

Kinetic Study of Radical Polymerization. VII. Investigation into the Solution Copolymerization of Acrylonitrile and Itaconic Acid by Real-Time ^1H NMR Spectroscopy

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ABSTRACT: Free radical solution copolymerization of acrylonitrile (AN) and itaconic acid (IA) was performed with DMSO- d_6 as the solvent and 2,2'-azobisisobutyronitrile (AIBN) as the initiator. Weight ratio of the monomers to solvent and molar ratio of initiator to monomers were constant in all experiments. The initial comonomer composition was the only variable in this study. On-line ^1H NMR spectroscopy was applied to follow individual monomer conversion. Mole fraction of AN and IA in the reaction mixture (f) and in the copolymer chain (F) were measured with progress of the copolymerization reaction. Overall monomer conversion versus time and also compositions of monomer mixture and copolymer as a function of overall monomer conversion were calculated from the data of individual monomer conversion versus time. Total rate constant

for the copolymerization reaction was calculated by using the overall monomer conversion versus time data and then $k_p/k_t^{0.5}$ was estimated. The dependency of $k_p/k_t^{0.5}$ on IA concentration was studied and it was found that this ratio decreases by increasing the mole fraction of IA in the initial feed. The variation of comonomer and copolymer compositions as a function of overall monomer conversion was calculated theoretically by the terminal model equations and compared with the experimental data. Instantaneous copolymer composition curve showed the formation of alternating copolymer chain during copolymerization reaction. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3253–3260, 2007

Key words: free-radical copolymerization; ^1H NMR; kinetic; acrylonitrile; itaconic acid

INTRODUCTION

Acrylonitrile (AN)-based copolymers are widely used in the production of acrylic fibers. Polyacrylonitrile fibers suffer from poor hygroscopicity and low dye uptake. Suitable comonomers are thus incorporated into the polymer to overcome these shortcomings. Acidic comonomers not only improve the hygroscopicity but also help in the cyclization of the nitrile group to form a ladder structure during thermo-oxidation of acrylic fibers.¹ Among the various polymerization techniques used in the production of AN polymers, solution polymerization is one of the most common ones.² The advantage of solution polymerization over the other techniques is that the polymer solution can be converted directly to the spinning dope in the process of fiber production.³

Tsai and Lin^{4–7} used a solution polymerization technique to copolymerize AN with different monomers including acidic comonomer to produce hygroscopic fibers. In addition to solution polymerization, suspension polymerization is another popular method, which has been widely used to produce AN copolymers.^{8,9} Also free-radical aqueous slurry polymerization of AN has been reported by Ebdon et al.¹⁰

There are many reports in the literature about application of ^1H and ^{13}C NMR technique to analyze the copolymer structure and composition and also determination of reactivity ratios.^{11–16} Bajaj et al.¹⁷ have studied the copolymerization of AN with vinyl acids such as methacrylic acid, acrylic acid, and itaconic acid in dimethyl formamide (DMF) with the objective of improving the hygroscopicity of the resulting fibers. They used FTIR, CHNO analysis, and ^{13}C NMR to investigate copolymer composition, reactivity ratio, and tacticity of the chains.

One of the key comonomers recommended for the copolymerization with AN is itaconic acid (IA), which has been a subject of some previous studies.^{17–21} The major reason for the superiority of IA over other acidic comonomers is the presence of two carboxylic groups, which increases the possibility of

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interaction of the carboxylic group and the nitrile group during cyclization reaction.

The effect of reaction medium on radical polymerization has been well documented in previous reported studies, suggesting factors like electrostatic interactions, hydrogen bonding, polar–polar interactions, etc. as responsible for monomer and radical reactivity in copolymerization.²² It is noteworthy that the presence of water in the solvents such as DMF and DMSO also affects the reactivity ratio.²³

To our knowledge, all of the kinetic studies about copolymerization of AN and IA have discussed about deriving their reactivity ratios and there is not any report on calculation of the rate constant. In this article, kinetic data were obtained from on-line ¹H NMR spectroscopy, and overall rate constant and also $k_p/k_t^{0.5}$ were determined for copolymerization reaction of AN and IA. In addition, variation in the monomer and copolymer compositions versus conversion was calculated theoretically and compared with experimental data.

EXPERIMENTAL

Materials

Analytical grade acrylonitrile (AN), itaconic acid (IA), and 2,2'-azobisisobutyronitrile (AIBN) were obtained from Merck Chemical (Darmstadt, Germany). DMSO-d₆ as solvent was purchased from ARMAR Chemicals (Dottingen, Switzerland). AN was washed three times with a 2% sodium hydroxide solution followed by three times washing with distilled water to remove its inhibitor and then dried over CaCl₂. Other chemicals were used without further purification.

Equipments

All ¹H NMR experiments reported in this study were carried out on a Bruker Avance 400 NMR spectrometer (Bruker Instruments, Darmstadt, Germany). The sample cavity was equilibrated at 78°C (i.e., the temperature at which the kinetic NMR experiments were carried out) by a BVT 3000 (± 0.1°C) temperature control unit. After setting the cavity temperature at 78°C, the sample tube of 5 mm diameter containing the reaction mixture was inserted into the sample chamber.

