

Kinetic Study of Radical Polymerization. IV. Determination of Reactivity Ratio in Copolymerization of Styrene and Itaconic Acid by $^1\text{H-NMR}$

Ali Reza Mahdavian,^{1,*} Mahdi Abdollahi,^{1,**} Leila Mokhtabad,¹ Hamid Reza Bijanzadeh,²
Farshid Ziaee¹

¹Polymer Science Department, Iran Polymer and Petrochemical Institute, Tehran, Iran

²Chemistry Department, Tarbiat Modares University, Tehran, Iran

Received 8 June 2005; accepted 13 November 2005

DOI 10.1002/app.23795

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Here, online $^1\text{H-NMR}$ spectroscopy has been successfully applied to investigate the kinetic parameters of radical copolymerization of styrene (St) and itaconic acid (IA). This technique was used because it allowed us to individually map out the monomer conversions of St and IA during the course of the polymerization at various conversions. This was possible because the individual contributions to the overall monomer conversion from St and IA could be measured through their nonoverlapping vinylic proton signals. The results of monomer conversion during the time in the corresponding $^1\text{H-NMR}$ spectra was the basis of our analysis to determine the reactivity ratios of St and IA

in the solution and radical copolymerization reaction by several methods. In addition to linear least-squares methods, such as Finemann–Ross, inverted Finemann–Ross, Mayo–Lewis, Kelen–Tudos, extended Kelen–Tudos, and Mao–Huglin, a nonlinear least-square method (Tidwell–Mortimer) was used for this purpose, at low conversions. Extended Kelen–Tudos and Mao–Huglin were applied to determine the reactivity ratio values at high conversions too.
© 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2062–2069, 2006

Key words: radical copolymerization; $^1\text{H-NMR}$; reactivity ratio; solution polymerization

INTRODUCTION

Itaconic acid (IA) is one of the monomers, which is readily available at low cost. It is obtained from renewable resources by fermentation with *Aspergillus terreus*.¹ The commercial availability of IA gives it a clear advantage over monomers that have to be synthesized via a multiple-step reaction sequence.

The presence of carboxylic acid groups in the structure of IA is another advantage of this monomer. This could help in designing copolymers with specific characteristics, which is a hot research field in both industrial and academic fields.

In another point of view, controlling copolymerization reactions with respect to polydispersity and molecular weight by some techniques, such as atom transfer radical polymerization (ATRP) or reversible addition fragmentation chain transfer (RAFT), is of

great importance.^{2–4} Although these techniques allow for excellent molecular weight control, they suffer from controlling the microstructure and sequences of the repeating units in the polymeric chain. To our knowledge, no report could be found in the literature about the successful copolymerization of IA or its ester derivatives with styrene (St) via ATRP or RAFT processes.

Fordyce and Ham reported the polymerization of St and IA in 1,4-dioxane.⁵ Also, Barner-Kowollik et al. have published an extensive article about this copolymerization reaction and calculation of reactivity ratios by using Q,e-scheme.⁶ Although what they have proposed is applicable for this polymerization, DMF and DMSO are more suitable because of their better ability to dissolve IA and its corresponding copolymer.

The choice of IA is advantageous, as it represents a highly functionalized copolymeric material with carboxylic acid pendant groups.

There are some precautions about the polymerization of IA. The α -methylene group within IA could readily undergo chain transfer to a monomer and providing a high degree of end-group functionalization. Furthermore, IA propagates slowly by itself because of its sterically demanding nature. For example, its dimethyl ester has a propagation rate coefficient (k_p) of $7 \text{ mol L}^{-1} \text{ s}^{-1}$ at 20°C .⁷ Also it has been shown that $k_p/k_t^{0.5}$ varies from 5.2×10^{-2} for pure St to $2.0 \times 10^{-2} (\text{mol L}^{-1} \text{ s}^{-1})^{0.5}$ for pure IA.⁶

*Correspondence to: A. R. Mahdavian (a.mahdavian@ippi.ac.ir).

**Present address: Faculty of Engineering, Polymer Engineering Department, Tarbiat Modares University, P.O. Box 14965/115, Tehran, Iran.

Contract grant sponsor: TWAS; contract grant number: 01–094 RG/CHE/AS.

Contract grant sponsor: Iran Polymer and Petrochemical Institute.

Despite a large number of examples of the failure of many other 1,1-disubstituted ethylenes to produce high polymers because of a low ceiling temperature,⁸ dialkyl itaconates readily polymerize by radical polymerization.^{1,9,10} Their polymerization relativities, such as polymer yields and molecular weights, depend on the structure of the alkyl substituents.^{11,12}

In 1959, Marvel and Shepherd demonstrated that the molar masses of the resulting polymers of dialkyl esters of IA were, however, significantly lower than those of the structurally similar esters of methacrylic acid.¹³ They suggested that this could be due to the chain transfer to monomer as a result of the presence of allylic hydrogen atoms in the itaconate monomers.

Monomer reactivity ratios are important quantitative values to predict the copolymer composition for any starting feed in batch, semibatch, or continuous reactors and to understand the kinetic and mechanistic aspects of copolymerization.

