This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Kinetic Study of Radical Polymerization v. Determination of Reactivity Ratio in Copolymerization of Acrylonitrile and Itaconic Acid by ^{1}H-NMR

Ali Reza Mahdavian[a]; Mahdi Abdollahi[a]; Leila Mokhtabad[a]; Farshid Ziaee[a]
[a] Polymer Science Department, Iran Polymer and Petrochemical Institute, Tehran, Iran

To cite this Article Mahdavian, Ali Reza , Abdollahi, Mahdi , Mokhtabad, Leila and Ziaee, Farshid(2006) 'Kinetic Study of Radical Polymerization v. Determination of Reactivity Ratio in Copolymerization of Acrylonitrile and Itaconic Acid by ^{1}H-NMR', Journal of Macromolecular Science, Part A, 43: 10, 1583 — 1596

To link to this Article: DOI: 10.1080/10601320600896959

URL: http://dx.doi.org/10.1080/10601320600896959

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry, 43:1583–1596, 2006

ISSN 1060-1325 print/1520-5738 online
DOI: 10.1080/10601320600896959

Kinetic Study of Radical Polymerization v. Determination of Reactivity Ratio in Copolymerization of Acrylonitrile and Itaconic Acid by ^{1}H-NMR

ALI REZA MAHDAVIAN, MAHDI ABDOLLAHI,
LEILA MOKHTABAD, AND FARSHID ZIAEE

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

Many reports exist in the literature about the application of ^{1}H and ^{13}C-NMR techniques to analyze the copolymer structure and composition and also determination of reactivity ratios. In this work, on-line ^{1}H-NMR spectroscopy has been applied to identify reactivity ratios of itaconic acid and acrylonitrile in the solution phase (DMSO as the solvent) and in the presence of AIBN as the radical initiator. All the peaks corresponding to the existing protons were assigned quietly. Therefore, the kinetics of the copolymerization reaction was investigated by studying the variation of integral of two characteristic peaks regarding each monomer. The obtained data were used to find the reactivity ratios of acrylonitrile and itaconic acid by linear least-squares methods such as Finemann-Ross, inverted Finemann-Ross, Mayo-Lewis, Kelen-Tudos, extended Kelen-Tudos and Mao-Huglin. In addition, a non-linear least-square method (Tidwell-Mortimer) was used at low conversions. Extended Kelen- Tudos and Mao-Huglin were applied to determine reactivity ratio values at high conversions as well.

Keywords radical copolymerization, ^{1}H-NMR spectroscopy, reactivity ratio, acrylonitrile, itaconic acid

Introduction

Acrylonitrile-based copolymers are widely used in the production of acrylic fibers. Polyacrylonitrile fibers suffer from poor hygroscopictiy 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 thermoxidation of acrylic fibers (1). Among the various polymerization techniques used in the production of acrylonitrile polymers, solution polymerization is one of the most popular (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).

Received March 2006; Accepted May 2006.

Address correspondence to Ali Reza Mahdavian, Polymer Science Department, Iran Polymer and Petrochemical Institute, P.O. Box 14965/115, Tehran, Iran. Tel.: +9821 4458 0000; Fax: +9821 4458 0023; E-mail: a.mahdavian@ippi.ac.ir

Tsai and Lin (4–7) used a solution polymerization technique to copolymerize acrylonitrile 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 acrylonitrile copolymers (8, 9). In addition, free-radical aqueous slurry polymerization of acrylonitrile has been reported by Ebdon et al. (10).

There exists many reports in the literature about the application of ^{1}H and ^{13}C-NMR techniques to analyze the copolymer structure and composition and also determination of reactivity ratios (11–14). Bajaj et al. (15) have studied the copolymerization of acrylonitrile with vinyl acids such as methacrylic acid, acrylic acid and itaconic acid and in DMF with the objective of improving hygroscopicity of the resulting fibers. They used FT-IR, 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 acrylonitrile (AN) is itaconic acid (IA), which has been a subject of some previous studies (15–19). The major reason for the superiority of IA over other acidic comonomers is the presence of two carboxylic groups, which increases the possibility of interaction of the carboxylic group and the nitrile group during cyclization reaction.

The earlier published results on reactivity ratios of AN and IA appear to be ambiguous and different authors have reported different values (20).

The effect of the reaction medium on radical polymerization has been well documented in previously reported studies, suggesting factors like electrostatic interactions, hydrogen bonding, polar-polar interactions, etc. as responsible for monomer and radical reactivity in copolymerization (21). It is noteworthy that the presence of water in the solvent such as DMF and DMSO also affects the reactivity ratio (22).

The understanding of copolymerization kinetics has gained great importance in recent decades. Because of this fact, the prediction of monomer reactivity ratios becomes a valuable quantitative aspect. Most existing procedures for calculating reactivity ratios can be classified as linear least-squares (LLS), and non-linear least-squares (NLLS) methods. It is accepted that LLS methods such as those proposed by Finemann and Ross (23), and by Kelen and Tudos (24), can only be applied to experimental data at sufficiently low conversion, because the calculation is based on the differential copolymerization equation (25, 26). The only LLS method, as an exception, is an extended Kelen-Tudos method (27), which involves a rather more complex calculation. It could be applied to medium-high conversion experimental data ($\sim$40% conversion) without sufficient systematic error. If the copolymerization is carried to high conversions, the exact calculation of reactivity ratios can only be achieved by a NLLS method based on the integrated copolymerization equation (28). Compared to the LLS method, the NLLS method requires many iterations and a fairly good initial estimation of variables is always needed to attain convergence results. Even so, the different criteria of convergence, and the different initial estimates of reactivity ratios r_1, and r_2 can very often lead to conflicting results. As pointed out by Tudos et al. (27), application of NLLS methods may lead to severe conceptual errors. That is a fairly good estimation of reactivity ratios relative to initial input is always needed for any NLLS calculations.