Copolymerization reaction

The copolymerization reactions were conducted in the NMR tubes. The prepared solutions in NMR tubes were degassed with nitrogen gas (99.9% purity) to exclude oxygen from the solutions, which acts as a retardant in radical polymerization reactions. Sample preparation and degassing were

TABLE I
Initial Reaction Mixture and Copolymer Compositions for AN/IA Copolymerization System^{a,b}

Sample	f_{IA}^0	[AIBN] (mol L ⁻¹)	F_{IA}^c
AN-IA-1	0.1245	0.0113	0.2214 (10.86)
AN-IA-2	0.2190	0.0122	0.3175 (10.36)
AN-IA-3	0.4143	0.0134	0.4658 (9.65)
AN-IA-4	0.4745	0.0141	0.4918 (7.24)
AN-IA-5	0.5435	0.0150	0.5470 (10.53)
AN-IA-6	0.6157	0.0167	0.5952 (10.29)
AN-IA-7	0.7167	0.0177	0.6523 (9.87)

^a Reaction temperature was set at 78°C.

^b The weight ratios of monomers to solvent in all experiments were almost 1 : 1.

^c Values in parentheses indicate conversion % values.

performed at 0°C to inhibit initiation reaction before inserting in the NMR chamber. After setting the cavity temperature at 78°C, the sample tube containing the reaction mixture was inserted into the sample chamber. The spectra were recorded at different time intervals. All the data have been listed in Table I.

RESULTS AND DISCUSSION

During our investigation on kinetic studies of radical polymerization by several instrumental techniques in different media and conditions,^{24–28} we were notified to the great potential of ¹H NMR spectroscopic technique, for these kinetic studies. Especially, on-line ¹H NMR spectroscopy gives us the most reliable data about the variation of conversion during the progress of reaction, with high accuracy.

We have applied this method for calculating the reactivity ratios of AN and IA in free-radical copolymerization in DMSO-d₆, using AIBN at 78°C, previously.²⁸ A typical ¹H NMR spectrum of a sample during copolymerization reaction, which contains three components (monomers and copolymer), has been shown in Figure 1 and assignment of the peaks were performed according to the different types of protons. Also carboxylic acid proton appears as a broad peak above 10 ppm that has not been shown in Figure 1.

H_c and H_e, which are the characteristic peaks of AN and IA respectively (Scheme 1), are far enough from each other in the corresponding spectrum and have no overlapping. H_c appears at 5.75–5.9 ppm as a doublet of doublet and H_e could be found at 5.6–5.65 ppm as a singlet. So, these two peaks could be considered as the basis of conversion calculations. Individual monomer conversion was calculated by measuring the specific peak areas in the recorded spectra at different time intervals with respect to the first spectrum for each reaction mixture.²⁸ It is observable that area of the peaks in the aliphatic

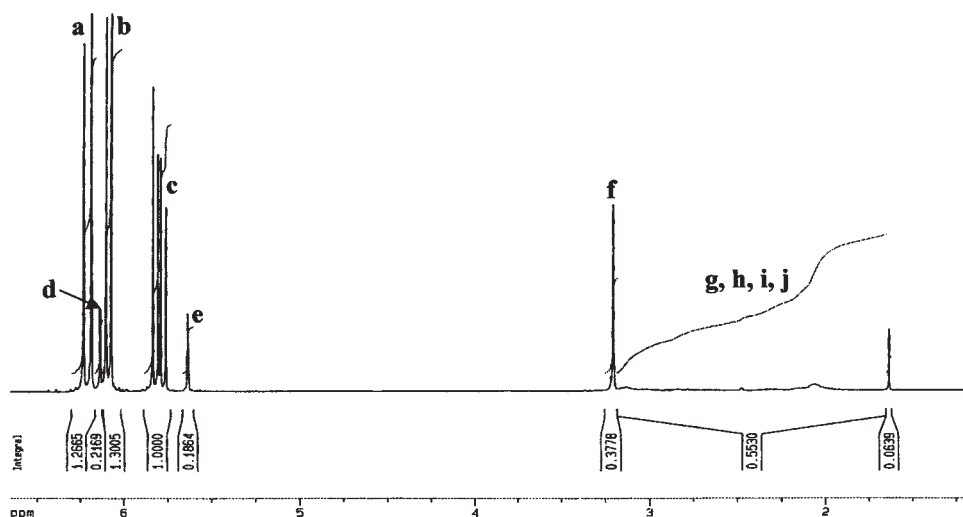


Figure 1 A typical ^1H NMR spectrum of acrylonitrile-itaconic acid copolymer and the corresponding unreacted monomers.

region (Fig. 2), which shows the progress of copolymerization reaction, is growing up during the time.