Monomer reactivity ratios are generally determined at low conversion. In the classic terminal model of copolymerization, it has been suggested that, for a given pair of monomers, the instantaneous copolymer composition is a function of instantaneous feed only.^{14,15}

Among several procedures available to determine monomer reactivity ratio, the methods of Mayo–Lewis,¹⁴ Finemann–Ross,¹⁶ inverted Finemann–Ross,¹⁷ Kelen–Tudos,¹⁸ extended Kelen and coworkers,^{19–21} Tidwell–Mortimer,²² and Mao–Huglin²³ are extensively used for the determination of monomer reactivity ratios at low conversions. Extended Kelen–Tudos (K-T) and Mao–Huglin (M-H) methods are applicable for the manipulation of high conversion data.

¹H-NMR spectroscopy has proven to be one of the most informative techniques for the investigation of copolymer composition.²⁴ The online ¹H-NMR technique has been successfully applied by us to study the kinetics of radical polymerization previously.²⁵ In this study, ¹H-NMR spectroscopy was used because it allowed us to individually map out the monomer conversions of St and IA during the course of the polymerization up to medium monomer conversions. This was possible because the individual contributions to the overall monomer conversion from St and IA could be measured through their nonoverlapping vinylic proton signals.

There were no absorptions of the generated copolymer material in the vinylic proton region, which would invalidate the kinetic analysis.

EXPERIMENTAL

Materials

St monomer from Merck Chemical Co. (Darmstadt, Germany) was washed three times with 5% sodium hydroxide, followed by washing three times with dis-

TABLE I
Mole Fractions of Each Monomer for Different Samples^{a,b}

	Itaconic acid	Styrene
St-IA-1	0.71	0.29
St-IA-2	0.59	0.41
St-IA-3	0.49	0.51
St-IA-4	0.40	0.60
St-IA-5	0.27	0.73
St-IA-6	0.24	0.76

^a The polymerization temperature was set at 78°C.

^b The amount of AIBN was 0.6% relative to the total amount of monomers for all the samples.

tilled water to remove its inhibitor, and then dried over CaCl₂. Analytical grade IA and 2,2-azobisisobutyronitrile were obtained from Merck chemical Co. and used without further purification. DMSO-*d*₆ (as solvent) was purchased from ARMAR Chemicals (Dottingen, Switzerland).

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, with 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 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 15°C to inhibit the 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 I.

RESULTS AND DISCUSSION

In continuum to our previous research on kinetic study of radical polymerization,^{25–27} we have developed the ¹H-NMR technique for copolymerization reaction and the determination of reactivity ratios in such systems. The advantageous and disadvantageous application of this method has been discussed earlier.²⁵