In 1993, Mao and Huglin represented a new calculation method, which can provide the determination of reactivity ratios at high conversion and still uses the LLS method without systematic error (29).

In most cases, spectroscopic methods such as UV and IR spectroscopy would not be very useful in the estimation of copolymer composition because of the similarity in the comonomer units. However, NMR spectroscopy offers simple and rapid evaluation of copolymer composition compared to the other techniques. Here, we have applied the kinetic data, extracted from ^{1}H-NMR spectra to evaluate reactivity ratios of acrylonitrile and itaconic acid in their radical copolymerization in solution phase.

Experimental

Materials

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

Equipments

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. 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.

Table 1
Mole fraction of monomers in each sample[a,b]

	Acrylonitrile	Itaconic acid
AN-IA-1	0.8755	0.1245
AN-IA-2	0.7810	0.2190
AN-IA-3	0.5857	0.4143
AN-IA-4	0.5255	0.4745
AN-IA-5	0.4565	0.5435
AN-IA-6	0.3843	0.6157
AN-IA-7	0.2833	0.7167

[a] The polymerization temperature was set at 78°C.
[b] The initiator (AIBN) concentration was set about 0.16% relative to the total amount of monomers.

Results and Discussion

During our investigation on kinetic studies of radical polymerization by several instrumental techniques in different media and conditions (30–33), we were notified to the great potential of ^{1}H-NMR spectroscopic technique, for these kinetic studies. Especially on-line ^{1}H-NMR spectroscopy gives us the most reliable data about the variation of conversion during the progress of reaction with high accuracy. Nevertheless, there are some limitations that could be mentioned as: i) in the case that polymerization reaction rate is much higher than the scanning rate, ii) in precipitation polymerization reactions that make the system heterogeneous and, iii) when the differentiation between overlapped characteristic peaks is not possible precisely. By selection of proper systems that can achieve the above problems, one could have the most accurate data for following the kinetics of polymerization reaction and obtaining kinetic parameters.

Here, we have applied this method for calculating the reactivity ratios of itaconic acid and acrylonitrile radical copolymerization in solution phase. A typical ^{1}H-NMR spectrum of a sample during copolymerization reaction, which contains three components (monomers and copolymer) has been shown in Figure 1 and the assignment of the peaks were performed according to the different types of protons represented in Scheme 1. Also, carboxylic acid proton appears as a broad peak above 8 ppm that has not been shown in Figure 1.

H_c and H_e, which are the characteristic peaks of AN and IA respectively, are far enough from each other in the corresponding spectrum and have no overlapping that causes any problem for the integrations. H_c appears at 5.7–5.9 ppm as a doublet of doublet and H_e could be found at 5.6–5.7 ppm as a doublet. So, these two peaks could be considered as the basis of conversion calculations. The expanded region of 5.4–6.4 ppm reveals the position of H_c relative to H_e and variation of their intensities with time comparatively (Figure 2).

It is visible that the area of the peaks in the aliphatic region (Figure 3) (except the peak at 3.2 ppm relating to the CH_2 in monomeric IA), which shows the progress of copolymerization reaction, is rising during the time.

As mentioned above, the conversion of each monomer will be obtained from the comparison between the modified peak area of H_c and H_e at different time intervals.

The method of calculating f (mole ratio of AN to IA in the feed) and F (mole ratio of AN to IA in the copolymer chain) have been discussed in our previous article in detail (33). The measured amounts of f and F in these series of experiments have been listed in Table 2.

Determination of Reactivity Ratios by Linear Least-Square Methods

Finemann-Ross (F-R) method is the earliest way for determining reactivity rations (23). In this method, two parameters (G and H) are defined and have a linear relationship with each other according to the following equation (Equation 1).

$$G = Hr_{AN} - r_{IA} \tag{1}$$

The obtained G and H from corresponding equations (33) in our system will result in a plot (G vs. H), where the intercept gives reactivity ratio of IA ($r_{IA} = 0.45$) and its slope shows r_{AN} ($r_{AN} = 0.38$) (Figure 4).

