Effect of Acrylonitrile Water Solubility on the Suspension Copolymerization of Acrylonitrile and Styrene

Qun Lu,[1] Zhi-xue Weng,[2] Guo-rong Shan,[2] Guo-qiao Lai,[1] Zu-ren Pan[2]

[1]*Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Department of Chemistry, Hangzhou Teachers College, Hangzhou 310012, Peoples' Republic of China*
[2]*Institute of Polymer Engineering, Zhejiang University, Hangzhou 310027, Peoples' Republic of China*

Received 15 March 2005; accepted 30 August 2005
DOI 10.1002/app.23648

ABSTRACT: Effect of acrylonitrile water solubility on the suspension polymerization of acrylonitile and styrene was investigated. It was found that the copolymer composition produced in the suspension polymerization of acrylonitrile and styrene was significantly different from that in the bulk polymerization at the same monomer feed ratio, since acrylonitrile is partially soluble in water. To predict accurately and then control the copolymer composition in the suspension polymerization, a model to calculate the copolymer composition was proposed based on considering the phase partition of actylonitrile between monomer and aqueous phases. The results calculated by the model are in agreement with the experimental data. The real reactivity ratios in monomer phase used in the model are the same as that in the bulk polymerization, but the apparent reactivity ratios used in the classical theory for the suspension polymerization vary significantly with water/oil ratio. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4270–4274, 2006

Key words: acrylonitrile; styrene; suspension polymerization; copolymer composition

INTRODUCTION

Oil-soluble initiator was usually used in suspension polymerization, and so the polymerization takes place within the monomer droplets.[1] For water-insoluble monomers (such as styrene), the suspension copolymer composition may be quantitatively predicted by using the same model for the corresponding bulk polymerization. However, partially water-soluble comonomer (such as acrylonitrile) may be used in the suspension copolymerization, such as styrene-acrylonitrile system.[2,3] In such case, the copolymer composition will be significantly different from that in the bulk polymerization at the same monomer feed ratio,[2–7] since the locus concentration of water-soluble monomer at the polymerization site (monomer droplets) is lower than that in the feed.

In suspension polymerization, salt may be used to depress the monomer water solubility, but it can not be used in every case, since some suspension copolymers are expected to be prepared in deionized water[8] and moreover in some cases, it is preferable that monomers are partially dissolved in aqueous phase for preparing certain copolymer.[6,8] Therefore, it is necessary to study the phase partition of water-soluble monomer between monomer and aqueous phases and its effects on suspension polymerization. Mino[3] and Smith[9] studied the partition of AN between monomer and aqueous phases at room temperature and its effect on AN/St emulsion polymerization. Kalfas[7,4] and Zhang[2] studied the suspension polymerization of some other partially water-soluble monomers. However, the phase partition of AN at the higher temperature and its effect on AN/St suspension polymerization weren't investigated. It is more unluckily that the authors did not take notice of the effect of water/oil ratio on copolymer composition and apparent reactivity ratios in suspension polymerization.

In the present work, AN/St suspension polymerization system was adopted to investigate the partition of AN between monomer and aqueous phases at various temperatures, especially at polymerization temperature higher than room temperature, and its effect on copolymer composition and apparent reactivity ratios. To predict accurately and then control the copolymer composition in AN/St suspension polymerization, a model to calculate AN/St copolymer composition was proposed based on considering the phase partition of AN between monomer and aqueous phases. The results calculated by the model are in agreement with the experimental data. The present investigation is mainly to provide the theoretical foundation for the preparation of new suspension copolymer[8,10]

Correspondence to: Q. Lu (Luqun@263.net).
Contract grant sponsor: National Nature Science Foundation of China; contract grant number: 20166001.

