frac{\text{mol. wt. of monomer} - 2}{\text{mol. wt. of monomer} - 1} \tag{5}$$

The initial feed composition f is defined in Eq. (6) as the ratio of mole fraction of monomer 1 in the feed to that of monomer 2. The average copolymer composition F is defined similarly in Eq. (7) in terms of mole fractions F_1 and F_2 of monomer units in the copolymer:

$$f = \frac{f_1}{f_2} = \frac{[M_1]_0}{[M_2]_0} \tag{6}$$

$$F = \frac{F_1}{F_2} = \frac{\Delta[M_1]}{\Delta[M_2]} \tag{7}$$

From Eq. (1) a plot of η vs. ξ yields r_1 as the value of η at $\xi = 1$ and $-r_2/\alpha$ as the extrapolated intercept at $\xi = 0$ or alternatively r_1 can be obtained as (slope + intercept). The 95% confidence limits of the values of r_1 and r_2 may be estimated by the confidence interval estimation technique of the linear least-squares method [17]. Thus the 95% limits

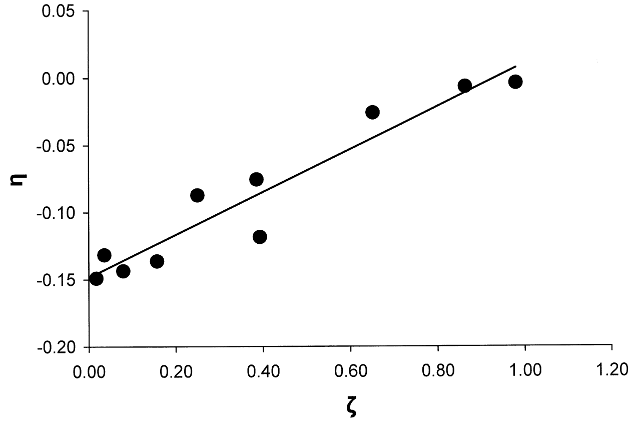

Fig. 1. The Ex. K–T plot for NIPA/MAA copolymerisation.

can be calculated by the following unified equations:

$$\Delta r_1 = \pm t_{0.025}(n-2)\sqrt{\frac{S_R}{n-2}\frac{\sum(1-\xi_i)^2}{D}} \tag{8}$$

$$\Delta r_2 = \pm\alpha\times t_{0.025}(n-2)\sqrt{\frac{S_R}{n-2}\frac{\sum\xi_i^2}{D}} \tag{9}$$

where $t_{0.025}(n-2)$ is the Student's t distribution with $(n-2)$ degrees of freedom and with each tail area probability equalling 0.025, n is the number of experimental points. All summations of ξ are carried out from $i = 1$ to $i = n$.The quantities S_R and D are

$$S_R = \sum\left[\eta_i - r_1\xi_i + \frac{r_2}{\alpha}(1-\xi_i)\right]^2 \tag{10}$$

$$D = \sum\xi_i^2\sum(1-\xi_i)^2 - \left[\sum\xi_i(1-\xi_i)\right]^2 \tag{11}$$

The ellipse, according to the following equation, encloses the 95% joint confidence interval [17]:

$$(r_1-R_1)^2\sum\xi_i^2 + \frac{2}{\alpha}(r_1-R_1)(r_2-R_2)\sum\xi_i(\xi_i-1) + \left(\frac{r_2-R_2}{\alpha}\right)^2\sum(\xi_i-1)^2 = \frac{2S_R}{n-2}F_{0.05}(2, n-2) \tag{12}$$

where $F_{0.05}(2, n-2)$ is the F distribution having 2 and $n-2$ degrees of freedom and R_1, R_2 are the least-squares estimation of r_1, r_2, respectively.

The Ex. K–T plot according to Eq. (1) is linear ($R^2 = 0.92$) for all the three systems, but is illustrated here only for NIPA/MAA (Fig. 1). The linearity affords some measure of support for the Ex. K–T method and the terminal model on which it is based.

Fig. 2 (relating to the NIPA/AMPS) is an example of the ellipse for 95% joint confidence interval according to Eq. (12). The values of the derived reactivity ratios are listed in Table 3.