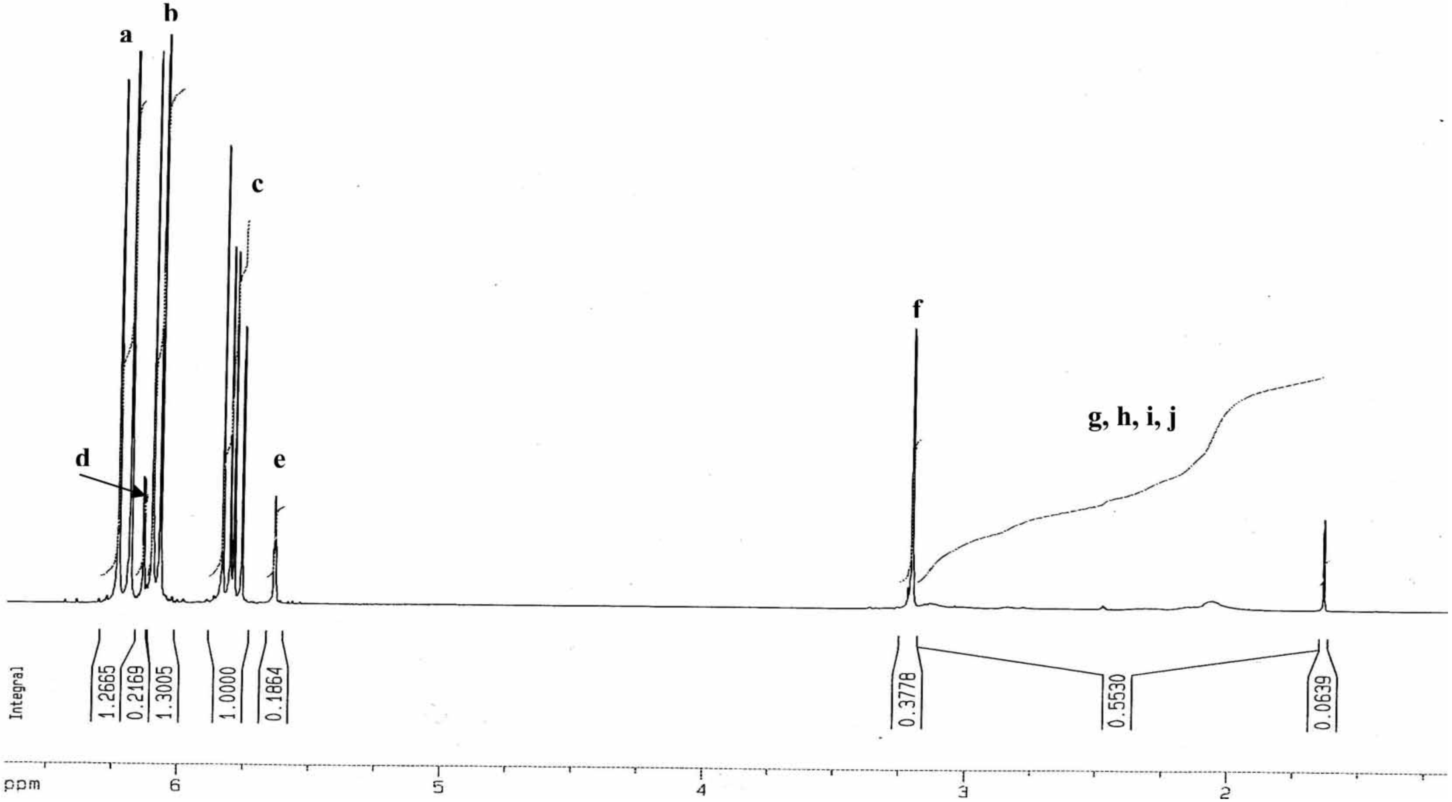
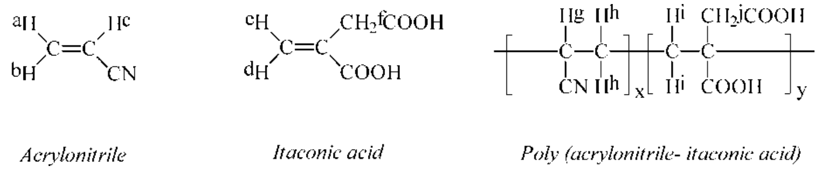


Figure 1. A typical spectrum of acrylonitrile- itaconic acid copolymer and unreacted corresponding monomers.



Scheme 1. The chemical structure of monomers and corresponding copolymer.

Inverted Finemann-Ross in another linear method in which the parameter G/H is plotted against 1/H (34). It has been figured out for our system (Figure 5) and r_{AN} and r_{IA} were found to be 0.37 and 0.46, respectively.

Kelen and Tudos introduced mathematical parameters into the linearized copolymerization equation such as η, ζ and α (Equation (2) (Figure 2) (24).

$$\eta = \left[r_{AN} + \frac{r_{IA}}{\alpha} \right] \xi - \frac{r_{IA}}{\alpha} \tag{2}$$

Here, the domain for variation of η and ζ is 0 and 1 with respect to G and H, where the domain was between 0 and ∞.

The plot relating to the variation of η vs. ζ has been shown in Figure 6. Hence, the best fitted line through the points will give r_{AN} equals to 0.38 and $r_{IA} = 0.48$.

Extended Kelen-Tudos (K-T) is another linear least-square method (27), where the effect of conversion is considered directly in determination of G, H and subsequently, η and ζ by definition of the parameter Z (Equations 3–5):

$$Z = \frac{\log(1 - \theta_{AN})}{\log(1 - \theta_{IA})} \tag{3}$$

$$G = \frac{(F - 1)}{Z} \tag{4}$$

$$H = \frac{F}{Z^2} \tag{5}$$

θ_{AN} and θ_{IA} are partial molar conversion of these monomers.