Journal of Applied Polymer Science, Vol. 101, 4270–4274 (2006)

EXPERIMENTAL

Materials

AN (Hangzhou Gaojin Chemical Industry Co.) was distilled under purified nitrogen atmosphere, and St (Shanghai Chemical Reagent Co.) was distilled under vacuum before use. Benzoyl peroxide (BPO) (Shanghai Chemical Reagent Co.) as initiator was recrystallized from methanol. Hydroxy-propyl methyl cellulose (HPMC, 90SH100) (Dow Chemical Co.), as received, was used as suspending agent. HPMC was dissolved in water before polymerization. *N*,*N*-dimethylformamide (DMF), isopropyl alcohol, methanol, dodecyl mercaptan, potassium hydroxide, potassium iodide, and iodine were all of analytical reagent grade and used as received. Deionized water was used in the experiments.

Measurement of partition of AN between monomer and aqueous phases

Water and AN/St solution of known composition were added to a glass vessel and stirred for equilibrium under constant temperature for 1 h. The water samples were removed from the glass vessel by means of a syringe and then mass percentage of AN in the water samples (C_w) was determined. The method to determine C_w was improved based on the information from the literatures[3,11] as follows

25 g of dodecyl mercaptan was dissolved in 1 L of isopropyl alcohol and 50 mL of this solution was poured into a 250-mL iodine flask. 2–5 g of water sample was added to 1 mL of alcoholic potassium hydroxide solution (0.9 mol/dm^3) and was poured into the flask. Oxygen was removed by sweeping with nitrogen. The flask was stoppered and the solution was allowed to stand for about 10 min for completion of reaction. The solution was acidified with 1 mL of glacial acetic acid and was diluted with isopropyl alcohol to about 75 mL. The excess of mercaptan was titrated with 0.1 mol/L iodine solution to a faint yellow end point, permanent for 30 s of swirling.

Then, the same volume of mercaptan solution as was used for the experimental determination was diluted to be about 75 mL using isopropyl alcohol and a blank was run by direct titration with iodine. Mass percentage of AN in the water samples (C_w) may be computed as follows:

$$C_w = \frac{53.06(V_0 - V)N}{m \times 1000} \times 100\% \qquad (1)$$

where V is ml of iodine solution required for the unknown, V_0 ml of iodine solution required for the direct mercaptan blank, N molarity of ½ I_2, and m the weight of water sample. At the temperature higher than room temperature, the water sample should rapidly be diluted with cold deionized water to prevent AN separating out of water when cooled, and here m is the weight of the water sample before diluted. The mass percentage of AN in the monomer phase (C_s) was calculated from C_w by material balance.

Preparation of AN/St copolymer

AN/St copolymer was prepared in the batch suspension polymerization in a 500-mL jacketed glass reactor fitted with a stirrer, a reflux condenser, and a nitrogen inlet. Water, HPMC water solution (1%), and AN/St mixture containing BPO were added into the glass reactor in turn. To ensure an inert atmosphere and to prevent inhibition effect from oxygen, the reactor was swept with a continuous follow of nitrogen at least 20 min before and during the course of the reaction. The polymerization temperature was well controlled in a water bath.

After reacting for a certain time, the reactor was cooled rapidly to room temperature. Then the reactant was taken out and dried under vacuum. The obtained copolymer was purified by dissolving with DMF and precipitating in methanol, and then dried at 60°C. The mass conversion X_w was measured gravimetrically. Note that the measured conversion was based on the total initial monomer feed, and unreacted monomer dissolved in water was also counted.

Determination of AN/St copolymer composition

Carlo Erba 1106 element analyzer was employed to determine the nitrogen content in AN/St copolymer and AN content was calculated from nitrogen content. The St content was then calculated from the AN content. As long as the copolymer composition is known, the mass conversion X_w can be converted to the molar conversion X_m.

RESULTS AND DISCUSSION

Partition of an between monomer and aqueous phases

To analyze and discuss the effect of AN water solubility on the AN/St copolymer composition in suspension polymerization, the phase partition of AN between monomer and aqueous phases was determined at various temperatures, and given in Figure 1.

