Kinetic Study of Radical Polymerization VI. Copolymer Composition and Kinetic Parameters for Coplymerization of Styrene-Itaconic Acid by On-Line 1H-NMR

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Kinetic Study of Radical Polymerization VI. Copolymer Composition and Kinetic Parameters for Coplymerization of Styrene-Itaconic Acid by On-Line ^{1}H-NMR

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Free radical solution copolymerization of styrene (St) and itaconic acid (IA) in dimethylsulfoxide-d₆ (DMSO-d₆) as the solvent and the use of 2,2′-azobisisobutyronitrile (AIBN) as the initiator at 78°C was investigated by an on-line ^{1}H-NMR spectroscopy technique. Individual monomer conversion vs. reaction time, which was calculated from the ^{1}H-NMR spectra data, was used to study the drift in monomer mixture composition vs. conversion. It was found that in general, both monomers were incorporated almost equally into the copolymer. However, when the mole fraction of IA was low, the tendency of IA toward incorporation into the copolymer chain was somewhat higher than St and by increasing the mole fraction of IA in the reaction mixture, the inverse tendency was observed. Overall monomer conversion as a function of time was calculated from individual monomer conversion data and used for the estimation of $k_p/k_t^{0.5}$ for various monomer mixture compositions. This ratio was decreased with increasing the amount of IA in the initial feed, indicating a decrease in the rate of copolymerization. Changes in the copolymer composition vs. overall monomer conversion were investigated experimentally from the NMR spectra. This was in good agreement with the changes in monomer mixture composition vs. reaction progress. Plotting the copolymer composition vs. initial monomer feed showed tendency of the system toward alternating copolymerization.

Keywords styrene, itaconic acid, radical copolymerization, ^{1}H-NMR, kinetics

Introduction

Copolymerization of styrene and itaconic acid may represent a possible candidate for the production of highly functionalized copolymers. IA is chosen as a comonomer because it

introduces an acid functionality. Furthermore, IA is readily available at low cost. It is obtained from renewable resources by fermentation with Aspergillus terrus (1). The polymerization of IA derivatives (especially its esters) has been studied extensively over the past decades (2–5). According to these investigations, IA only propagates slowly because of its sterically demanding nature. For example, its dimethyl ester has a propagation rate coefficient (k_p) of $7 \, \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at 20°C (6). It is very likely that IA has a k_p value similar to that of dimethyl ester, although no study on this matter currently exists. However, α-methylene group within IA could contribute to readily undergo chain transfer to a monomer, hopefully providing a high degree of end-group functionalization. For industrial applications, it is desirable to achieve molecular weight control and a high degree of end group functionality (featuring a variety of possible end group, e.g. acids, alcohols, or amines) via simpler polymerization technique such as conventional free radical polymerization. The design of copolymer with specific characteristics has always been a research field of both industrial and academic interest. Controlling polymerizations with respect to polydispersity, molecular weight and chemical composition distribution (in the case of copolymerization) can be achieved if the kinetics of (co)polymerization is known.

NMR spectroscopy has proven to be one of the most important techniques for studying copolymer composition and determination of monomer reactivity ratios (7–13). On-line ^{1}H-NMR monitoring of reaction progress has been successfully used for kinetic studies of free radical homo- and copolymerization (14–18). Kowollik et al. applied this technique in free radical copolymerization of styrene/itaconic acid system and derived the overall rate coefficient of copolymerization. These authors did not achieve determination of the copolymer composition and consequently, monomer reactivity ratios. Here, we have determined the copolymer composition successfully. Discussion on the determination of monomer reactivity ratios has been reported elsewhere (17). The present research focuses on gathering kinetic information of the styrene/itaconic acid copolymerization system with respect to overall rate coefficient of copolymerization, changes in the reaction mixture composition and specifically the copolymer composition vs. overall monomer conversion.

Experimental

Materials

Styrene monomer from Merck Chemical Co. (Darmstadt, Germany) was washed three times with a 5% sodium hydroxide followed by washing with distilled water three times to remove its inhibitor and then dried over $CaCl_2$. Analytical grade itaconic acid and 2,2′-azobisisobutyronitrile (AIBN) were obtained from Merck Chemical Co (Darmstadt, Germany) and used without further purification. DMSO-d_6 as solvent was purchased from ARMAR Chemicals (Dottingen, Switzerland).