Therefore, this method has the potential to be used for either low conversion (<15%) or high conversions (<40%). Above 40% conversion, the fluctuations in the composition will cause high level of uncertainty. As a consequence, the plot for extended K-T method has been shown in Figure 7 and the obtained reactivity ratios for AN and IA in the extended K-T (low conversion) were 0.36 and 0.46, respectively.

According to the above method for high conversion and due to the relating curve (Figure 8), $r_{AN} = 0.44$ and $r_{IA} = 0.67$ were obtained too.

The last linear least-square method used in this work was Mayo-Lewis (M-L) (25). Here, different amounts of r_{IA} with r_{AN} were investigated and plotted (Figure 9) for each calculated G and H value. The cross-point of the lines plotted by considering arbitrary values for r_{AN} ($0.10 < r_{AN} < 1.00$) will result in the real amounts of reactivity ratios.

$$r_{IA} = Hr_{AN} - G \tag{6}$$

In this method, r_{AN} and r_{IA} were found to be 0.38 and 0.48, respectively. Mao-Huglin (M-H) method is one of the most recent techniques for determination of reactivity ratios at low and high conversions (29). It has been based upon some corrections on copolymer

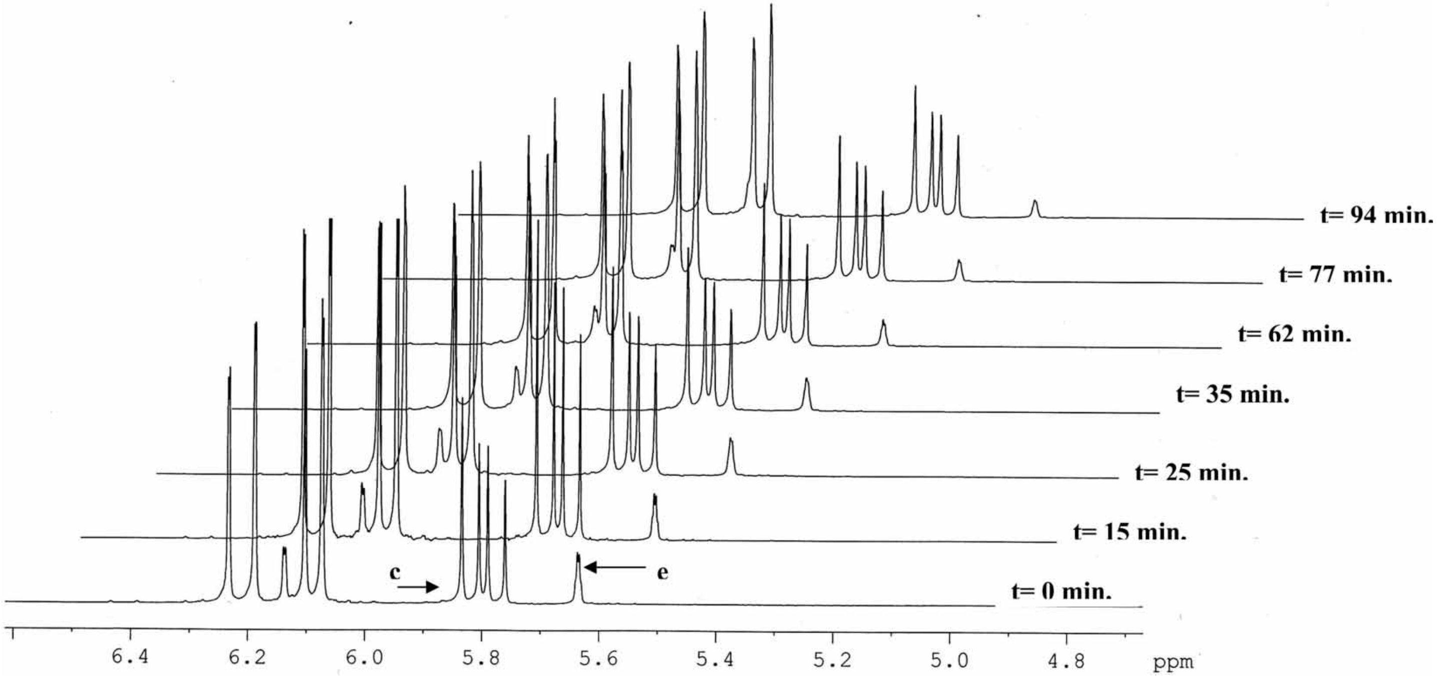


Figure 2. Expanded region of vinylic protons during the copolymerization reaction.