It was found that the experimental data in Figure 1 fitted the following Marker equations:[12]

$$25°\mathrm{C}: \left(\frac{A_s}{S}\right) \Big/ \left(\frac{A_w}{W}\right)\left(0.075 - \frac{A_w}{W}\right) = 0.28 + 4.4\frac{A_w}{W} \qquad (2)$$

$$50°\mathrm{C}: \left(\frac{A_s}{S}\right) \Big/ \left(\frac{A_w}{W}\right)\left(0.089 - \frac{A_w}{W}\right) = 0.35 + 5.2\frac{A_w}{W} \qquad (3)$$

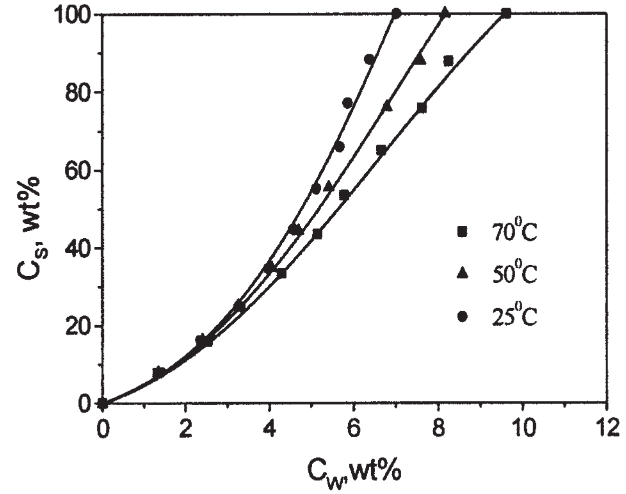

Figure 1 Mass percentage of AN in monomer phase as a function of mass percentage of AN in water at various temperatures.

$$70°\text{C}: \left(\frac{A_s}{S}\right)\Big/\left(\frac{A_w}{W}\right)\left(0.106-\frac{A_w}{W}\right) = 0.40 + 6.3\frac{A_w}{W} \quad (4)$$

where S and W are the masses of St and water, and A_s and A_w the masses of AN in St and aqueous phases. According to the definitions, one has

$$\frac{A_w}{W} = \frac{C_w}{1 - C_w} \quad (5)$$

$$C_s = \frac{A_s}{S}\Big/\left(1 + \frac{A_s}{S}\right) \quad (6)$$

C_s can be calculated from the determined C_w using the eqs. (2)–(6). The curves in Figure 1 are the results calculated.

Figure 1 shows that C_w increases with the increase in C_s at various temperatures. When C_s increases to 100%, C_w becomes solubility of pure AN (C_w^*). It is found that the values of C_w^* at 25, 50, and 70°C are 7.0, 8.2, and 9.6% (wt), which are approximately equal to those from the literature,[11] respectively. It indicates that the phase partition determined is reasonable.

Figure 1 also shows that the temperature hardly influences phase partition of AN at low concentration of AN, but obviously does with the increase in the concentration. It indicates that the effect of temperature on AN phase partition should be considered at higher concentration of AN. Both Smith[9] and Marker[12] investigated the AN phase partition at room temperature, but the AN phase partition at polymerization temperature higher than room temperature has not been investigated in detail. One knows from this work that it should bring error for studying the effect of AN water solubility on AN/St suspension polymerization at higher concentration of AN. To accurately predict the copolymer composition in AN/St suspension polymerization at 70°C, eq. (4) will be infra employed to calculate the partition of AN between monomer and aqueous phases.

In suspension polymerization, the real initial composition of monomer droplets f_1 (mole fraction of AN) is lower than the composition of monomer feed f_{10}, because AN is partially dissolved in water. Suppose the phase equilibrium has been set up before polymerization,[2,4,7] the relationship of f_1 and f_{10} can be calculated using eq. (4) as shown in Figure 2. It can be seen that the greater the water/oil ratio, the larger the difference between f_1 and f_{10}. If monomer ratio in the feed (AN : St) is 45.7:54.3 (mol) and the water/oil ratios are 2 : 1, and 4 : 1 (wt), the AN content dissolved in water accounts for 31.9% and 49.7% (wt) of the initial total AN content, respectively. The AN contents dissolved in water are so much as to remarkably influence AN/St suspension polymerization.