The method of calculating f_i (mole fraction of monomer i in the feed) and F_i (mole fraction of monomer i in the copolymer chain) has been discussed in our previous article in detail.^{27,28} The measured amounts of f_{IA}^0 (mole fraction of IA in the initial feed) and F_{IA} in these series of experiments are listed in Table I that have been used before for determination of reactivity ratios.²⁸

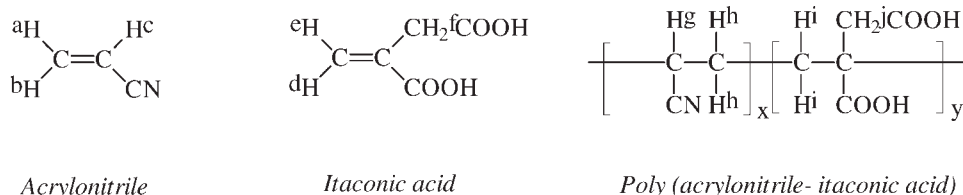
Kinetic studies of the copolymerization reaction

The analysis of the peaks in ^1H NMR spectra for vinylic protons of AN and IA would give the conversion of each monomer as a function of reaction time. Individual conversion of AN and IA versus time for some samples have been plotted in Figure 3. Reaction temperature was set at 78°C in all experiments and the initiator concentration was in the range of 0.011–0.018M. The individual conversion curves for AN and IA show that they are incorporated into the copolymer chain as the polymerization reaction proceeds. When mole fraction of IA (f_{IA}) in the initial feed was less than 0.5435, this monomer is copolymerized with higher rate than AN and this

trend is inverted if f_{IA} in the initial feed is more than 0.5435. This will be discussed more in the next.

These individual monomer conversions could be used to obtain overall monomer conversion and investigation of variation in the monomer mixture and copolymer compositions. Overall monomer conversion as a function of time for different f_{IA} in the initial feed has been shown in Figure 4. It is clear that the copolymerization rate decreases considerably with increasing mole fraction of IA in the initial monomer mixture. It has also been found in Figure 3 from the decrease in the slope of each individual monomer conversion versus time curves by increasing the amount of IA in the initial feed. This was expected as the homopolymerization rate for AN^{29,30} is much greater than that for IA.^{31–35}

Propagation rate constant (k_p) for homopolymerization of AN at 25 and 50°C in DMSO and at 75°C in bulk has been reported to be 1910, 3200,²⁹ and $4600 \text{ L mol}^{-1} \text{ s}^{-1}$,³⁰ respectively. With considering the Arrhenius dependency of k_p on the temperature, k_p value for homopolymerization of AN at 78°C will be about $4883 \text{ L mol}^{-1} \text{ s}^{-1}$, meanwhile this rate constant for dimethyl itaconate (DMI) is about $20 \text{ L mol}^{-1} \text{ s}^{-1}$.^{32–35} To our knowledge, there exists no data about the amounts of k_p and termination rate constant (k_t) for homopolymerization of IA. How-



Scheme 1

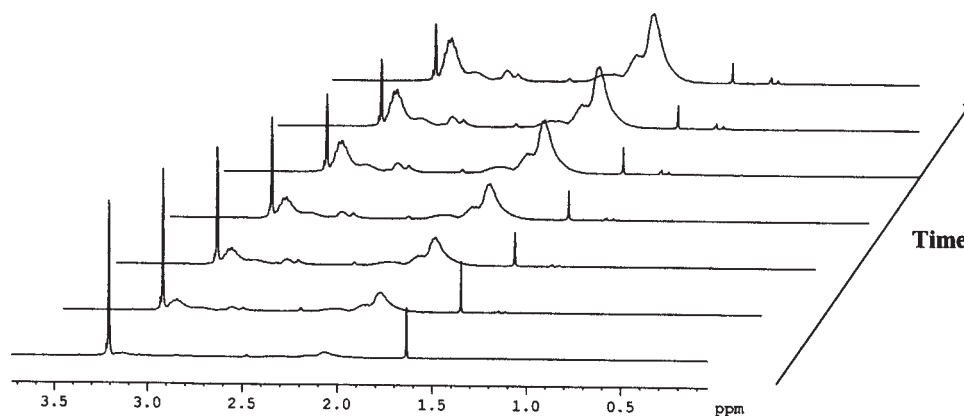


Figure 2 Expanded region of aliphatic protons for AN and IA in the produced copolymer, indicating the progress of copolymerization reaction with time.

ever, it is assumable that k_p and k_t for DMI and IA would be close to each other.³¹ Also k_p for AN could be predicted to be about 244 times greater than k_p for IA.

k_t value for homopolymerization of AN in DMSO at 25 and 50°C is 2.9×10^8 and 3.0×10^8 L mol⁻¹ s⁻¹,²⁹ respectively. From this data, it is clear that k_t is not almost sensitive to temperature. Hence, k_t for homopolymerization of AN in DMSO at 78°C will be close to 3.1×10^8 L mol⁻¹ s⁻¹. Value of k_t (purely disproportionation) for homopolymerization of DMI at 78°C has been reported to be 3.0×10^5 L mol⁻¹ s⁻¹.³² Therefore, k_t for AN is about 1033 times greater than that for IA. The comparison between k_p and k_t shows clearly that from pure AN toward pure IA in the feed composition, the decreasing in square root of k_t is less than k_p remarkably. Thus, it is expected that the polymerization rate decrease with increasing the amount of IA in the initial feed [see eq. (1)] as observed in Figure 4.