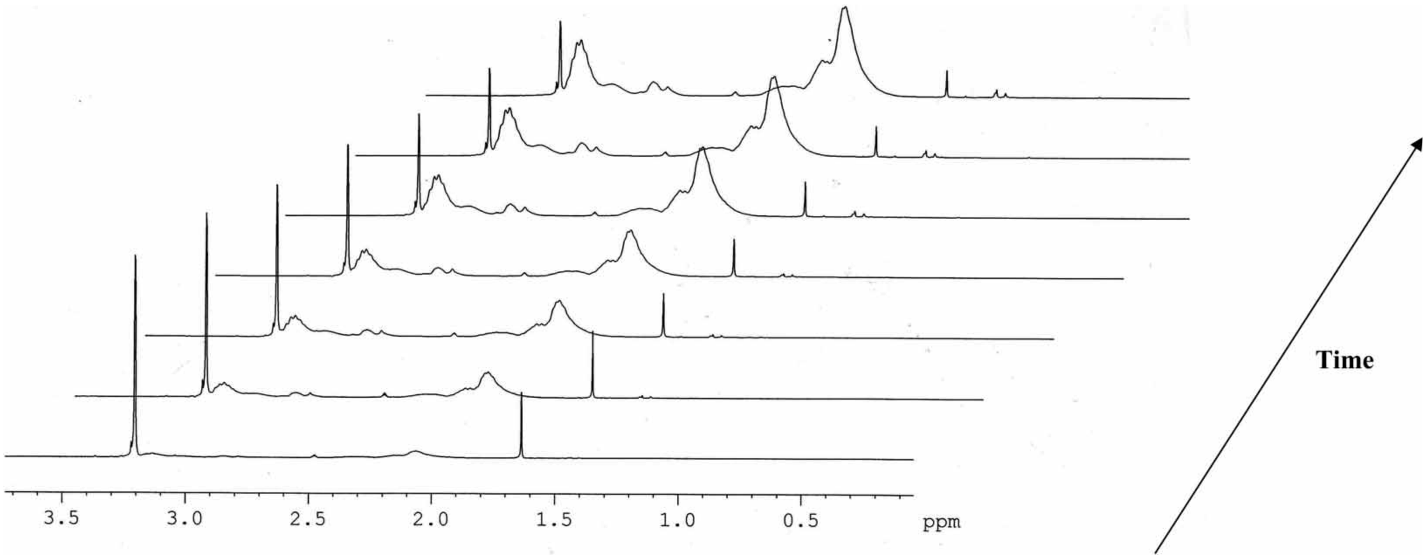


Figure 3. Expanded region of aliphatic protons showing the progress of copolymerization reaction with time.

Table 2
Initial acrylonitrile composition in the feed (f) and copolymer chain (F) at low and high conversions

	f^{AN}	F^{AN} (Conversion %)	$F^{AN a}$ (Conversion %)
AN-IA-1	0.8755	0.7786 (10.86)	0.8254 (40.11)
AN-IA-2	0.7810	0.6825 (10.36)	0.8202 (34.93)
AN-IA-3	0.5857	0.5342 (9.65)	0.7133 (34.64)
AN-IA-4	0.5255	0.5082 (7.24)	0.6915 (21.18)
AN-IA-5	0.4565	0.4530 (10.53)	0.5121 (20.01)
AN-IA-6	0.3843	0.4048 (10.29)	0.3940 (20.04)
AN-IA-7	0.2833	0.3477 (9.87)	—

[a] These quantities were used for high-conversion calculations.

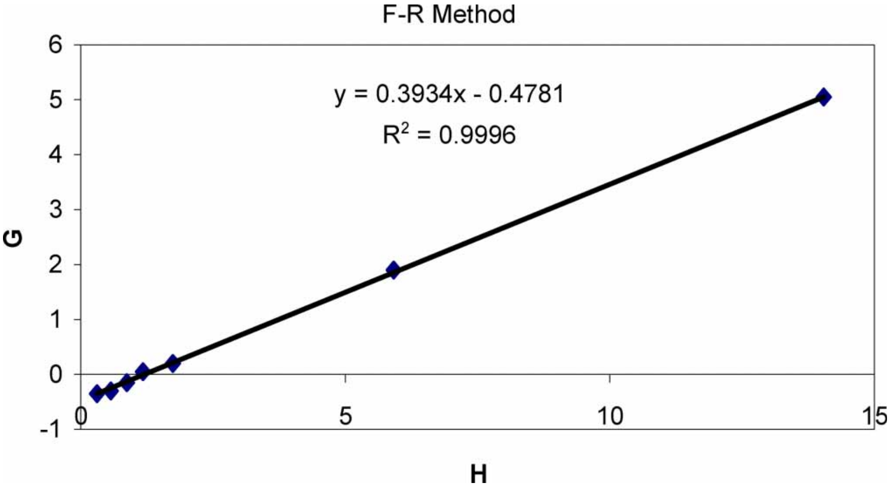


Figure 4. G vs. H in the Finemann-Ross method.

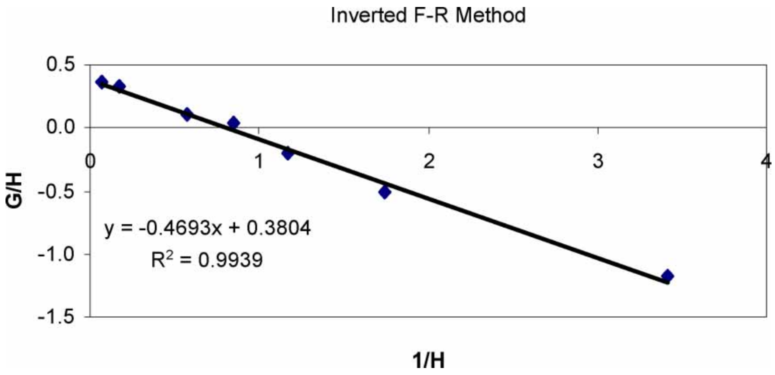


Figure 5. G/H vs. 1/H in the Inverted Finemann-Ross method.