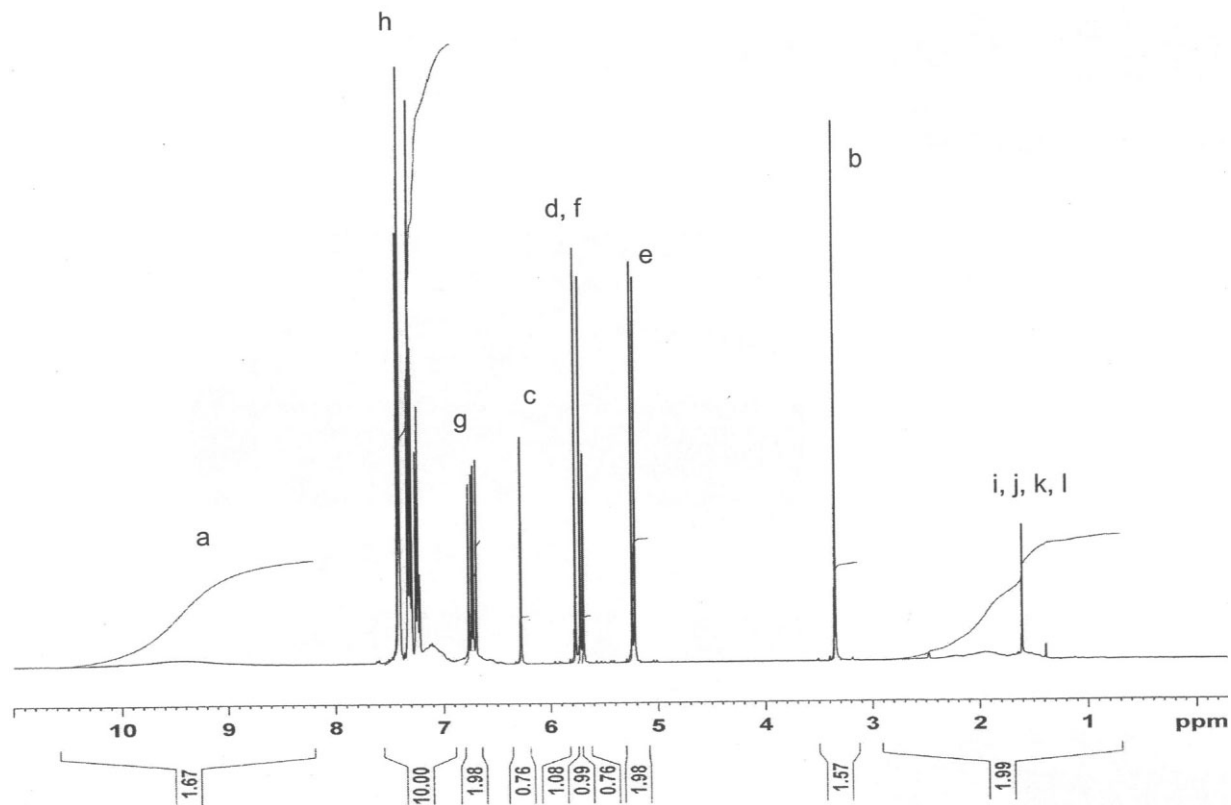


Figure 1 A typical spectrum of St-IA copolymer and unreacted corresponding monomers.

Here, a $^1\text{H-NMR}$ spectrum of a mixture of St and IA and also its corresponding copolymer have been shown in Figure 1. The assignment of each proton in the monomer and copolymer chain (Scheme 1) was carried out perfectly.

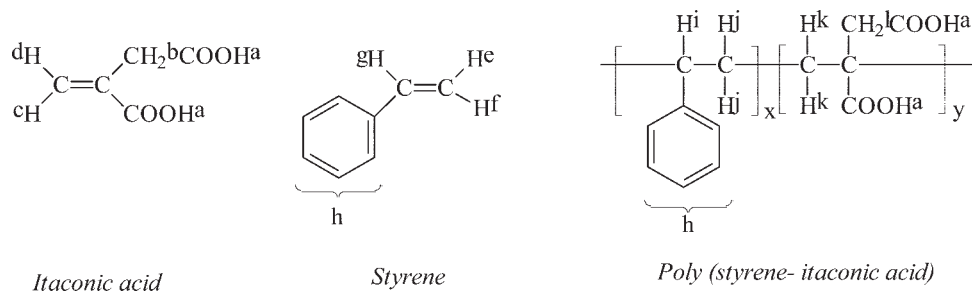
H_c and H_e were considered as characteristic peaks of IA and St for following the conversion of the copolymerization reaction, respectively. H_c appears at 6.3 ppm as a singlet, and H_e could be found at 5.2 ppm as a doublet. H_f and H_d overlap with each other at 5.7 ppm and could be used as the basis of conversion calculation. The expanded region of 5.1–6.4 ppm shows that H_c and H_e are far enough from each other, and the variation of integral of the characteristic peaks could be investigated with good accuracy (Fig. 2).

The comparative $^1\text{H-NMR}$ spectra have been revealed in Figure 3. It is apparent that as the copolymerization reaction is progressing, the intensity of the peaks in the aliphatic range (1.0–2.0 ppm), relevant to copolymer chain protons, is growing up. In other words, the progress of the reaction with time is observable.

Calculation of conversion, f and F

The calculations were built upon the integral of characteristic peaks H_c and H_e . The comparison between normalized total integral of peaks in each spectrum led to minimize the error in our calculations.

In fact, after normalization, the conversion of each monomer in the feed could be directly related to the



Scheme 1

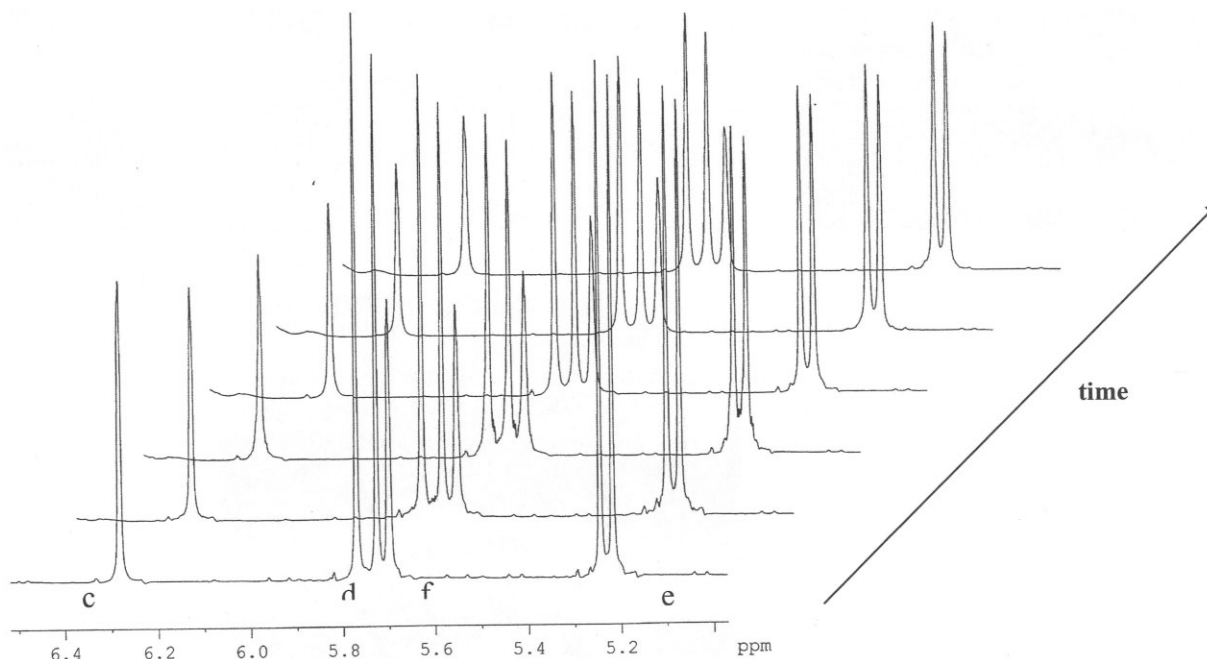


Figure 2 Expanded region of vinylic protons during the progress of copolymerization reaction.