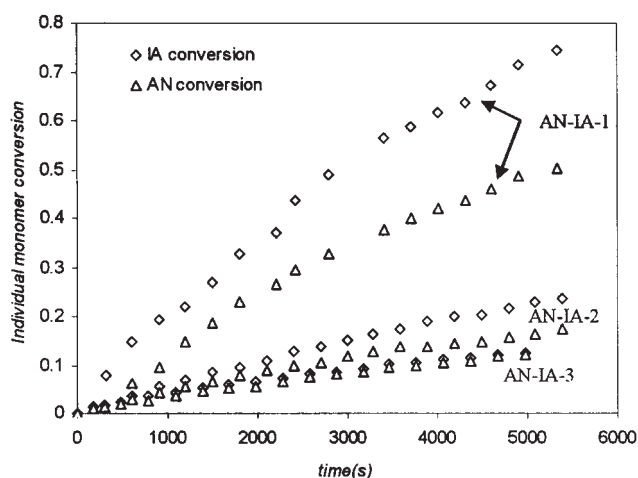


Figure 3 Individual monomer conversion versus reaction time for different mole fractions of IA in the initial feed of AN/IA copolymerization system.

The polymerization rate equation (R_p) at the steady-state condition (steady-state concentration of free radicals) is [eq. (1)]:

$$R_p = k_p[M][R^{\cdot}] = k_p[M] \left(\frac{f'k_d[I]}{k_t} \right)^{0.5} \quad (1)$$

where R_p : polymerization rate; k_p : average propagation rate constant; k_t : average termination rate constant; f' : initiator efficiency; k_d : decomposition rate constant for the initiator; $[R^{\cdot}]$: free-radical concentration; $[M]$: overall monomer concentration; $[I]$: initiator concentration.

Since the polymerization rate is proportional to $k_p/k_t^{0.5}$, a decrease in overall polymerization rate would be expected with the increase in the mole fraction of IA (f_{IA}) in the initial feed. For further investigation into the effect of f_{IA} on R_p (or equivalently on $k_p/k_t^{0.5}$), the linear part of the curves of

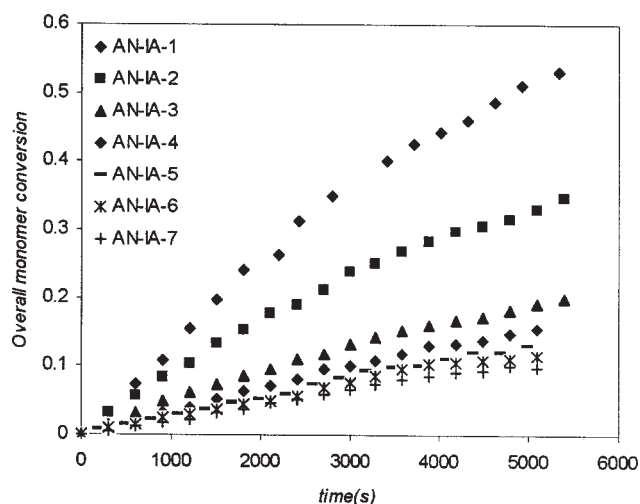


Figure 4 Overall monomer conversion as a function of time for various mole fractions of IA in the initial reaction mixture calculated by ¹H NMR data.

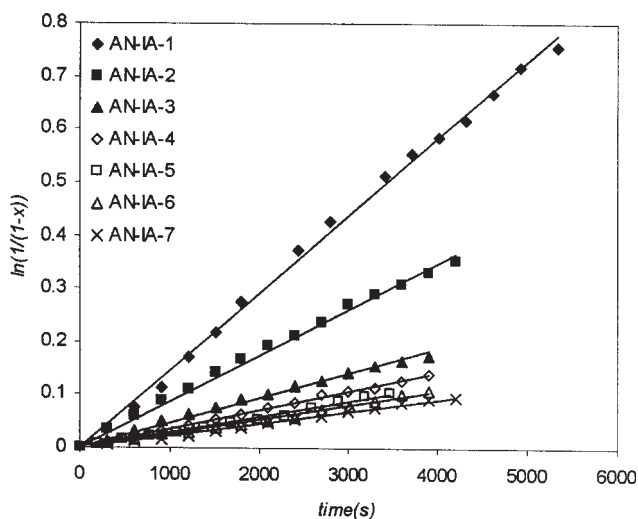


Figure 5 Dependency of $\ln [1/(1-x)]$ versus t plots on the mole fractions of IA in the initial monomer mixture.

overall monomer conversion versus time were plotted as the first-order curves [derived from integration of eq. (1)]:

$$\ln \left(\frac{1}{1-x} \right) = k_{\text{obs}} t \quad (2)$$

$$k_{\text{obs}} = k_p \left(\frac{f' k_d [I]}{k_t} \right)^{0.5} \quad (3)$$

where x is the overall monomer conversion and k_{obs} is the observed rate constant. k_{obs} could be obtained from the slope of the curve of $\ln [1/(1-x)]$ versus t . The corresponding plots have been shown in Figure 5.