Equipment

All ^{1}H-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 with 5 mm in diameter containing the reaction mixture was inserted into the sample chamber).

Copolymerization Reaction

The copolymerization reactions were conducted in the NMR tubes (5 mm in diameter). The prepared solutions in NMR tubes were deaerated with nitrogen gas (99.9% purity) to exclude oxygen from the solutions, which acts as a retardant in radical polymerization reactions. Sample preparation and deaeration were 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 of the data have been listed in Table 1.

Results and Discussion

Individual and overall conversion of monomers St and IA as a function of reaction time were measured by analysis of ^{1}H-NMR spectra through vinylic proton peak areas of St and IA. Method and equations for this analysis have been reported in our previous article (17). The copolymer composition was calculated and then used for determination of monomer reactivity ratios.
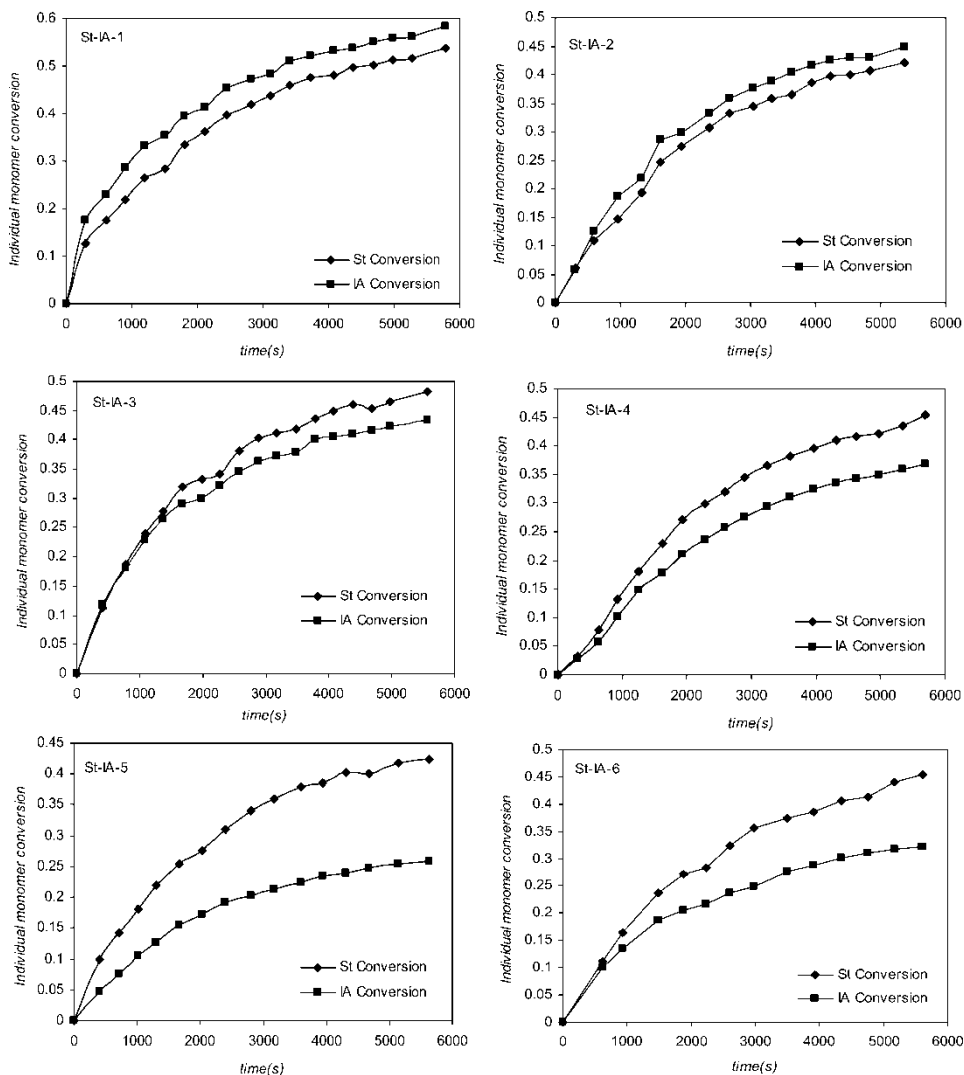
Figure 1 shows the individual monomer conversions vs. time for the copolymerization system containing various mole fractions of monomers in the initial feed. The reactions were done at 78°C and the concentration of initiator in all cases was in the range of 0.041–0.075 M. At this reaction temperature, the half-life time of initiator (AIBN) was about 5400 sec. (14, 19). All reactions were carried out up to about 5400 sec. and thus, the initiator concentration can be assumed to be constant in the initial stage of polymerization. When the mole fraction of IA in the initial monomer feed was lower than 0.51, IA was incorporated into the copolymer at a somewhat higher rate than St. In mole fraction of 0.51 for IA, both monomers were incorporated into the copolymer at almost the same rate. On the other hand, St/IA system shows an azeotropic point in mole