Effect of an water solubility on copolymer composition

The relationship between average copolymer composition F_1 (mole fraction of AN) and conversion X (mol %) was determined at various water/oil ratios as shown in Figure 3, in which the mole fraction of St (F_2) was calculated from F_1. Figure 3 is a typical example among the results determined at various initial monomer feed ratios in this work. In Figure 3, the curves B and C, which were obtained by fitting the corresponding experimental data, describe the relationships of F_1 and X in AN/St suspension polymerization, and the curve A, which is calculated with Mayo–Lewis[1,10]

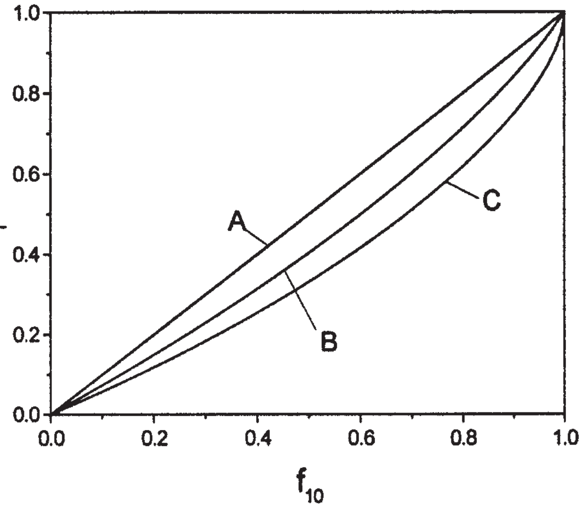

Figure 2 Relationship between initial composition in monomer phase and that in the monomer feed at 70°C. Monomer feed ratio: AN/St = 45.7 : 54.3 (mol), water/oil ratio (wt) : (A) 0 : 1 (bulk), (B) 2 : 1, (C) 4 : 1.

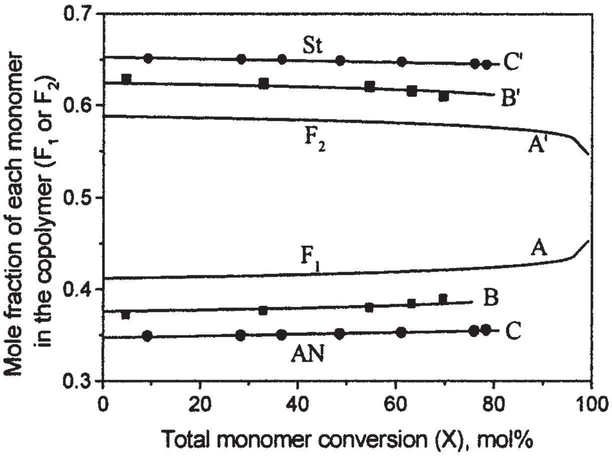

Figure 3 Comparison between the average copolymer composition in suspension polymerization and that in bulk polymerization at 70°C. Monomer feed ratio: AN/St = 45.7 : 54.3 (mol); water/oil mass ratio: (A) 0 : 1 (bulk), (B) 2 : 1, (C) 4 : 1.

equation taking $r_1 = 0.04$, $r_2 = 0.40$, describes that in bulk polymerization.

It is found that AN content in the copolymer prepared in the suspension polymerization is lower than that in the bulk polymerization, and decreases with the increase in water/oil ratio, since AN content in water increases with increase in water/oil ratio at the same monomer feed. Extrapolating F_1-X curves to X = 0, one can obtain the initial copolymer composition F_{10}, which will be infra used. On the other hand, the initial copolymer composition F_{10} can also be calculated using the following Mayo–Lewis equation:[1]

$$F_{10} = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + f_1 f_2 + r_2 f_2^2} \qquad (7)$$

where f_1 and f_2 are the real initial AN and St contents in monomer phase, r_1 and r_2 the real reactivity ratios in monomer phase. The curve A in Figure 4 was calculated using eq. (7), which describes the relationship between F_{10} and f_1 in bulk or suspension polymerization of AN and St.