It could be observed that increasing the mole fraction of IA in the initial feed has remarkable influence on the slope of the curve (i.e., k_{obs}). The decrease in k_{obs} becomes less pronounced after a certain concentration of IA. Since the efficiency of initiator (AIBN) and its concentration is known, $k_p/k_t^{0.5}$ could be calculated from eq. (3) and the experimental k_{obs} is obtained from Figure 5. Takenaka et al.³⁶ have studied homopolymerization of AN in DMSO- d_6 using AIBN up to complete conversion and found that f' for AIBN in this system is equal to unit up to 75% conversion (before β -scission of the primary radicals) and it is independent of initiator concentration. The maximum conversion in our experiments was about 53% and it is convincing to assume that f' equals to 1.

Kinetic of homopolymerization of AN in dimethyl formamide (DMF) and DMSO have been investigated at 40–60°C.³⁷ Initiation rate of polymerization has been determined for AN/AIBN/DMF at 40, 50, and 60°C and for AN/AIBN/DMSO at 50°C by inhibition method. Czajlik et al.³⁷ have concluded that

TABLE II
The Observed Polymerization Rate Constants (k_{obs}) and $k_p/k_t^{0.5}$ as a Function of Mole Fraction of IA in the Initial Feed

Sample	f_{IA}^0	k_{obs} (10^5) (s^{-1})	$k_p/k_t^{0.5}$ (10^2) ($L^{0.5} \text{mol}^{-0.5} s^{-0.5}$)
Pure AN	0	–	27.73 ^a
AN-IA-1	0.1245	14.569	17.76
AN-IA-2	0.2190	8.7484	10.27
AN-IA-3	0.4143	4.6956	5.26
AN-IA-4	0.4745	3.5490	3.87
AN-IA-5	0.5435	2.9424	3.11
AN-IA-6	0.6157	2.6561	2.66
AN-IA-7	0.7167	2.2712	2.21
Pure IA	1	–	2.00 ^a

^a Values obtained from the reported data.^{29–31}

$2f'k_d$ does not depend on monomer concentration and depends on the type of the solvent. $2f'k_d$ in DMSO is 10% less than that in DMF. The Arrhenius dependency of $2f'k_d$ on temperature for AN/AIBN/DMF system was calculated by using experimental data from Banfield radical inhibitor ($E_d = 30,272.73 \text{ cal mol}^{-1}$, $A = 5.6682 \times 10^{20} \text{ min}^{-1}$, correlation coefficient = 0.999, in which E_d is the activation energy of initiator decomposition and A is the frequency factor).³⁷ Then $2f'k_d$ for DMF at 78°C was found to be $1.3227 \times 10^{-4} \text{ s}^{-1}$. According to the above data, $2f'k_d$ for DMSO at 78°C was estimated to be $1.1904 \times 10^{-4} \text{ s}^{-1}$. If we consider $f' = 1$,³⁶ then k_d would be $5.95 \times 10^{-5} \text{ s}^{-1}$. The estimated k_d seems to be reasonable with regard to the reported k_d values for AN/AIBN/DMSO at 50 and 60°C, which were 1.325×10^{-6} ³⁶ and $2.0 \times 10^{-5} \text{ s}^{-1}$,³⁷ respectively.

$k_p/k_t^{0.5}$ value could be obtained with the above data and the initiator concentration (Table I). The calculated $k_p/k_t^{0.5}$ amounts have been listed in Table II and plotted in Figure 6 as a function of f_{IA} in the initial feed. Also the value of $k_p/k_t^{0.5}$ for homopolymer-

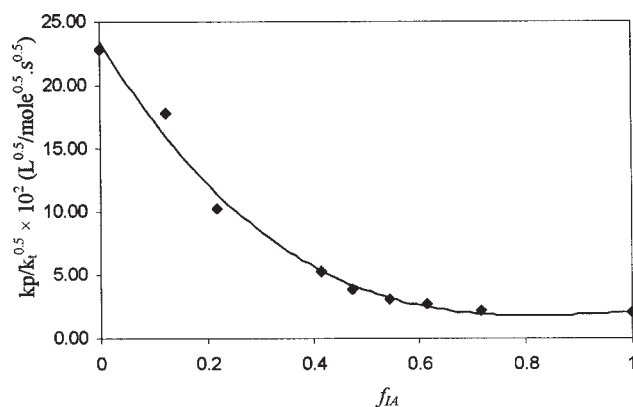


Figure 6 Plot of $k_p/k_t^{0.5}$ as a function of mole fraction of IA in the initial feed (solid curve is the best fitted curve to experimental data).

rization of AN in DMSO at 78°C was calculated to be about $2.77 \times 10^{-1} \text{ L}^{0.5} \text{ mol}^{-0.5} \text{ s}^{-0.5}$.^{29,30} This ratio for homopolymerization of IA in DMSO at 78°C has been reported to be $2.0 \times 10^{-2} \text{ L}^{0.5} \text{ mol}^{-0.5} \text{ s}^{-0.5}$.³¹ These values along with the experimental data have been given in Table II.

It could be observed from Figure 6 that $k_p/k_t^{0.5}$ decreases with the increase in the IA concentration, indicating that square root of k_t decreases less than k_p . In addition, Figure 6 shows that lowering in k_p with increasing the mole fraction of IA in the initial feed to about 0.40 is more sensed than the other ranges.