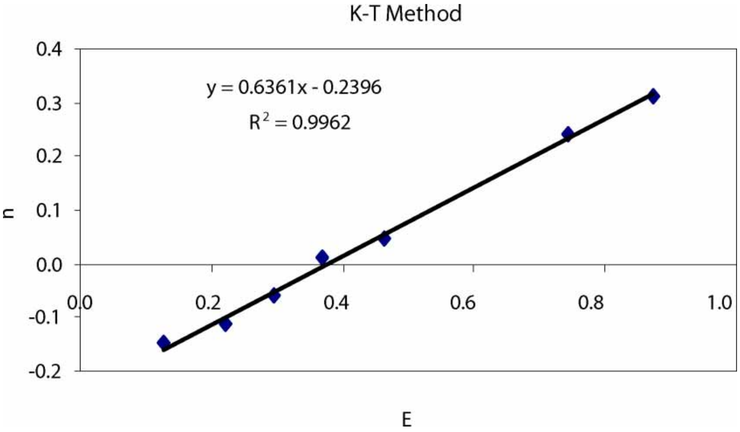


Figure 6. η vs. ξ in the Kelen-Tudos method ($\alpha = 2.03$).

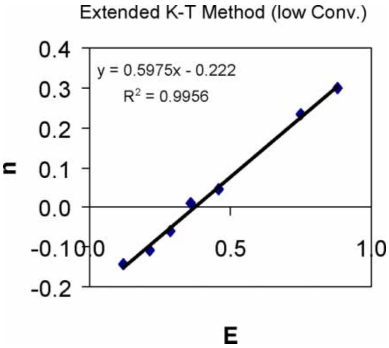


Figure 7. η vs. ξ in the extended Kelen-Tudos method at low conversion ($\alpha = 2.11$).

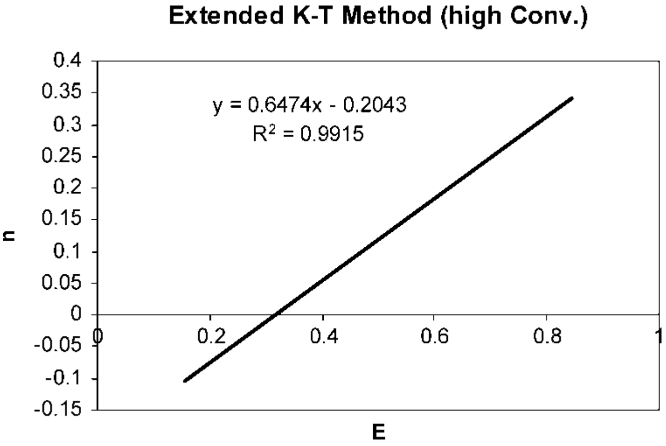


Figure 8. η vs. ξ in the extended Kelen-Tudos method at high conversion.

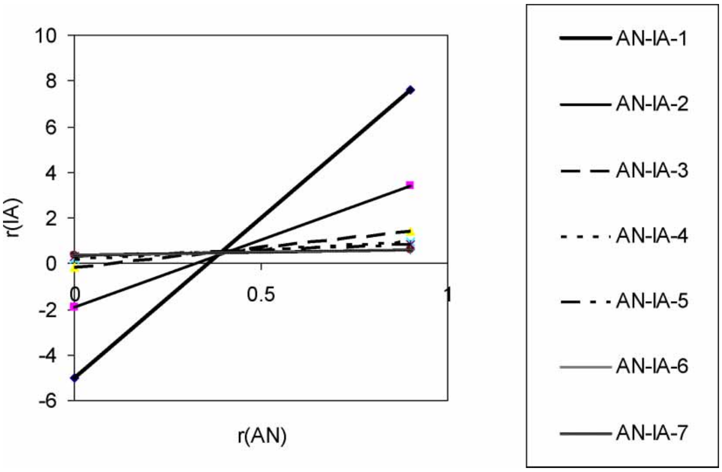


Figure 9. r_{IA} vs. r_{AN} in the Mayo-Lewis method.

composition equation. Nevertheless, the procedure is almost similar to T-M method i.e. an initial estimation of r_{AN} and r_{IA} is required and the computations are progressed until to reach the minimum $\langle d_i^2 \rangle$.

The preference of M-H rather than T-M method is that in the former, the effect of conversion on the comonomer and copolymer compositions are considered. Hence, this method is applicable for both low and high conversions. This is similar to extended K-T method but with higher accuracy and precision. $r_{AN} = 0.36$ and $r_{IA} = 0.43$ were obtained from M-H method at low conversion. The values at high conversions were 0.44 and 0.63, respectively (Table 3).

Table 3

Determination of reactivity ratios by Mao-Huglin method*

r_{AN}	r_{IA}	$\langle d_i^2 \rangle$
At low conversion		
0.3762073	0.4543263	16.63511
0.3573177	0.4292122	2.803425 E-2
0.3561786	0.4274875	1.347122 E-2
0.3561077	0.4273766	1.365566 E-2
0.3561042	0.4273690	1.367251 E-2
At high conversion		
0.5765761	0.9426328	17.23388
0.4829214	0.7767996	0.8969141
0.4520277	0.6870533	0.1404513
0.4407789	0.648707	7.648955 E-2
0.4365414	0.6333979	7.416974 E-2

*The initial assumption was $r_{AN} = r_{IA} = 1.0$.