aforementioned characteristic peak areas in the corresponding spectrum. The conversion at each time (χ_t) for St and IA could be obtained according to the following equation [eq. (1)].

$$\chi_t = \frac{A_0 - A_t}{A_0} \quad (1)$$

where A_0 is the primary normalized integral of the characteristic monomer peak ($t = 0$) and A_t is the normalized integral of the characteristic monomer peak at time t .

It is notable in our determination for low conversions that χ_t does not exceed more than 15% for each monomer. Therefore, the mole fraction of St and IA in

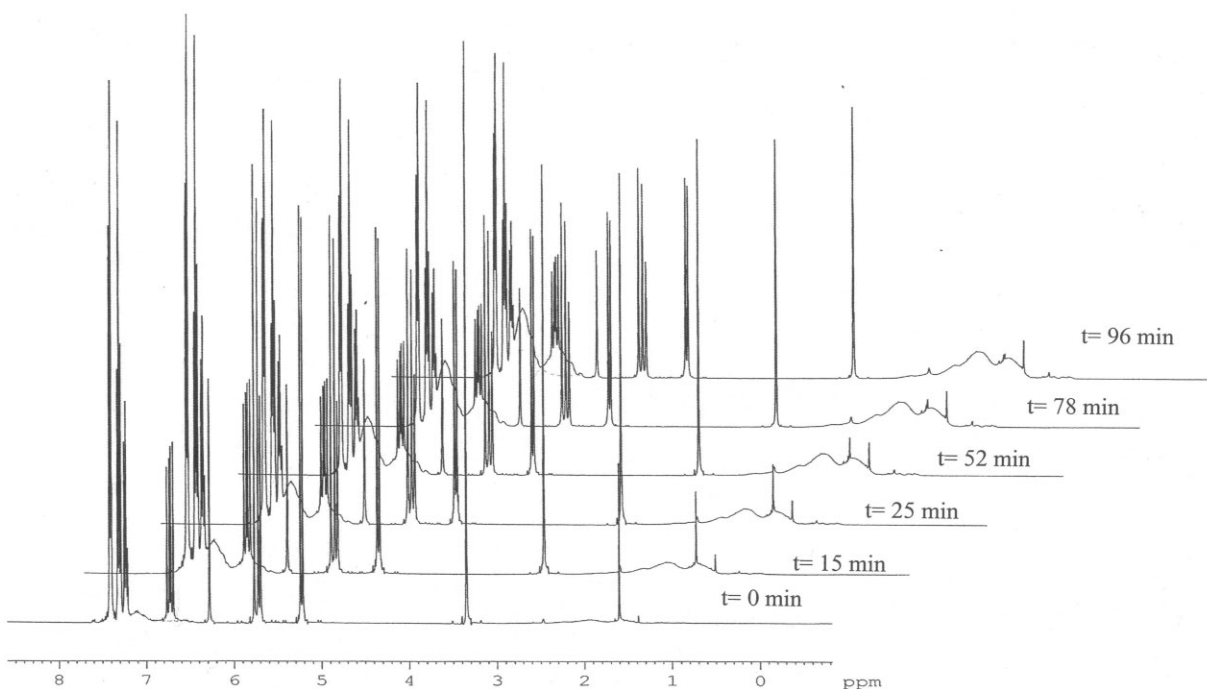


Figure 3 Progress of the copolymerization reaction with time.

TABLE II
The Calculated Parameters Needed for the Determination of Reactivity Ratios at Low Conversion

	f	F	G	H	Z	ξ^a	η^a
St-IA-1	2.43	1.67	0.98	3.54	0.66	0.82	0.22
St-IA-2	1.43	1.24	0.28	1.65	0.86	0.67	0.11
St-IA-3	0.97	1.00	0.00	0.94	1.03	0.53	0.00
St-IA-4	0.66	0.78	-0.18	0.56	1.20	0.39	-0.13
St-IA-5	0.37	0.60	-0.25	0.23	1.67	0.20	-0.23
St-IA-6	0.32	0.52	-0.29	0.20	1.68	0.18	-0.28

^a The amount of α is 0.84.

the copolymer chain (F_{St} and F_{IA}) could be found using the following equations [eqs. (2) and (3)]:

$$F_t^{St} = \frac{A_0^{St} - A_t^{St}}{[A_0^{St} - A_t^{St}] + [A_0^{IA} - A_t^{IA}]} \quad (2)$$

$$F_t^{IA} = \frac{A_0^{IA} - A_t^{IA}}{[A_0^{St} - A_t^{St}] + [A_0^{IA} - A_t^{IA}]} \quad (3)$$