The compositional drift of copolymers with increasing fractional conversion (θ) of unreacted total monomers was determined from the copolymer composition [18] and Skeist [19] equations (Eqs. (13) and (14), respectively).

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2} \tag{13}$$

$$\ln(1-\theta) = \int_{f_{1i}}^{f_{1j}} \frac{\mathrm{d}f_1}{F_1 - f_1} \tag{14}$$

The calculation of θ with fractional change in feed composition during an interval of conversion from a value of f_{1i} to a value of f_{1j} utilises Eq. (14), and thereby, the integrated expression (Eq. (15)) of Meyer and Lowry [20].

$$\theta = 1 - \left(\frac{f_{1j}}{f_{1i}}\right)^{\alpha}\left(\frac{1-f_{1j}}{1-f_{1i}}\right)^{\beta}\left(\frac{f_{1i}-\delta}{f_{1j}-\delta}\right)^{\gamma} \tag{15}$$

where

$$\alpha = \frac{r_2}{(1-r_2)};\quad \beta = \frac{r_1}{(1-r_1)};$$

$$\gamma = \frac{(1-r_1r_2)}{[(1-r_1)(1-r_2)]};\quad \text{and } \delta = \frac{(1-r_2)}{(2-r_1-r_2)}.$$

Further details have been given by us previously [7].

Seven different feed compositions were considered for each of the three copolymerisations and curves were computed of instantaneous copolymer composition as a function of conversion. The general form of the set of seven curves is similar for each of the three copolymerisations and the set is reproduced here for the NIPA/AA system only (see Fig. 3).

4. Discussion

Despite the rather large uncertainty limits in the reactivity ratios, the following features hold: (a) in no case is there an azeotropic composition (because $r_1 > 1$ and $r_2 < 1$)), (b) $1 > r_1r_2 > 0$ in all three cases and hence the copolymerisations are neither ideal nor alternating, although NIPA/AA is close to the former and NIPA/AMPS is close to the latter, (c) $r_1 > r_2$, i.e. NIPA has a strong propensity to enter the

Table 3
Values of reactivity ratios for copolymerisations of NIPA (monomer-1) with acidic comonomers (monomer-2)

Comonomer	r_1	r_2	r_1r_2
AA	14.0 ± 1.9	0.07 ± 0.09	0.98
MAA	10.2 ± 1.4	0.01 ± 0.03	0.10
AMPS	2.4 ± 0.8	0.03 ± 0.02	0.07

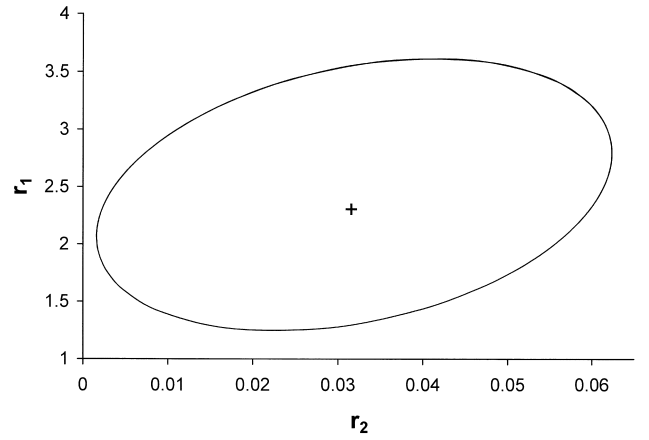

Fig. 2. The 95% joint confidence intervals for the reactivity ratios for the copolymer system NIPA(1)/AMPS(2) ($r_1 = 2.4$, $r_2 = 0.03$). The equation is $3.81(r_1 - 0.03)^2 - 0.19(r_1 - 0.03)(r_2 - 2.4) + 2.60 \times 10^{-2}(r_2 - 2.4)^2 = 6.06 \times 10^{-3}$.