Table 4
Determination of reactivity ratios by Tidwell- Mortimer method[a]

r_{AN}	r_{IA}	$\langle d_i^2 \rangle$
1.0	1.0	2.862442 E-2
0.6836824	0.7388293	1.095195 E-2
0.4197332	0.509784	4.870986 E-4
0.3859792	0.4764565	2.41266 E-4
0.3849437	0.475437	2.411192 E-4
0.3850766	0.4755678	2.411113 E-4
0.3850807	0.4755718	2.411112 E-4

[a] The initial assumption was $r_{AN} = r_{IA} = 1.0$.

Determination of Reactivity Ratios by Non-linear Least-square Methods

The non-linear method outlined by Tidwell and Mortimer is one of the most accurate procedures for determination of reactivity ratio (35). In the Tidwell-Mortimer (T-M) method, one should have an initial estimation of r_{AN} and r_{IA} and computations are performed in such a way that minimum $\langle d_i^2 \rangle$ is obtained (d_i is the difference between computed and observed copolymer composition). In this case, several interactions will lead to the best r_{AN} and r_{IA} and for our system r_{AN} and r_{IA} were found to be 0.39 and 0.48, respectively (Table 4).

As a summary, the reactivity ratios obtained from various methods for acrylonitrile and itaconic acid have been tabulated below (Table 5).

Joint confidence limit of the reactivity ratio values were calculated for each method and have been plotted in Figure 10. The corresponding detail has been mentioned elsewhere (36, 37). These parameters are preferred to simple limits of precision because of simultaneous estimation of reactivity ratios. Hence, they should not be considered independent statistically. The results interpret that the certainty to calculated reactivity ratios at low conversion is more than those of high conversion.

Table 5
A summary of the calculated reactivity ratios by different methods

	r_{AN}	r_{IA}
Finemann-Ross	0.3934	0.4781
Inverted Finemann-Ross	0.3804	0.4693
Kelen-Tudos	0.3965	0.4865
Extended Kelen-Tudos (low conversion)	0.3755	0.4682
Extended Kelen-Tudos (high conversion)	0.4431	0.6863
Mayo-Lewis	0.3963	0.4859
Mao-Huglin (low conversion)	0.3561	0.4274
Mao-Huglin (high conversion)	0.4365	0.6334
Tidwell-Mortimer	0.3851	0.4756

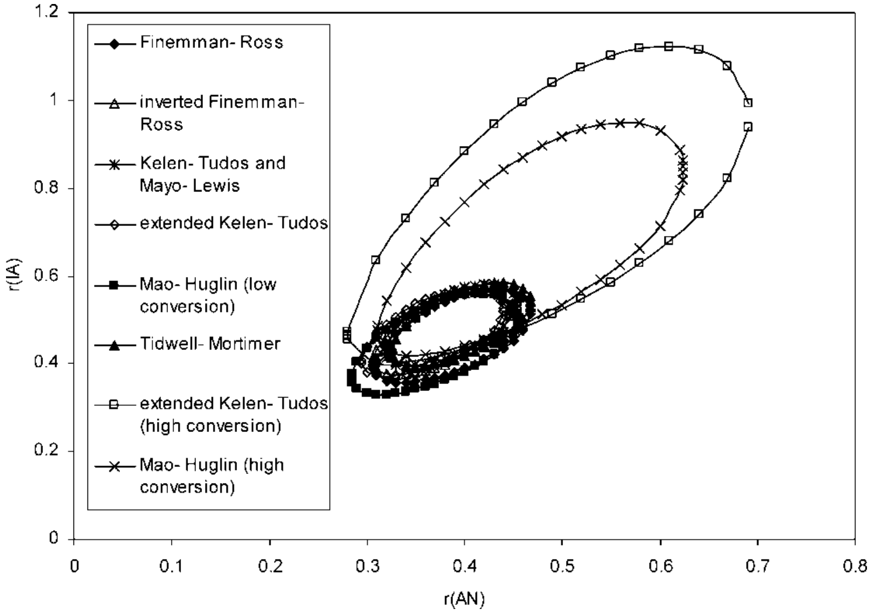


Figure 10. Joint confidence limit for each method at low and high conversions.

Conclusions

Polyacrylonitrile fibers suffer from poor hygroscopicity and low dye uptake. Suitable comonomers are thus incorporated into the polymer to overcome these problems. Acidic comonomers not only improve the hygroscopicity, but also help in the cyclization of the nitrile group to form a ladder structure during thermoxidation of acrylic fibers. One of the candidate comonomers recommended for the copolymerization with acrylonitrile is itaconic acid. The major reason for the superiority of IA over other acidic comonomers is the presence of two carboxylic groups, which increases the possibility of interaction of the carboxylic group and the nitrile group during cyclization reaction. According to the importance of this radical copolymerization reaction, reactivity ratios of acrylonitrile and itaconic acid were determined in DMSO as the solvent. ^{1}H-NMR spectroscopy was used to follow monomer conversion during the time. This was the basis of our analysis to determine reactivity ratios by different methods. In addition to linear least-squares methods such as F-R, inverted F-R, Mayo-Lewis, K-T, extended K-T and M-H and also a non-linear least-square method, 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. The summary of the obtained reactivity ratios by above methods have been listed in Table 5. The certainty of obtained reactivity ratios at low conversion are more than those of high conversion methods. The proximity of r_{AN} and r_{IA} shows that the copolymer structure will be somewhat like a alternating copolymer structure.