For this copolymerization reaction, f and F that will be used in the next steps would be obtained by using the following equations [eqs. (4) and (5)]:

$$f = \frac{A_0^{St}}{A_0^{IA}} \quad (4)$$

$$F = \frac{F_t^{St}}{F_t^{IA}} = \frac{A_0^{St} - A_t^{St}}{A_0^{IA} - A_t^{IA}} \quad (5)$$

Determination of r_{St} and r_{IA}

Finemann–Ross (F-R) method¹⁶

The values of f and F [eqs. (4) and (5)] from ¹H-NMR spectra (Table II) were used to calculate G and H according to the following equations [eqs. (6) and (7)]:

$$G = \frac{f}{F}(F - 1) \quad (6)$$

$$H = \frac{f^2}{F} \quad (7)$$

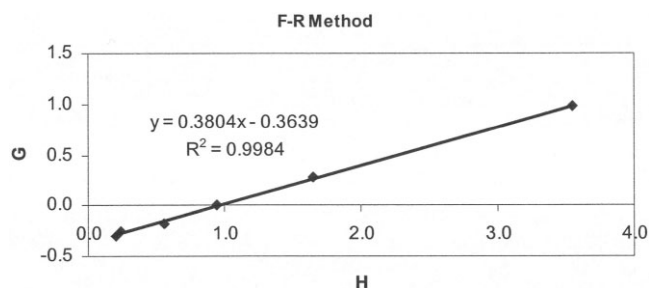


Figure 4 G versus H in the F-R method.

The linear relationship between G and H could be [eq. (8)] given as follows:

$$G = Hr_{St} - r_{IA} \quad (8)$$

Substituting G and H from Table II will result in a plot, in which its slope is r_{St} and the intercept is r_{IA} (Fig. 4). The obtained values of r_{St} and r_{IA} by this method were 0.38 and 0.36, respectively.

Inverted Finemann–Ross (F-R) method¹⁷

The linear relationship in the Finemann–Ross (F-R) method between r_{St} and r_{IA} could be shown as eq. (9) for inverted F-R method.

$$G/H = r_{St} - \left(\frac{1}{H}\right)r_{IA} \quad (9)$$

According to the data available in Table II, G/H versus $1/H$ has been plotted in Figure 5. The reactivity ratios could be obtained from the slope ($r_{IA} = 0.36$) and intercept ($r_{St} = 0.37$) of the best-fitted line (Fig. 5).

Mayo–Lewis (M-L) method¹⁴

This method uses the calculated values of G and H in F-R method. The difference is that, for each G and H value, the corresponding line should be plotted using eq. (10) by substituting an arbitrary value for r_{St} in the range of 0.10–1.00 (for low conversion). Then the position of the crossing point of all lines will show a real amount of reactivity ratios (Fig. 6).

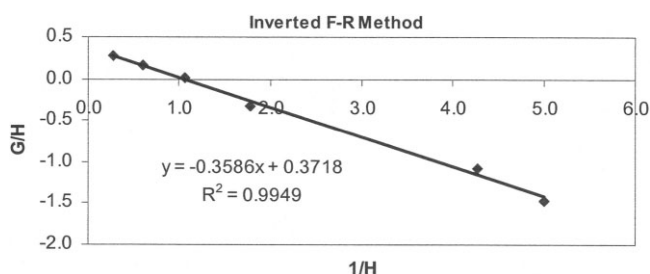


Figure 5 G/H versus $1/H$ in the inverted F-R method.

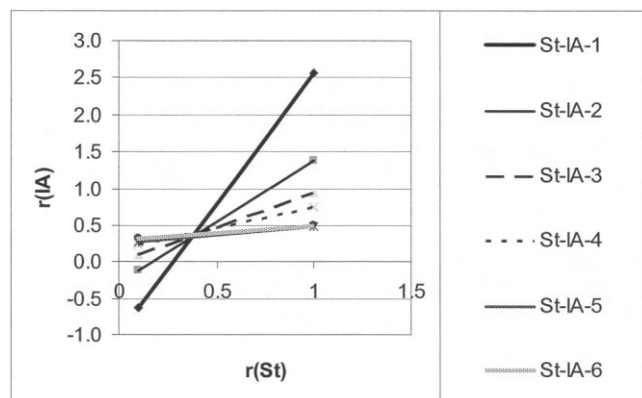


Figure 6 r_{IA} versus r_{St} in the Mayo-Lewis method.

$$r_{IA} = Hr_{St} - G \quad (10)$$

where $r_{St} = 0.43$ and $r_{IA} = 0.38$.