Table 1
Concentration of components in the initial reaction mixture^{a,b}

Samples	f_{IA}^0	[AIBN] (mol · lit^{-1})
St-IA-1	0.2913	0.04138
St-IA-2	0.4113	0.04346
St-IA-3	0.5070	0.07471
St-IA-4	0.6018	0.05484
St-IA-5	0.7280	0.05168
St-IA-6	0.7557	0.05450

^{a}The reaction temperature was set at 78°C.
^{b}Weight ratio of monomer to solvent in all experiments was about 1 : 1.

Figure 1. Individual monomer conversion vs. reaction time for different mole fractions of IA in initial feed of St/IA copolymerization system.

fraction of about 0.51 for IA. Above this, the rate of incorporation of St into the copolymer was higher than IA and speeds up with increasing the mole fraction of IA in the feed. This result was different from those obtained by Kowollik et al. (14). The differences come from the lower amount of IA in the initial feed. They have reported that both monomers are copolymerized with about the same rate but our observations reveal that at such conditions, IA is incorporated at a somewhat lower rate than St.

Total monomer conversion as a function of reaction time for different mole fractions of IA in the initial reaction mixture has been shown in Figure 2. It is clear that the rate of copolymerization reaction decreases considerably by increasing the amount of IA in the initial feed due to the reduction of slope in the individual monomer conversion curves. The results are similar to the previous one (14), but the total higher rate is attributed to
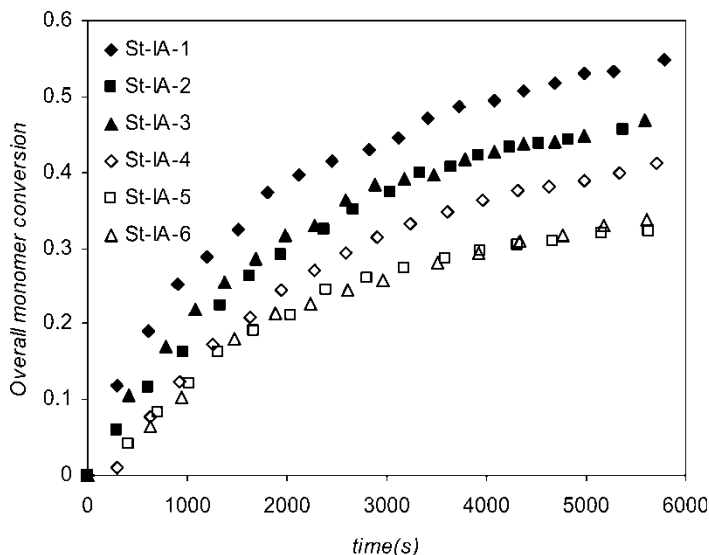
Figure 2. Overall monomer conversion as a function of time curves for various mole fractions of IA in the initial reaction mixture calculated by ^{1}H-NMR data.

the higher concentration of the initiator in this study. These observations, i.e., decrease in polymerization rate with increasing mole fraction of IA in the initial feed, were predictable with the reported data on propagation and termination rate coefficients for homopolymerization of St (20, 21) and IA derivatives (2–4,6). The propagation rate coefficient for styrene at 78°C is close to $606 \, L \cdot mol^{-1} \cdot s^{-1}$, whereas the corresponding value reported for dimethyl itaconate (DMI) is close to $20 \, L \cdot mol^{-1} \cdot s^{-1}$. Unfortunately, there is no k_p data available for IA in the literature. However, it is assumable that the amount of k_p for DMI is close to that of IA (14). There is a difference in k_p of approximately a factor of 30 between St and IA.