For AN/St bulk polymerization, the curve A in Figure 4 can also describe the relationship between F_{10} and f_{10}, because $f_1 = f_{10}$ in bulk polymerization. In Figure 4, the symbols ■ are the experimental F_{10}–f_{10} data in bulk polymerization from the literatures.[9,11]

However, for AN/St suspension polymerization, the real initial AN content in monomer phase f_1 is lower than the monomer composition of feed f_{10} as a result of the different partitions of AN between monomer and aqueous phases. Suppose the real reactivity ratios ($r_1 = 0.04$, $r_2 = 0.40$) in monomer phase were the same as that in bulk polymerization, the curve A in Figure 4 can be used to describe the relationship between F_{10} and f_1 in suspension polymerization, but can not F_{10} and f_{10}.

To obtain the relationship between F_{10} and f_{10} in suspension polymerization, the real initial composition f_1 in monomer phase should be first calculated from the monomer composition of the feed f_{10} using eq. (4), and then F_{10} was calculated from f_1 using eq. (7). Thus, F_{10}–f_{10} data can be obtained as shown in Figure 4 (curves B, C, and D). Figure 4 shows that the greater the water/oil ratio, the larger the difference between the F_{10}–f_{10} curves of suspension polymerization and that of bulk polymerization (curve A), since AN content dissolved in water increases with the increase in water/oil ratio. Symbols ● and ▲ linked by curves B and C in Figure 4 are our experimental data for F_{10}–f_{10} relationship. It can be seen that the theoretical F_{10}–f_{10} curves (B, C, and D) are in agreement with experimental data.

In Figure 4, the relationship of F_{10} and f_1 determined in suspension polymerization was plotted with the symbols ○ and △ linked by curve A. It can be seen that F_{10}–f_1 relationship in suspension and F_{10}–f_{10} relationship in bulk are identical within the accuracy of the data and can be plotted by a same curve. This indicates that the composition difference between suspension and bulk polymerization was only caused by AN water solubility, and the real reactivity ratios in suspension polymerization should be equal to those in bulk polymerization.

Effect of water/oil ratio on apparent reactivity ratios

In the previous section, the following assumptions were made for the suspension polymerization: (1) The

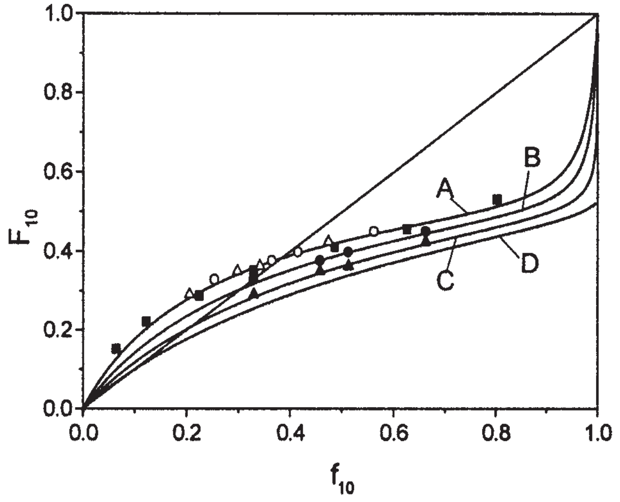

Figure 4 The initial copolymer composition F_{10} as a function of monomer composition f_{10} in the feed at 70°C. Water/oil mass ratio: (A) 0 : 1 (bulk), (B) 2 : 1, (C) 4 : 1, (D) 6 : 1 (Curve A also indicates the relationship between F_{10} and f_1 in suspension polymerization).

TABLE I
Effects of Water/Oil Ratio on the Apparent Reactivity Ratios (70°C)