Kelen-Tudos method¹⁸

The major criticism that can be expressed against such linearization methods is that r_{St} and r_{IA} do not play symmetrical roles, for instance, eq. (10). K-T method aims at preventing the nonsymmetrical characteristic of the composition equation from affecting the reactivity ratio values determined experimentally. In this method, the reactivity ratios are related to each other due to the following equation [eq. (11)]:

$$\eta = \left(r_{St} + \frac{r_{IA}}{\alpha} \right) \xi - \frac{r_{IA}}{\alpha} \quad (11)$$

where

$$\alpha = (H_{\max} \cdot H_{\min})^{1/2}$$

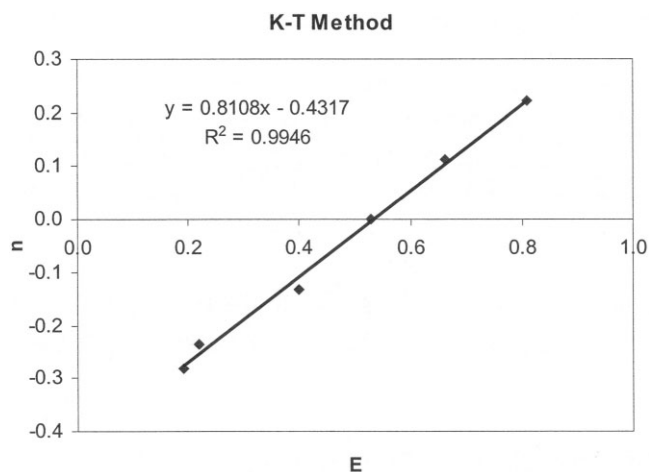


Figure 7 η versus ξ in the K-T method.

$$\xi = \frac{H}{\alpha + H}$$

$$\eta = \frac{G}{\alpha + G}$$

The domain for variation of η and ξ is between 0 and 1, meanwhile, this domain for G and H is 0 and ∞ .

The amount of G and H could be extracted from Table II, and the result of calculations has been plotted in Figure 7. According to this plot, r_{St} and r_{IA} were obtained as 0.38 and 0.36, respectively.

Extended K-T method¹⁹

It is accepted that linear least squares (LLS) methods, such as F-R and K-T, can only be applied to experimental data at sufficiently low conversion, because the calculation is based on differential copolymerization equation. The only exception is the extended K-T method, which involves a rather more complex calculation, but is still a LLS method. It can be applied from low (<15%) to medium-high (<40%) conversions without significant systematic error.

Hence, the partial molar conversion of monomers (θ_{St} and θ_{IA}) could be obtained from the following equations [eqs. (12) and (13)]:

$$\theta_{IA} = \frac{W(\mu + F)}{(\mu + F)} \quad (12)$$

$$\theta_{St} = \theta_{IA} \left(\frac{F}{f} \right) \quad (13)$$

where W is the total conversion (by weight) and μ shows the molecular weight ratio of IA to St.

The parameter Z could be calculated as given later [eq. (14)]:

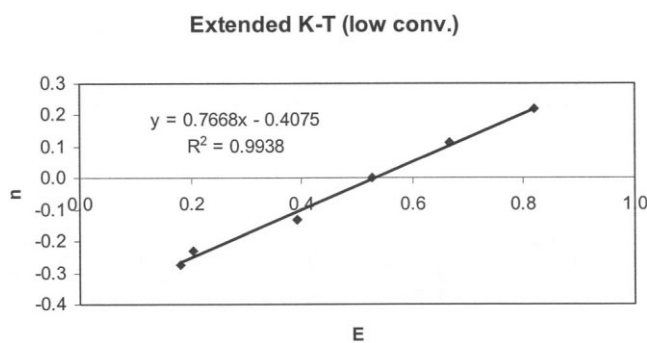


Figure 8 η versus ξ in the extended K-T method at low conversion.

TABLE III
The Calculated Parameters Needed for the Determination of Reactivity Ratios at High Conversion by Extended Kelen–Tudos Method

	f	F	Z	ξ^a	η^a
St-IA-1	2.43	2.07	0.81	0.81	0.34
St-IA-2	1.43	1.42	0.99	0.67	0.19
St-IA-3	0.97	1.07	1.13	0.53	0.04
St-IA-4	0.66	0.80	1.26	0.41	-0.13
St-IA-5	0.37	0.60	1.80	0.20	-0.24
St-IA-6	0.32	0.49	1.69	0.19	-0.33

^a The amount of α is 0.73.

$$Z = \frac{\log\left(\frac{[M_{St}]}{[M_{St}]_0}\right)}{\log\left(\frac{[M_{IA}]}{[M_{IA}]_0}\right)} = \frac{\log(1 - \theta_{St})}{\log(1 - \theta_{IA})} \quad (14)$$

Then

$$G = \frac{(F - 1)}{Z} \quad \text{and} \quad H = \frac{F}{Z^2} \quad (15)$$

By substituting the new G and H values in eq. (11), the corresponding reactivity ratios, at low conversion, would be obtained from the consequent plot of η versus ξ (Table II and Fig. 8)

The obtained reactivity ratio is 0.36 for St and 0.34 for IA. Similar method could be applied for the determination of reactivity ratios at high conversion, which have been tabulated in Table III and the corresponding curve could be seen in Figure 9. r_{St} and r_{IA} were 0.53 and 0.37, respectively.