With respect to the average termination rate coefficient (k_t), a large difference between the respective values for St and IA may be also expected. The k_t value (purely bimolecular combination) reported for pure St bulk polymerizations at 78°C is close to $1.2 \times 10^8 \, L \cdot mol^{-1} \cdot s^{-1}$ (14, 21), whereas k_t (purely disproportionation) for DMI has been reported to be near to $3.0 \times 10^5 \, L \cdot mol^{-1} \cdot s^{-1}$ (2, 14). Therefore, the difference in k_t between pure St (in bulk) and pure IA may be close to a factor of 400.

On-line ^{1}H-NMR based kinetic studies are carried out, usually up to a long reaction time (14, 15). We tried to keep sufficient data as short as possible. Hence, the concentration of AIBN was adjusted to limit the reaction time to about 3 h. It is necessary to perform the polymerization reaction at isothermal conditions to obtain the most reliable kinetic data. Since the polymerization rate was relatively high in these experiments, the isothermal conditions may not remain steady completely. Thus, the exact temperature of the reaction solution may deviate from the probe temperature. However, since the determination of monomer reactivity ratios, monomer feed composition, and copolymer composition were the main purposes of this article, it is expected that such a deviation in reaction temperature does not affect the above mentioned parameters remarkably.

Overall rate coefficient and $k_p/k_t^{0.5}$ the for St/IA system at 78°C have been previously reported (14). These kinetic parameters were also determined in this study to be evidence

for non-isothermal conditions in our reactions. The rate of polymerization reaction in the steady state condition (steady concentration of free radical) is expressed as below:

$$R_p = k_p[M]\left(\frac{R_i}{2\,k_t}\right)^{1/2} \tag{1}$$

in which R_p is the polymerization rate, R_i is the initiation rate, k_t is (average) rate coefficient for termination, k_p is (average) rate coefficient for propagation, and $[M]$ is the overall concentration of monomers.

Since the rate of polymerization (or equivalent slopes of curves in Figure 2) is proportional to the $k_p/k_t^{0.5}$, it is clear that by variation of mole fraction of IA in the feed from 1 to 0, a total decrease in the rate of polymerization and thereby, decrease in overall rate constants ($k_p/k_t^{0.5}$) is expected. In order to investigate the effect of St amounts in the reaction mixture on the rate of polymerization (and then on the $k_p/k_t^{0.5}$ ratio), the linear parts of overall monomer conversion vs. time were considered as the first-order curves (that was derived by integration from Equation (1) via the following equation.

$$\ln\left(\frac{1}{1-x}\right) = k_{obs} \times [I]^{0.5} \times t \quad \text{where} \quad k_{obs} = k_p\left(\frac{f' \cdot k_d}{k_t}\right)^{1/2} \tag{2}$$

x is the total monomer conversion, f' is the efficiency of initiator, k_d is the rate constant for initiator dissociation, $[I]$ is the concentration of initiator and k_{obs} is the observed overall polymerization rate constant. k_{obs} could possibly be obtained from the slope of curve of $\ln(1/(1-x))$ vs. $[I]^{0.5} \times t$. The corresponding curves are shown in Figure 3.

The straight lines in Figure 3 were obtained through fitting Equation (2) with the experimental data. Accordingly, k_{obs} decreases with increasing the mole fraction of IA in the initial feed. With the further addition of IA, the decrease in k_{obs} become less
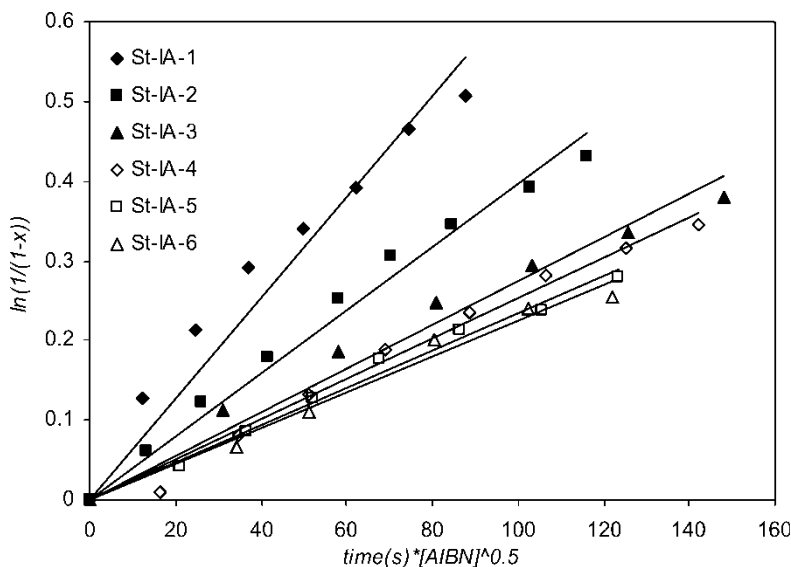
Figure 3. Dependency of $\ln(1/(1-x))$ to $[I]^{0.5} \times t$ at different mole fractions of IA in the initial monomer mixture.