The variation in monomer composition with overall monomers conversion could be followed by on-line ¹H NMR spectroscopy. These compositions have been determined from individual conversions of AN and IA (Fig. 3) according to the following equation.³¹

$$f_{\text{AN}}(x) = \frac{n_0^{\text{AN}} - n_x^{\text{AN}}}{(n_0^{\text{AN}} - n_x^{\text{AN}}) + (n_0^{\text{IA}} - n_x^{\text{IA}})} \quad (4)$$

where

$$n_x^i = n_0^i x^i \quad (5)$$

n_0^i indicates the presence of mole monomer i in the initial feed, n_x^i gives the number of consumed moles of monomer i at the individual monomer conversion (x^i), and $f_i(x)$ represents the mole fraction of monomer i in the monomer mixture at the individual conversion x^i .

Figure 7 shows the experimental variation of monomer mixture composition versus overall monomer conversion for different amounts of IA in the

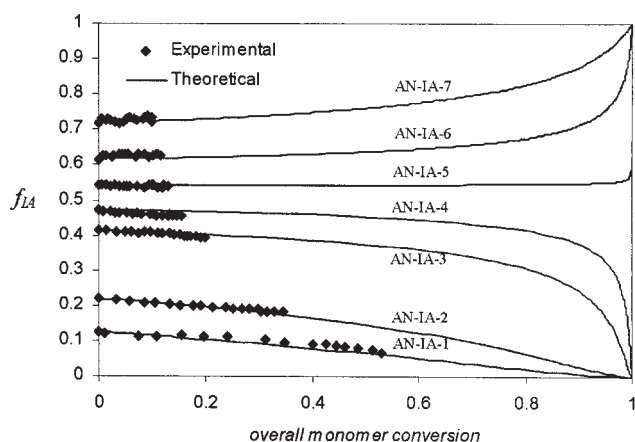


Figure 7 Experimental and theoretical changes in comonomer mixture composition versus overall monomer conversion for different amounts of IA in the initial reaction mixture (points: experimental data; dotted curves: theoretical data).

initial feed up to 53% overall monomer conversion. It could be observed that IA enters into the copolymer chain with higher rates than AN in the low mole fractions of IA in the initial feed. With increasing f_{IA} in the initial feed, this entrance rate decreases and at f_{IA} above 0.5435 becomes less than that of AN. It should be noted that changes in monomer mixture composition versus conversion for all mole fractions of IA in the initial feed is small.

Mao and Huglin³⁸ reported a method for the determination of monomer reactivity ratios that can be used for calculation of comonomer and copolymer compositions as a function of reaction progress. According to this method, whole copolymerization process is divided into many very small steps during which, the feed composition is assumed to be constant and the copolymer composition is calculated by the following equation:

$$F = \frac{r_{\text{St}} f^2 + f}{r_{\text{IA}} + f} \quad \text{where} \quad F = \frac{F_{\text{St}}}{F_{\text{IA}}} \quad \text{and} \quad f = \frac{f_{\text{St}}}{f_{\text{IA}}} \quad (6)$$

In eq. (6), f is the ratio of the molar concentrations of monomers St and IA in the feed ($[M_{\text{St}}]/[M_{\text{IA}}]$) or, equivalently, the ratio of their mole fractions (f_{St} and f_{IA}). F is in fact the ratio of instantaneous rates of consumption of the monomers ($d[M_{\text{St}}]/d[M_{\text{IA}}]$) and also expresses the instantaneous composition of the produced copolymer. If the conversion is sufficiently low, F represents the average copolymer composition. F_{St} and F_{IA} are the average values of the mole fractions of the monomer units in the copolymer chain.

After each step, the feed composition is readjusted by considering the amount of both monomers that have entered into the copolymer chain. The process is repeated to the complete conversions and then the copolymer composition is averaged over all steps.

The theoretical values of f_{IA} versus overall monomer conversion were calculated by Mao-Huglin method using reactivity ratios obtained at low conversions ($r_{\text{AN}} = 0.3754$, $r_{\text{IA}} = 0.4682$ with extended Kelen-Tudos²⁸). The corresponding plots are shown in Figure 7. There is a good fitting between experimental and theoretical data.

The copolymer composition can also be calculated according to the following equation:

$$F_{\text{IA}}(x) = \frac{n_x^{\text{IA}}}{n_x^{\text{IA}} + n_x^{\text{AN}}} \quad (7)$$

in which $F_{\text{IA}}(x)$ is the mole fraction of IA in the produced copolymer at conversion x .

A plot of experimental and theoretical changes in the copolymer composition versus overall monomer conversion for different amounts of IA in the initial feed has been shown in Figure 8. It should be noted

that experimental data of the copolymer composition versus overall monomer conversion for samples containing the mole fraction above 0.41 for IA in the initial feed have been omitted because of scattering of the data. However, the trend in experimental data was similar to theoretical ones. The comparison between Figures 7 and 8 reveals their good agreement and confirms the calculated reactivity ratios. This accurate prediction of the copolymer composition with progress of reaction was one of the main purposes in this study.