Water/oil ratios (wt)	0 : 1 (bulk)	1 : 1	2 : 1	3 : 1	4 : 1
r_{1a} (AN)	0.040	0.030	0.022	0.013	0.009
r_{2a} (St)	0.400	0.486	0.570	0.660	0.760

polymerization takes place within the monomer droplets; (2) The real reactivity ratios (r_1, r_2) in monomer droplets are the same as those of bulk polymerization. However, the values of apparent reactivity ratios (r_{1a}, r_{2a}) in the classical theory for suspension polymerization are significantly different from those of the real reactivity ratios (r_1, r_2),[3,7] since the real reactivity ratios (r_1, r_2) are defined based on eq. (7), whereas the apparent reactivity ratios (r_{1a}, r_{2a}) are defined according to the following equation:

$$F_{10} = \frac{r_{1a}f_{10}^2 + f_{10}f_{20}}{r_{1a}f_{10}^2 + f_{10}f_{20} + r_{2a}f_{20}^2} \qquad (8)$$

where f_{10} and f_{20} are the monomer compositions in the feed but not the real compositions f_1, f_2 in monomer droplets (1-AN, 2-St). Comparing eqs. (7) and (8), it can be seen that in bulk polymerization, the real initial monomer composition is equal to the monomer composition in the feed ($f_1 = f_{10}$) and eqs. (7) and (8) are identical, and so $r_{1a} = r_1$, $r_{2a} = r_2$. However, in suspension polymerization, $r_{1a} \neq r_1$, $r_{2a} \neq r_2$, since $f_1 \neq f_{10}$, $f_2 \neq f_{20}$, due to partial AN water solubility.

The apparent reactivity ratios (r_{1a}, r_{2a}) can be determined by the method of Fineman and Ross[13] from the experimental (F_{10}–f_{10}) data in AN/St suspension polymerization. On the other hand, since the calculated (F_{10}–f_{10}) data in Figure 4 are in agreement with the experiments, r_{1a}, r_{2a} can also be obtained from the calculated (F_{10}–f_{10}) data. The apparent reactivity ratios (r_{1a}, r_{2a}) thus obtained at various water/oil ratios were shown in Table I.

Table I shows that the apparent reactivity ratio of AN (r_{1a}) decreases and that of St (r_{2a}) increases with increase in water/oil ratio, but do not keep constant like bulk polymerization at a certain temperature, since the greater the water/oil ratio, the more AN dissolved in water.

It is obviously discommodious to study suspension polymerization using the apparent reactivity ratios, which drift with the water/oil ratio. Moreover, the method of treating suspension polymerization using the apparent reactivity ratios is only an approximate one. The above calculation indicates that the greater the water/oil or AN content, the more the AN content dissolved in water, the greater the error caused by this approximate method. Therefore, a satisfactory discussion of the suspension copolymerization of monomer with significant water solubility requires the information of the partition of monomer between monomer and aqueous phases and its effect on the suspension copolymerization.

References

1. Pan, Z.; Weng, Z.-x.; Huang, Z. Suspension Polymerization; Chem Industry Press: Beijing, 1997 [in Chinese].
2. Zhang, S. X.; Ray, W. H. Ind Eng Chem Res 1997, 36, 1310.
3. Mino, G. J Polym Sci 1956, 22, 369.
4. Kalfas, G.; Ray, W. H.; Ind Eng Chem Res 1993, 32, 1831.
5. Hagberg, C. G. Third Chem Congr North Am 1988, 58, 614.
6. Lu, Q.; Weng, Z.-x.; Zhou, S.; Huang, Z.; Pan, Z. Eur Polym Mater 2002, 38, 1337.
7. Kalfas, G.; Ray, W. H. Ind Eng Chem Res. 1993, 32, 1822.
8. Ichiro, I.; Hitoshi, N (Asahi Chem Ind). Jpn Kodai Tokkyo Koho JP, C08j, 06,136,177; 1994–05-17.
9. Smith, W. V. J Am Chem Soc 1948, 70, 2177.
10. Lu, Q.; Weng, Z.-x.; Huang, Z.; Zhou, S. Acta Polym Sin 2000, 6, 736 [in Chinese].
11. Wang, J.; Sun, W.; Guo, X. Encyclopedia of Chem Industry, Chem Industry Press: Beijing, 1997; Vol. 1, pp 806–807 [in Chinese].
12. Marker, L.; Sweeting, O. J. J Polym Sci 1962, 57, 855.
13. Ying, S.; Yu, F. Principle of Copolymerization; Chem Industry Press: Beijing, 1984 [in Chinese].