pronounced. The values of $k_p/k_t^{0.5}$ were calculated from the experimental data of k_{obs} along with the values reported for f' (0.7) and k_d ($8.87 \times 10^5\,\text{s}^{-1}$) at 78°C for AIBN (14, 19, 22) (Table 2). $k_p/k_t^{0.5}$ as a function of mole fraction of IA in the initial monomer feed has been plotted in Figure 4. It is clear that this ratio decreases with increasing the mole fraction of IA in the initial feed. Similar trend has been observed before [14], but $k_p/k_t^{0.5}$ values obtained in this study are greater. This could be anticipated to the non-isothermal condition in our experiments. The faster the polymerization rate, the higher the generation of heat during polymerization and thereby the thermal equilibrium is set up later. That is, the real reaction temperature is higher than the probe temperature. This has a positive effect on the rate coefficients especially k_p and k_d. This is the source of scattering of the data from the straight line in Figure 3.

Changes in monomer mixture composition vs. overall monomer conversion could be followed by on-line ^{1}H-NMR spectroscopy. These data were calculated through individual conversion of monomers St and IA (Figure 1) based on the following equation (17):

$$f_x^{St} = \frac{A_0^{St} - A_x^{St}}{(A_0^{St} - A_x^{St}) + (A_0^{IA} - A_x^{IA})} \quad \text{where} \quad A_x^i = A_0^i \times x^i \tag{3}$$

f_x^{St} is the mole fraction of St in the reaction mixture at total conversion of x. The A_0^i value shows the intensity of one (vinylic) proton resonance from comonomer i in the first spectrum of each sample (or equivalently, moles of comonomer i in the initial reaction mixture), A_x^i shows the intensity of one (aliphatic) proton resonance of consumed monomer i at total conversion x (that is proportional to the consumed moles of monomer i at total conversion x) and x^i represents the individual conversion of monomer i. In fact, $A_0^{St} - A_x^{St}$ represent the intensity of the one proton of residual (unreacted) monomer i.

Figure 5 shows the experimental and theoretical changes of comonomer composition in the reaction mixture vs. overall monomer conversion for different amounts of IA (or St) in the initial feed. Theoretical calculation of comonomer mixture composition vs. conversion will be discussed below. It is obvious that the rate of incorporation of IA into the copolymer chain was higher than St for lower amounts of IA in the initial feed. With increasing the amount of IA, its tendency toward incorporation into the copolymer decreased and at mole fractions of IA above 0.51, the rate of incorporation of IA into the copolymer was lower than St. These results were in good agreement with individual

Table 2
The observed overall rate of polymerization (k_{obs}) and ratio $k_p/k_t^{0.5}$ for copolymerization of St/IA at 78°C