To obtain more information about the copolymer structure or monomer sequence distribution in the copolymer structure, the instantaneous copolymer composition curve with respect to IA (F_{IA} versus f_{IA}) has been plotted in Figure 9 due to the experimental data at low conversions presented in Table I. r_{AN} and r_{IA} are both less than unity and from the shape of the curve, it would be understood that the alternating copolymer structure is the predominant sequence distribution of the repeating units.

The unstable azeotropic point, in which $f_{IA} = F_{IA}$, could be observed in Figure 9. Composition of the feed and copolymer at this point could be obtained by the following equation.

$$f_{IA} = F_{IA} = \frac{1 - r_{AN}}{2 - r_{IA} - r_{AN}} \quad (8)$$

The previously calculated r_{IA} and r_{AN} by extended Kelen–Tudos method, which were 0.4682 and 0.3754 respectively,²⁸ were used for determination of copolymer composition at azeotropic point. Consequently, the composition at this point was calculated to be $f_{IA} = F_{IA} = 0.540$.

The instantaneous copolymer composition is [eq. (9)]:³⁹

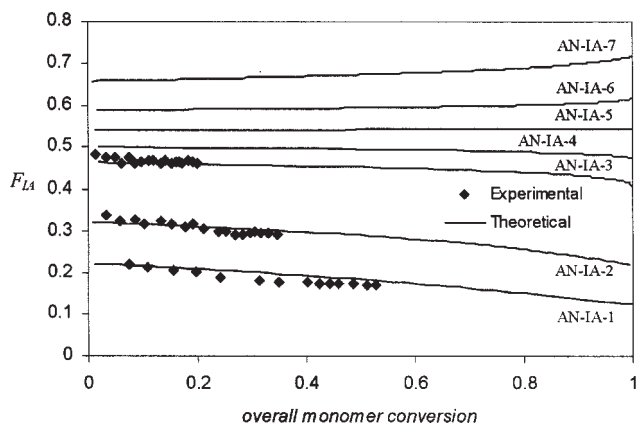


Figure 8 Copolymer composition as a function of overall monomer conversion for different amounts of IA in the initial feed (points: experimental data; dotted curves: theoretical data).

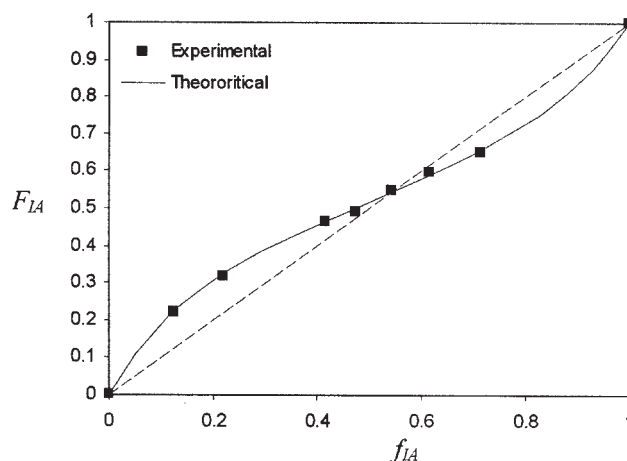


Figure 9 Variation of the copolymer composition (F_{IA}) as a function of monomer composition expressed as a mole fraction of IA in the feed (f_{IA}) for AN/IA copolymerization reaction (points: experimental data; solid curve: theoretical data calculated by terminal model equation).

$$F_{IA} = \frac{r_{IA}f_{IA}^2 + f_{IA}f_{AN}}{r_{IA}f_{IA}^2 + 2f_{IA}f_{AN} + r_{IA}f_{IA}^2} \quad (9)$$

According to the eq. (9) and with regard to the obtained reactivity ratios by extended Kelen–Tudos method (at low conversion), theoretical copolymer composition as a function of monomer composition in the initial feed has been plotted in Figure 9. As could be seen, the experimental and theoretical data conform to each other. These results confirm the accuracy of the calculated reactivity ratios with the emphasis that the terminal model could predict the copolymer composition well.

As a consequence when both the monomer reactivity ratios are less than unity, their tendency toward homopolymerization is less than copolymerization. But this does not mean that the rate of copolymerization must be certainly more than homopolymerization. Of course, there are some limitations for terminal model in prediction of rate constants and penultimate model shows more accuracy and precision.

CONCLUSION

Free-radical copolymerization of AN and IA was performed in DMSO- d_6 , using AIBN as initiator at 78°C. The kinetic studies of this system were investigated by on-line ^1H NMR spectroscopy. Individual and overall monomers conversion, compositions of monomer mixture, and copolymer were plotted against progress of reaction by using the obtained data from this spectroscopic technique. Overall polymerization rate constant for samples containing different mole fractions of monomers in the initial feed

was calculated from the overall monomer conversion versus time and $k_p/k_t^{0.5}$ was estimated subsequently. It was observed that $k_p/k_t^{0.5}$ value decreases with the increase in mole fraction of IA in the initial reaction mixture and this illustrates the reduction in copolymerization rate with increasing IA concentration in the initial feed. From our previously reported r_{IA} and r_{AN} , f_{IA} and F_{IA} were calculated as a function of monomer conversion by terminal model equations and they were comparable with those obtained experimentally. The instantaneous copolymer composition versus initial feed composition graph confirms the formation of alternating copolymer structure during copolymerization reaction.