It is noteworthy that despite the difference in the calculative routes, the r_{St} and r_{IA} from different method are about the same. This shows the accuracy and precision of the obtained experimental data from ¹H-NMR spectroscopy that fit well with such a variety of theoretical methods. On the other hand, this is the strength point of such an online technique for kinetic

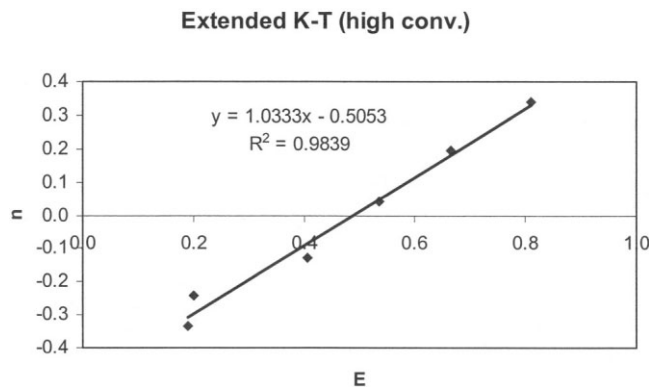


Figure 9 η versus ξ in the extended K-T method at high conversion.

TABLE IV
The Parameters Needed for the Determination of Reactivity Ratios at Low and High Conversions for T-M and M-H Methods

	f^{St}	F^{St}	
		Low conversion	High conversion
St-IA-1	0.71	0.63 (14.4) ^a	0.67(35.3)
St-IA-2	0.59	0.55 (11.5)	0.59 (34.8)
St-IA-3	0.49	0.48 (11.6)	0.52 (33.6)
St-IA-4	0.40	0.43 (13.7)	0.44 (33.1)
St-IA-5	0.27	0.37 (14.6)	0.37 (32.3)
St-IA-6	0.24	0.34 (11.5)	0.33 (32.4)

^a Values in parentheses indicate conversion percentages.

studies of copolymerization reactions with respect to its limitations.

The values of r_{St} and r_{IA} which have been reported by Barner-Kowollik et al.⁶ in almost similar conditions were 0.287 and 0.105, respectively. They applied the Q,e-scheme for their estimation. It is worthwhile to say that this is a rather quantitative method and gives only an approximation of reactivity ratio. Hence, we convince that the obtained reactivity ratios in this work are very close to the real values, because of the online data collection and processing.

Also the comparison between the reactivity ratios illustrates that $r_{St} \approx r_{IA}$. In this special case, the instantaneous composition of the copolymer coincides with that of the monomer mixture over the entire composition range. Consequently, no fluctuation in composition would be expected. That is, the affinity of each of the radicals for both monomers is the same. However, this condition implies a truly random displacement of St and IA units in the copolymer chain.

Tidwell–Mortimer (T-M) method²⁸

The Tidwell–Mortimer (T-M) procedure is considered to be one of the most accurate procedures for determination of monomer reactivity ratio values.²⁸ The method is a modification of the curve-fitting procedure. So, the sum of squares of the difference between observed and computed polymer compositions are

TABLE V
A Summary of the Calculated Reactivity Ratios by Different Methods

	r_{IA}	r_{St}
Finemann–Ross	0.36	0.38
Inverted Finemann–Ross	0.36	0.37
Kelen–Tudos	0.36	0.38
Extended Kelen–Tudos (low conversion)	0.34	0.36
Extended Kelen–Tudos (high conversion)	0.37	0.53
Mayo–Lewis	0.38	0.43
Mao–Huglin (low conversion)	0.37	0.36
Mao–Huglin (high conversion)	0.42	0.56
Tidwell–Mortimer	0.37	0.35

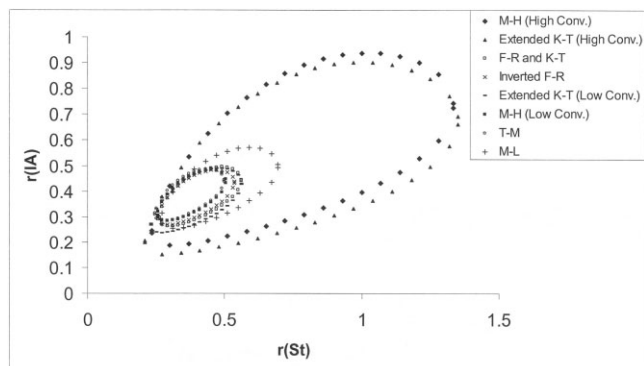


Figure 10 Joint confidence limit for each method at low and high conversions.

minimized. The computation procedure is basically a Gauss–Newton nonlinear least-squares method, which was modified by Box,²⁹ to assure rapid convergence to a pair of values. As a summary, the method consisting initial estimates of r_{St} and r_{IA} and a set of computations is performed to yield the sum of squares of the differences between the observed and computed polymer compositions. The summation is then minimized by iteration to yield reactivity ratios. More detailed data about calculation method and the way to reach real reactivity ratios have been discussed by Ziaee and Nekoomanesh.³⁰

For our system, the initial estimate of reactivity ratios were $r_{St} = r_{IA} = 1$, and several iterations were performed to obtain the minimum difference. These values have been given in Table IV. The amounts of r_{St} and r_{IA} were found to be 0.35 and 0.37, respectively.