Samples	f_{IA}^0	$k_{obs} \times 10^3$ (mol$^{0.5} \cdot l^{-0.5} \cdot$ sec)	$k_p/k_t^{0.5}$ (L$^{0.5} \cdot$ mol$^{-0.5} \cdot$ sec$^{0.5}$)
St-IA-1	0.2913	6.362	0.8074
St-IA-2	0.4113	3.970	0.5038
St-IA-3	0.5070	2.755	0.3496
St-IA-4	0.6018	2.536	0.3218
St-IA-5	0.7280	2.344	0.2975
St-IA-6	0.7557	2.239	0.2842
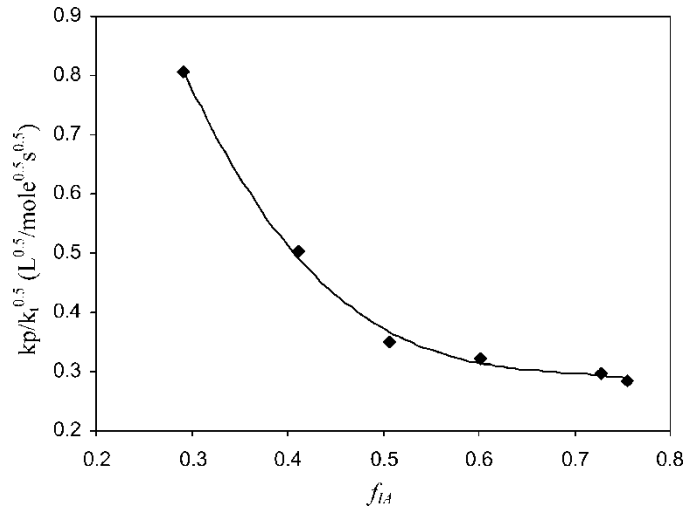
Figure 4. Plot of the $k_p/k_t^{0.5}$ as a function.

monomer conversion versus time curves. It should be noted that the total changes in comonomer mixture composition with progress of reaction is small.

Mao and Huglin (23) reported a method for determination of monomer reactivity ratios that can be used for calculation of comonomer and copolymer compositions as a

Figure 5. Experimental and theoretical changes in comonomer mixture composition vs. overall monomer conversion for different amounts of IA in the initial reaction mixture (points: experimental data; dash lines: theoretical data).

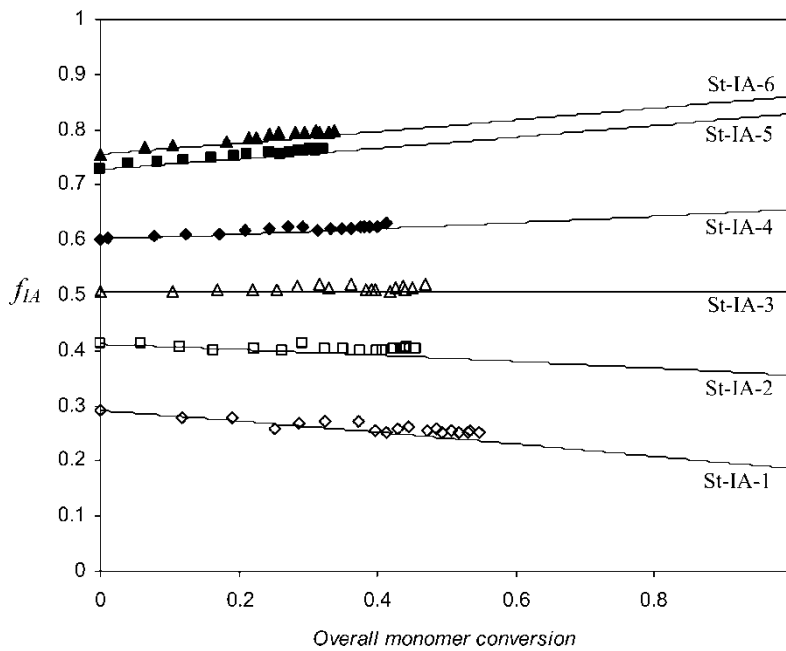function of reaction progress. According to this method, the entire copolymerization process is divided into many very small steps during which, the feed composition is assumed to be constant and the copolymer composition is calculated by the following equation:

$$F = \frac{r_{St}f^2 + f}{r_{IA} + f} \quad \text{where} \quad F = \frac{F_{St}}{F_{IA}} \quad \text{and} \quad f = \frac{f_{St}}{f_{IA}} \tag{4}$$

In Equation (4), f is the ratio of the molar concentrations of monomers St and IA in the feed ($[M_{St}]/[M_{IA}]$) 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 ($d\,[M_{St}]/d\,[M_{IA}]$) 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.

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 several times to reach the complete conversions and then the copolymer composition is averaged over all steps.