growing chain at the expense of the comonomer. (d) Consequently there is compositional heterogeneity. Thus in Fig. 3, $F_1 \gg 0.01$ at low conversion, when $f_1^0 = 0.01$ and the value of F_1 decreases thereafter with increasing level of the conversion. At medium values of f_1^0 there is a very wide spread of instantaneous copolymer composition over a medium range of θ. When the feed mixture is very high in NIPA (Fig. 3(f) and (g)), the copolymer is very rich in NIPA immediately and stays so up to ca. $\theta = 0.9$. Over the remaining short interval of conversion the instantaneous copolymer composition covers an extremely wide range of values. These observations have practical relevance since, even if the form of the composition–conversion curves may not be quantitatively exact due to some uncertainty in r_1, r_2, the general form indicates compositional homogeneity up to quite high conversion for those copolymers exhibiting marked thermosensitivity, i.e. those from feeds of high f_1^0.

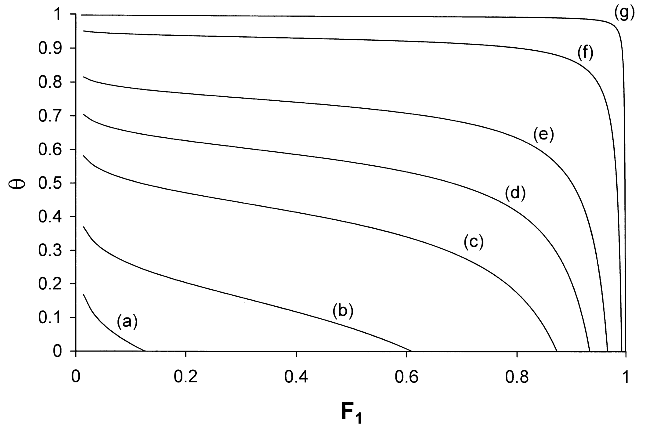

Fig. 3. The variation in instantaneous mole fraction (F_1) of NIPA in the copolymer system NIPA(1)/AA(2) with fractional conversion θ using the derived reactivity ratios ($r_1 = 14.0$, $r_2 = 0.07$). Curves (a)–(g) relate to initial feed compositions f_1^0 of 0.01, 0.10, 0.33, 0.50, 0.67, 0.90 and 0.99, respectively.

(e) In principle it should be possible to derive the copolymerisation parameters Q and e for NIPA using the literature values of 0.83 and 0.88, respectively for AA [21] and 0.98 and 0.62, respectively, for MAA [21]. Separate calculations involving $r_1 r_2$ for NIPA/AA and NIPA/MAA should yield a unique set of values of Q, e specific to NIPA. However, in practice use of the mean values in Table 3 gives disagreement between Q_1, e_1 derived via data for NIPA(1)/AA(2) and Q_1, e_1 calculated from data for NIPA(1)/MAA(2). Exact accord can only be forced by arbitrary selection of specific values of r_1 and r_2 within the overall uncertainty limits.

(f) Some measure of support for the application of the terminal model used here has been mentioned earlier in the text. However, it is not possible to discount entirely the possibility that the penultimate model (requiring two additional reactivity ratios) might be more appropriate. Solvent effects such as those in the ‘bootstrap model’ are particularly prevalent in polar systems wherein some form of interactions or association, characterised by an equilibrium constant K, exists between radical end of a growing chain and a monomer in its immediate vicinity [22]. In such an instance the derived values of r_1, r_2 depend on the nature of the solvent; for a fixed f_1^0, copolymerisation in two different solvents can lead to two different, experimentally determined, values of F_1 (but, surprisingly, identical microstructures). Essentially, the values of r_1, r_2 contain a contribution due to K. Although these reactivity ratios might thus be considered as only ‘apparent ones’, from the practical standpoint they are really the usable ones, provided the practitioner adopts the same solvent. For the present three polar systems it should be noted that each copolymerisation was conducted in only one solvent; hence prediction of F_1 from f_1^0 and r_1, r_2 should be satisfactory, if future copolymerisations involving AA, MAA and AMPS are conducted in ethanol, ethanol and water, respectively.

We discuss finally aspects of the small number of publications in which reactivity ratios for copolymerisations involving NIPA appear either explicitly or implicitly (generally as a topic subsidiary to the main theme) in order to (i) ascertain if others had encountered experimental difficulties and if sufficient attention had been paid to obtaining pure copolymer, (ii) compare, where possible, the values of r_1, r_2 reported (or derived by us from reported data) with those obtained here, (iii) examine the feasibility of deriving values of Q, e for NIPA.