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References

- Sen, K.; Hajir Bahram, S.; Bajaj, P. *J Macromol Sci Polym Rev* 1996, 36, 1.
- Nuyken, O.; Lattermann, G. In *Handbook of Polymer Synthesis, Part A*; Hricheldorf, H. R., Ed.; Marcel Dekker: New York, 1992; Chapter 4, p 284.
- Lewin, M.; Pearce, E. M. In *Fiber Chemistry, Handbook of Fiber Science and Technology, Vol. IV*; Marcel Dekker: New York, 1985.
- Tsai, J. S.; Lin, C. H. *J Appl Polym Sci* 1991, 42, 3039.
- Tsai, J. S.; Lin, C. H. *J Appl Polym Sci* 1991, 42, 3045.
- Tsai, J. S.; Lin, C. H. *J Mater Sci Lett* 1990, 9, 921.
- Tsai, J. S.; Lin, C. H. *J Appl Polym Sci* 1991, 43, 679.
- Mikolajczyk, T.; Krucinska, I. *Text Res J* 1989, 59, 536.
- Bajaj, P.; Paliwal, D. K.; Gupta, A. K. *J Appl Polym Sci* 1993, 49, 823.
- Ebdon, J. R.; Huckerby, T. N.; Hunter, C. *Polymer* 1994, 35, 250.
- Borbely, J. D.; Hill, D. J.; Lang, A. P.; O'Donnell, J. H. *Macromolecules* 1991, 24, 2208.
- Brar, A. S.; Kapur, G. S.; Dubey, S. K. *Eur Polym J* 1988, 24, 807.
- Brar, A. S.; Saini, A. K.; Kapur, G. S. *Polym J* 1989, 21, 689.
- Brar, A. S.; Dutta, K. *Macromol Chem Phys* 1998, 199, 2005.
- Brar, A. S.; Charan, S. *Polymer* 1996, 37, 2451.
- Brar, A. S.; Charan, S. *J Polym Sci Part A: Polym Chem* 1995, 33, 109.
- Bajaj, P.; Sen, K.; Hajir Bahrami, S.; *J Appl Polym Sci* 1996, 59, 1539.
- Li, P.; Shan, H.; *J Appl Polym Sci* 1995, 56, 877.
- Bajaj, P.; Sreekumar, T. V.; Sen, K. *J Appl Polym Sci* 2001, 79, 1640.
- Zhang, C.; Gilbert, R. D.; Fornes, R. E. *J Appl Polym Sci* 1995, 58, 2067.
- Bajaj, P.; Sreekumar, T. V.; Sen, K. *Polymer* 2001, 42, 1707.
- Plochocka, K. *J Macromol Sci Chem* 1981, C20, 67.
- Cowie, J. M. G.; Mc Ewan, I. J.; Yule, D. J. *Eur Polym J* 2000, 36, 1795.
- Mahdavian, A. R.; Abdollahi, M.; Bijanzadeh, H. R. *J Appl Polym Sci* 2004, 93, 2007.
- Mahdavian, A. R.; Zandi, M. *J Appl Polym Sci* 2003, 87, 2335.
- Mahdavian, A. R.; Zandi, M. *J Appl Polym Sci* 2003, 90, 1648.
- Mahdavian, A. R.; Abdollahi, M.; Mokhtabad, L.; Bijanzadeh, H. R.; Ziaee, F. *J Appl Polym Sci*, 2006, 101, 2062.
- Mahdavian, A. R.; Abdollahi, M.; Mokhtabad, L.; Ziaee, F. *J Macromol Sci A: Pure Appl Chem* 2006, 43, 1583.
- Brandrup, J.; Immergut, E. H.; Grulke, E. A. In *Polymer Handbook*, 4th ed.; Wiley: New York, 1999.
- Zetterlund, P.; Busfield, W.; Jenkins, I. *Macromolecules* 1999, 32, 8041.
- Barner-Kowollik, C.; Heuts, J. P. A.; Davis, T. P. *J Polym Sci Part A: Polym Chem* 2001, 39, 656.
- Otsu, T.; Yamagishi, K.; Matsumoto, A.; Yoshioka, M.; Watanabe, H. *Macromolecules* 1993, 26, 3026.
- Matsumoto, A.; Yamagishi, K.; Otsu, T.; *Eur Polym J* 1995, 31, 121.
- Otsu, T.; Yamagishi, K.; Yoshioka, M. *Macromolecules* 1992, 25, 2713.
- Yee, L. H.; Coote, M. L.; Chaplin, R. P.; Davis, T. P. *J Polym Sci Part A: Polym Chem* 2000, 38, 2192.
- Takenaka, M.; Johnson, A. F.; Kamide, K. *Polymer* 1994, 35, 3899.
- Czajlik, I.; Foldes-Bereznich, T.; Tudos, F.; Szakacs, S. *Eur Polym J* 1978, 14, 1059.
- Mao, R.; Huglin, M. B. *Polymer* 1993, 34, 1709.
- Mayo, F. P.; Lewis, F. M. *J Am Chem Soc* 1944, 66, 1594.