The theoretical values of f_{IA} vs. overall monomer conversions were calculated by the Mao-Huglin method using reactivity ratios obtained at low conversions ($r_{St} = 0.35$, $r_{IA} = 0.37$ with the Tidwell-Mortimer method (17)). The corresponding plots are shown in Figure 5. There is a good fit between experimental and theoretical data. By knowing the individual conversion of monomers, the copolymer composition can be also calculated according to the following equation:

$$F_x^{St} = \frac{A_x^{St}}{A_x^{St} + A_x^{IA}} \tag{5}$$

in which F_x^{St} is the mole fraction of St in the growing copolymer chain at conversion x. The experimental changes in the copolymer composition as a function of total monomer conversion for different amounts of IA in the initial feed up to 55% conversion are shown in Figure 6. It is clear that the trend of changes in the copolymer composition is similar to that of the monomer mixture composition.

Copolymer composition vs. overall monomer conversion for St/IA system has formerly been investigated using monomer reactivity ratios calculated from Q-e scheme ($r_{St} = 0.287$, $r_{IA} = 0.105$) (14). Since both r_{St} and r_{IA} are smaller than unity, it is expected that the monomer mixture and copolymer compositions show azeotropic composition. However, in the earlier study (14), this behavior has not been observed in the cases of experimental changes in monomer mixture composition vs. overall monomer conversion. Thus, monomer reactivity ratios from the Q-e scheme could not be used for investigation of the copolymer composition. Previously, these reactivity ratios for St/IA system were calculated experimentally by us (17). These results are applicable to predict the copolymer composition as a function of overall monomer conversion accurately. The correct prediction of copolymer composition during the progress of reaction was one of the main purposes of this study.

To gain better insight into the structure of the produced copolymer, instantaneous copolymer composition vs. initial monomer composition has been plotted in Figure 7 according to the obtained data from on-line ^{1}H-NMR spectroscopy listed in Table 3 (17). The experimental data of F_{IA} vs. f_{IA} at low conversions were fitted to the
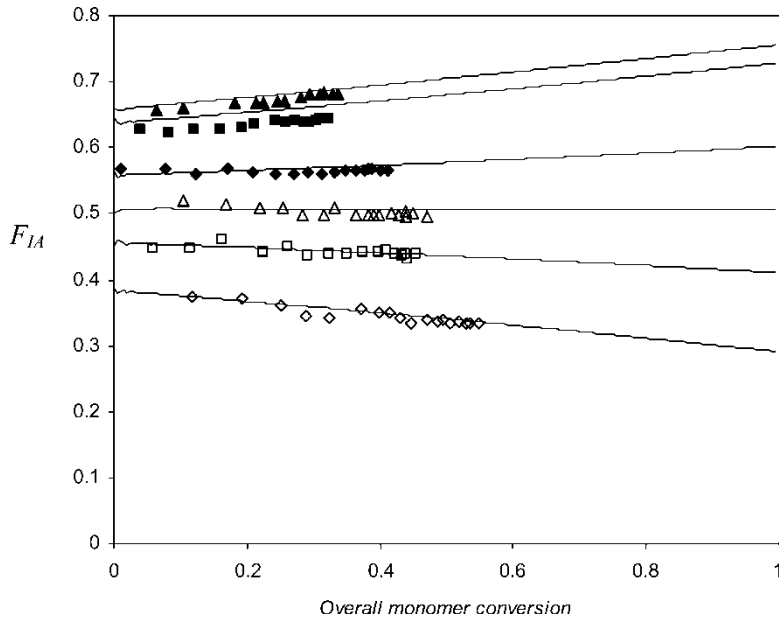
Figure 6. Copolymer composition as a function of overall monomer conversion for different amounts of IA in initial feed (points: experimental data; dash lines: theoretical data).