In his study geared primarily to the lower critical solution behaviour of the linear copolymers in aq. solution at different pH values, Jones prepared samples of P(NIPA-*co*-AA) [23] using three different values of f_1^0 and high conversions. Good accord was obtained among different techniques for analysis of copolymer composition, but it seems likely that the samples analysed were not pure. Copolymer separated from the solvent, toluene, during polymerisation. The expedient of washing with hexane is inadequate for removing unreacted monomers (see Table 1). Moreover, it emerged

[24] that some crosslinked material was produced (particularly at high values of f_1^0) and filtered off. The data provided are insufficient to enable any values of r_1, r_2 to be derived reliably.

Other work on the same system was geared primarily to control of molecular weight by incorporating ethanol as a chain transfer agent into the main solvent, benzene [25]. Omission of relevant conversions etc does not allow us to derive values of r_1, r_2. Isolation of copolymer by precipitation into *n*-hexane from solution in acetone was adopted and the same objection raised earlier in connection with the work of Jones on this system applies here. Note that copolymer precipitates during its formation, when toluene is solvent. Use of benzene (or presumably toluene also)/ethanol retains solubility, but induces reduction in molecular weight by chain transfer [25]. Finally in the situation where content of benzene (or toluene) is zero and that of ethanol in solvent is 100%, the chain transfer is probably high and molecular weight of copolymer low. Accordingly our decision to use ethanol as appropriate solvent for the copolymerisation was vindicated. In this connection also the aqueous solutions of the copolymers for conductometric titration were not very viscous, but the corresponding aq. solutions of P(NIPA-*co*-AMPS) that had been synthesised in water, rather than ethanol, were viscous and presumably contained high molecular weight polymer.

An otherwise excellent report [26] on the swelling behaviour of chemically crosslinked hydrogels of P(NIPA-*co*-MAA) contains within it a small section on the relevant reactivity ratios that seems somewhat flawed in several aspects: (a) no information is given on θ and the mode of isolating copolymers; indeed, if anything, the text implies that high conversion crosslinked samples were used. (b) Copolymer composition was obtained by elemental analysis for nitrogen; values are not quoted, but a plot indicates that F_1 does not deviate very greatly from f_1^0. Such a situation would inevitably be true (irrespective of values of r_1, r_2) if conversions were very high. (c) Five values of f_1^0 are quoted, but the corresponding plot of f_1^0 vs. F_1 contains twelve data points. (d) A plot similar to that of F–R yielded $r_1 = 0.891$ and $r_2 = 1.128$, (e) the authors used these values, in conjunction with literature values of Q_2 and e_2 quoted earlier here, to yield values of $Q_1 = 0.695$ and $e_1 = 0.26$ for NIPA. We do not agree that these or any values are possible by calculation from the definitions of Q and e [27] for the case where r_1r_2 ($= 1.005$) exceeds unity. If r_1r_2 is approximated reasonably to 1.0, then it follows that $e_1 = e_2 (= 0.62)$ and $Q_1 = 0.87$. The authors' assertion from their findings that MAA is more reactive than NIPA does not accord with our findings on the same system.

Recently Neradovic et al. [28] investigated the systems NIPA(1)/2-hydroxyethyl methacrylate (HEMA)(2) and NIPA(1)/HEMA lactate (2) in two separate sections. For the latter system in dioxan at 60°C the copolymer was not isolated but its composition was calculated by mass balance using the measured concentration of residual monomers. A F–R plot afforded $r_1 = 0.36$ and $r_2 = 1.22$, but no information was given on F_1, θ or confidence limits. In another section on NIPA(1)/HEMA lactate(2) full details were provided and the copolymer was isolated and analysed. Similar considerations apply to NIPA(1)/HEMA(2) in this section. The present authors have analysed all the data via the Ex. K–T method and obtained $r_1 = 1.85$, $r_2 = 1.05$ for NIPA(1)/HEMA lactate(2) and $r_1 = 1.58$, $r_2 = 1.81$ for NIPA(1)/HEMA(2). The difference between the two sets of values for NIPA/HEMA lactate may well be due to the small number of data points and narrow range of feed compositions available to the present authors for calculating r_1, r_2. The values of r_1, r_2 calculated here for NIPA/HEMA are not meaningful, since each is greater than unity.