Acknowledgments

A.R. Mahdavian wishes to express his gratitude to TWAS for partial financial support of this work (RGA No. 01-094 RG/CHE/AS). Also support of Iran Polymer and Petrochemical Institute (IPPI) is greatly acknowledged.

References

1. Sen, K., Hajir Bahram, S., and Bajaj, P. (1996) *J. Macromol. Sci.–Rev.*, C36: 1.
2. Nuyken, O. and Lattermann, G. (1992) In *Handbook of Polymer Synthesis Part A*; Hricheldorf, H.R. (ed.), Marcel Dekker: New York; p. 284, Chap. 4.
3. Lewin, M. and Pearce, E.M. (1985) Fiber chemistry. In *Handbook of Fiber Science and Technology*; Marcel Dekker: New York; Vol. IV.
4. Tsai, J.S. and Lin, C.H. (1991) *J. Appl. Polym. Sci.*, 42: 3039.
5. Tsai, J.S. and Lin, C.H. (1991) *J. Appl. Polym. Sci.*, 42: 3045.
6. Tsai, J.S. and Lin, C.H. (1990) *J. Mater. Sci. Lett.*, 9: 921.
7. Tsai, J.S. and Lin, C.H. (1991) *J. Appl. Polym. Sci.*, 43: 679.
8. Mikolajezyk, T. and Krucinska, I. (1989) *Text. Res. J*, 59: 536.
9. Bajaj, P., Paliwal, D.K., and Gupta, A.K. (1993) *J. Appl. Polym. Sci.*, 49: 823.
10. Ebdon, J.R., Huckerby, T.N., and Hunter, C. (1994) *Polymer*, 35: 250.
11. Borbely, J.D., Hill, D.J., Lang, A.P., and O'Donell, J.H. (1991) *Macromolecules*, 24: 2208.
12. Brar, A.S., Kapur, G.S., and Dubey, S.K. (1988) *Eur. Polym. J*, 24: 807.
13. Brar, A.S., Saini, A.K., and Kapur, G.S. (1989) *Polym. J.*, 21: 689.
14. Brar, A.S. and Saini, A.K. (1986) *J. Appl. Polym. Sci.*, 32: 4607.
15. Bajaj, P., Sen, K., and Hajir Bahrami, S. (1996) *J. Appl. Polym. Sci.*, 59: 1539.
16. Li, P. and Shan, H. (1995) *J. Appl. Polym. Sci.*, 56: 877.
17. Bajaj, P., Sreekumar, T.V., and Sen, K. (2001) *J. Appl. Polym. Sci.*, 79: 1640.
18. Zhang, C., Gilbert, R.D., and Fornes, R.E. (1995) *J. Appl. Polym. Sci.*, 58: 2067.
19. Bajaj, P., Sreekumar, T.V., and Sen, K. (2001) *Polymer*, 42: 1707.
20. Devasia, R., Nair, C.P.R., and Ninan, K.N. (2002) *Eur. Polym. J*, 38: 2003.
21. Plochocka, K. (1981) *J. Macromol. Sci. Chem.*, C20: 67.
22. Cowie, J.M.G., McEwan, I.J., and Yule, E.J. (2000) *Eur. Polym. J*, 36: 1795.
23. Finemann, M. and Ross, S.D. (1950) *J. Polym. Sci.*, 5: 259.
24. Kelen, T. and Tudos, F. (1975) *J. Macromol. Sci.*, A9: 1.
25. Mayo, F.P. and Lewis, F.M. (1944) *J. Amer. Chem. Soc.*, 66: 1594.
26. Alfery, T. and Goldfinger, G.J. (1944) *J. Chem. Phys.*, 12: 205.
27. Kelen, T., Tudos, F., Foldes-Berezsnich, T., and Turcsanyi, B. (1976) *J. Macromol. Sci.*, A10: 1513.
28. Lowry, G.G. and Meyer, V.E. (1965) *J. Polym. Sci.*, 3: 2843, A-1.
29. Mao, R. and Huglin, M.B. (1993) *Polymer*, 34: 1709.
30. Mahdavian, A.R., Abdollahi, M., and Bijanzadeh, N.R. (2004) *J. Appl. Polym. Sci.*, 93: 2007.
31. Mahdavian, A.R. and Zandi, M. (2003) *J. Appl. Polym. Sci.*, 87: 2335.
32. Mahdavian, A.R. and Zandi, M. (2003) *J. Appl. Polym. Sci.*, 90: 1648.
33. Mahdavian, A.R., Abdollahi, M., Mokhtabad, L., Bijanzadeh, H.R., and Ziaee, F. *J. Appl. Polym. Sci.* In press.
34. Finemann, M. and Ross, S.D. (1964) *J. Polym. Sci.* (*A*), 2: 1687.
35. Tidwell, P.W. and Mortimer, G.A. (1970) *J. Macromol. Sci. Chem.*, 5: 135.
36. Kress, A.O., Mathias, L.J., and Gustavo, C. (1989) *Macromolecules*, 22: 537.
37. Fukuda, T., Yung, D.M., Keiji, K., and Inagaki, H. (1991) *Macromolecules*, 24: 370.