Mao–Huglin (M-H) method²³

Mao–Huglin (M-H) method is a more recent method that was presented in 1993.²³ By considering the corresponding equations, computer simulation was used to a series of data at low and high conversions (Table IV). The results were obtained with initial assumption of $r_{St} = r_{IA} = 1$. The value of reactivity ratios by M-H at low conversion for St was 0.36 and for IA was 0.37. These values at high conversion were 0.56 and 0.42 for St and IA, respectively.

As a result, the amounts of reactivity ratios obtained by each method have been summarized in Table V.

Joint confidence limit calculation for different methods

Joint confidence limit of the reactivity ratio values was calculated for each method and has been plotted in Figure 10. The corresponding detail has been mentioned elsewhere.^{31,32} These parameters are preferred to simple limits of precision because of simultaneous estimation of reactivity ratios. Hence, they should not be considered independent statistically.

CONCLUSIONS

It has been accepted that online gain of data is a better and reliable method for kinetic studies. In this manner, ¹H-NMR technique was used. The results of monomer conversion during the time in the corresponding ¹H-NMR spectra were the basis of our analysis to determine the reactivity ratios of St and IA in the solution and radical copolymerization reaction by different methods. In addition to linear least square (LLS) methods, such as F-R, inverted F-R, Mayo–Lewis, K-T, extended K-T, and M-H, also a nonlinear least-square methods, which is T-M, was used for this purpose at low conversions. Extended K-T and M-H were applied to determine reactivity ratio values at high conversions too.

References

- Tate, B. E. In *Vinyl and Diene Monomers, Part 1*; Leonard, E. C., Ed.; Wiley-Interscience: New York, 1971; p 204.
- Chong, Y. K.; Le, T. P. T.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* 1999, 32, 2071.
- Yijin, X.; Caiyuan, P. *Macromolecules* 2000, 33, 4750.
- Matyjaszewski, K. *Macromolecules* 1998, 31, 6046.
- Fordyce, R. G.; Ham, G. E. *J Am Chem Soc* 1947, 69, 695.
- Barner-Kowollik, C.; Heuts, J. P. A.; Davis, T. P. *J Polym Sci Part A: Polym Chem* 2001, 39, 656.
- Yee, L. H.; Coote, M. L.; Chaplin, P. R. D.; Davis, T. P. *J Polym Sci Part A: Polym Chem* 2000, 38, 2192.
- Odian, G. In *Principles of Polymerization*, 2nd ed.; Interscience: New York, 1981; p 268.
- Otsu, T.; Watanabe, H.; Yang, J.-Z.; Yoshioka, M.; Matsumoto, A. *Makromol Chem Macromol Symp* 1992, 63, 87.
- Otsu, T.; Yamagishi, K.; Matsumoto, A.; Yoshioka, M.; Watanabe, H. *Macromolecules* 1993, 26, 3026.
- Otsu, T.; Watanabe, H. *Eur Polym Mater* 1993, 29, 167.
- Otsu, T.; Yamagishi, K.; Yoshioka, M. *Macromolecules* 1992, 25, 2713.
- Marvel, C. S.; Shepherd, T. P. *J Am Chem Soc* 1959, 24, 599.
- Mayo, F. P.; Lewis, F. M. *J Am Chem Soc* 1944, 66, 1594.
- Alfery, G.; Goldfinger, J. *J Chem Phys* 1944, 12, 205.
- Finemann, M.; Ross, S. D. *J Polym Sci* 1950, 5, 259.
- Finemann, M.; Ross, S. D. *J Polym Sci Part A: Gen Pap* 1964, 2, 1687.
- Kelen, T.; Tudos, F. *J Macromol Sci Chem* 1975, 9, 1.
- Kelen, T.; Tudos, F.; Foldes-Berezsnich, T.; Turcsanyi, B. *J Macromol Sci Chem* 1976, 10, 1513.
- Kelen, T.; Tudos, F.; Turcsanyi, B.; Kennedy, J. *J Polym Sci Polym Chem Ed* 1977, 5, 3047.
- Kelen, T.; Tudos, F. *J Macromol Sci Chem* 1981, 16, 1238.
- Tidwell, P. W.; Mortimer, G. A. *J Polym Sci Part A: Gen Pap* 1965, 3, 369.
- Mao, R.; Huglin, M. B. *Polymer* 1993, 34, 1709.
- Brar, A. S.; Yadav, A. *J Polym Sci Part A: Polym Chem* 2001, 39, 4051.
- 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.
- Tidwell, P. W.; Mortimer, G. A. *J Macromol Sci Chem* 1970, 5, 135.
- Box, G. E. P. *Bull Inst Int Stat* 1958, 36, 215.
- Ziaee, F.; Nekoomanesh, M. *Polymer* 1998, 39, 203.
- Kress, A. O.; Mathias, L. J.; Gustavo, C. *Macromolecules* 1989, 22, 537.
- Fukuda, T.; Yung, D. M.; Keiji, K.; Inagaki, H. *Macromolecules* 1991, 24, 370.