Aggregation of linear copolymers in solution was the primary concern of Erbil et al. [29] in their copolymerisations of NIPA(1) with itaconic acid (IA)(2) in aqueous solution. The data on conversion and compositions are insufficient to derive values of r_1, r_2. The mode of purification of copolymers gives rise to some concern. For PIA and copolymers obtained from feeds in which $f_1^0 < 0.50$, isolation was by precipitation into acetone. Isolation of PNIPA and copolymers obtained from feeds having $f_1^0 > 0.50$ was by heating the aq. solution to a temperature $> T_c$. These devices may be insufficiently rigorous, because (a) it is assumed implicitly that the feed composition is the same as that of the copolymer being isolated. Hence, if NIPA has a high tendency to incorporation into the chain, even a copolymer produced from a feed of medium–high content of IA could be rich in NIPA and possibly soluble in acetone. This procedure promotes isolation of those copolymeric species, which have a similar composition to that of the feed. (b) Heating in water to above T_c may impose the additional problem that in a compositionally heterogeneous copolymer, species of different F_1 may possess different values of T_c. Uncertainty exists, since the value of T_c of a thermosensitive polymer must be established on a sample that has already been isolated and a supposed value of T_c should not be used as a route to effecting this isolation (note also the additional complications of concentration [30,31] and molecular weight [31] in solutions of thermosensitive copolymers).

Low conversion copolymers of NIPA(1) with an unusual monomer, acrylamidolactamine (ALA)(2), have been synthesised in water by Kurth et al. [32]. The copolymers, precipitated in acetone/methanol, were analysed by NMR and both linear and nonlinear methods afforded $r_1 = 1.22$ and $r_2 = 0.75$. It does not seem profitable to compare these values with those for NIPA/AMPS (Table 3), since AMPS is very strongly acidic, whereas ALA is weakly basic.

Finally, attention is drawn to the work of Chen and Hoffman [33] on the copolymerisation of NIPA(1) with 4-pentenoic acid (PA)(2) in methanol at 50°C with AIBN as initiator. Examination of the procedures employed indicates that the problems in copolymer purification and data analysis discussed previously do not apply, since conversion was allowed to proceed only to low values (($\theta < 0.15$), and the copolymer was isolated and washed in diethyl ether, a solvent for NIPA and PA but not apparently for the homo- or copolymers of these monomers. The composition was determined by acid–base titration and analysis of data by the F–R method afforded values of $r_1 = 10.58$, $r_2 = 0.035$ were obtained. They are of similar magnitude to the values obtained here for NIPA/AA. It is pertinent to note that PA differs from AA only in the presence within its side chains of two additional methylene groups.

5. Conclusions

1. A review of the rather limited literature on linear copolymerisations involving NIPA discloses flaws and uncertainties in some of the methodologies employed.
2. Problems associated with crosslinking, rapid uncontrollable copolymerisation to high conversion and isolation of copolymer for NIPA/AA have been addressed and overcome. The procedure is applicable equally to NIPA/MAA. The system NIPA/AMPS in aqueous solution followed by isolation of copolymer by dialysis is relatively straightforward.
3. Analysis of the data (including those for medium–high conversion) by the Ex. K–T method yields $r_1 = 14.0 \pm 1.9$, $r_2 = 0.07 \pm 0.09$; $r_1 = 10.2 \pm 1.4$, $r_2 = 0.01 \pm 0.03$; $r_1 = 2.4 \pm 0.8$, $r_2 = 0.03 \pm 0.02$ for systems in which NIPA is monomer-1 and AA, MAA and AMPS, respectively, are monomer-2.
4. Despite the rather large uncertainty limits, these data are novel and have useful ramifications in assessing the compositional homogeneity of linear and crosslinked copolymer that are thermosensitive.

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