Mayo-Lewis equation (Equation (6)) (24):

$$F_{IA} = \frac{r_{IA}f_{IA}^2 + f_{IA}f_{St}}{r_{St}f_{St}^2 + 2f_{St}f_{IA} + r_{IA}f_{IA}^2} \tag{6}$$
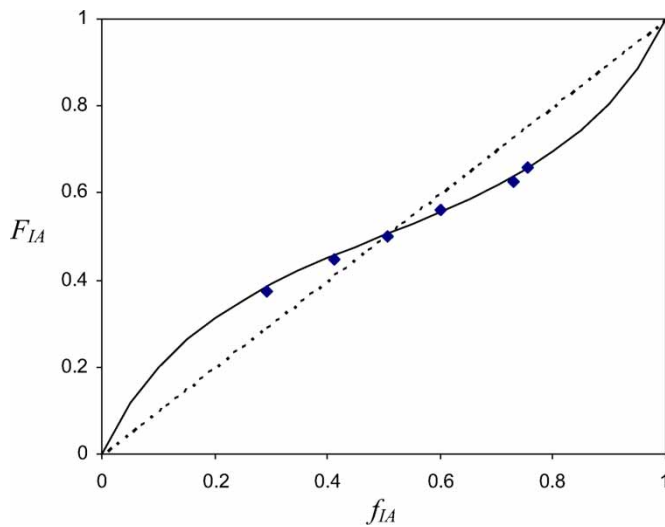
Figure 7. Variation of copolymer composition (F_{IA}) as a function of monomer composition in feed (f_{IA}) for itaconic acid (points: experimental data; dash lines: theoretical data calculated by terminal model equation) of mole fraction of IA in the initial feed.

Table 3
Mole fraction of IA in the initial feed and copolymer chain
for different samples at low conversion

	f_{IA}^0	F_{IA}	Conversion (mol%)
St-IA-1	0.2913	0.3743	14.4
St-IA-2	0.4113	0.4460	11.5
St-IA-3	0.5070	0.4995	11.6
St-IA-4	0.6018	0.5610	13.7
St-IA-5	0.7280	0.6264	14.6
St-IA-6	0.7557	0.6565	11.5

An optimum fit was obtained by using low conversion reactivity ratios (Tidwell-Mortimer method (17)), which means that the composition of this copolymerization system conforms to the terminal model. From monomer reactivity ratios (r_{St} and $r_{IA} \approx 0.35$), it is evident that at equal monomer concentrations, the adduct radical of either monomer is about 3 times more likely to react with the other monomer relative to its own monomer. This would indicate a random copolymer structure with a strong tendency toward alternation. Therefore, long blocks of homopolymers are not expected to any extent in the copolymers except at feed ratios far from 1 (i.e., far from azeotropic composition). This conclusion coincides with Figure 7, which graphically shows this behavior. Compositions of monomer feed and copolymer at azeotropic point (i.e., at point $F_{IA} = f_{IA}$) are represented by the following equation:

$$F_{IA} = \frac{1 - r_{St}}{2 - r_{IA} - r_{St}} \tag{7}$$

From known reactivity ratios ($r_{St} = 0.35$, $r_{IA} = 0.37$ with the Tidwell-Mortimer method (17)), composition of the azeotropic point was calculated to be 0.5078. This azeotropic composition is compatible with both the comonomer mixture and composition vs. overall monomer conversion curves in Figures 5 and 6, respectively.

Conclusions

Free radical solution copolymerization of St and IA was performed in DMSO-d_6 as a solvent in the presence of AIBN as an initiator at 78°C. Kinetics of polymerization was investigated by on-line ^{1}H-NMR spectroscopy. Individual and overall monomer conversions, mole ratio of St to IA in the reaction mixture *(f)* and in the copolymer chain *(F)* vs. progress of reaction were measured from ^{1}H-NMR spectra. It was found that by increasing the amount of IA in the initial feed, the rate of incorporation of IA into the copolymer chain was decreased and thereby St was incorporated into the copolymer with a higher rate. Overall monomer conversion vs. time decreased with increasing the mole fraction of IA in the initial feed. This was expected from propagation and termination rate coefficients of homopolymerizations of St and IA. Overall rate constant of the polymerization reaction was calculated by overall monomer conversion vs. time data and then $k_p/k_t^{0.5}$ was estimated. This ratio decreased with increasing the amount of IA in the initial monomer feed, indicating a decrease in the rate of polymerization

reaction. Changes in reaction mixture and copolymer compositions as a function of overall monomer conversion were determined experimentally and theoretically. The results were in good agreement with each other. This indicates that the terminal model equations, along with monomer reactivity ratios calculated by on-line ^{1}H-NMR data can be used for accurate prediction of copolymer composition. Instantaneous copolymer composition curve showed a tendency of the system toward producing alternating copolymer structure.

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