

Effects of Water Solubility of Acrylonitrile on Vinylidene Chloride/Acrylonitrile/Styrene Suspension Polymerization

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ABSTRACT: The water solubility of acrylonitrile (AN) and its effects on vinylidene chloride/acrylonitrile/styrene (VDC/AN/St) suspension copolymerization were investigated in this study. It shows that the VDC/St ratio and the presence of suspending agent have no obvious influences on AN phase partition between the monomer and aqueous phases, whereas the water solubility of AN increases as temperature increases. Polymerization in the aqueous phase occurs extensively with azobis(isobutyronitrile) (AIBN) as initiator, whereas with lauryl peroxide (LPO) as initiator, polymerization in the aqueous phase is negligible. Theoretical analysis and experimental results indicate that transport of the monomer molecule is possible during polymerization. Both VDC and AN transfer from the monomer phase to the aqueous phase when AIBN is used as initiator. AN transfers from the aqueous phase to the monomer phase for the polymerization system initiated by LPO. Sodium nitrite (NaNO_2), but not sodium sulfide (Na_2S), can be used to effectively inhibit polymerization in water and exerts less influence on the polymerization in the monomer phase. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 1431–1438, 2001

Key words: vinylidene chloride; acrylonitrile; styrene; suspension polymerization; phase partition; transport; inhibition

INTRODUCTION

Acrylonitrile (AN) is a commonly used monomer for producing acrylic fiber and also acts as comonomer in the synthesis of engineering plastics because of its high chemical resistance, barrier property, and high reactivity with other monomers such as vinylidene chloride (VDC) and styrene (St). In recent years, the VDC/AN/St terpolymer, used as the base resin for manufacturing organic hollow particles, was in most cases developed and synthesized by suspension polymerization. AN is a highly polar organic com-

pound and thus has a relatively substantial solubility in water (7.35 wt % at 20°C)¹ compared with that of other oil-soluble monomers. When used as a comonomer in suspension polymerization, AN dissolved in the water phase would polymerize if the initiator used has some degree of water solubility and no effective water-soluble inhibitor is added. However, AN polymerization in the aqueous phase has several disadvantages. First, the chemical composition of the copolymer would be different from that of the corresponding monomer and become more heterogeneous than the copolymer prepared in bulk polymerization.^{2,3} Second, the limiting conversion of copolymerization would be lowered as a result of the water solubility of AN if the AN monomer in the aqueous phase cannot revert to the monomer phase.⁴ The third disadvantage is that the water phase will have a

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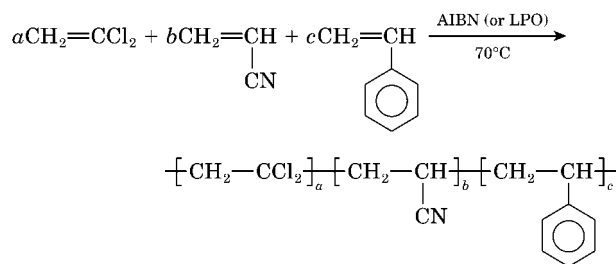
milk-like appearance as a result of polymerization in the aqueous phase. The polymer in the milk-like aqueous phase is not easy to recover and will be drained off to the surroundings, which causes the loss of polymer and pollution of the environment. So, it is important to investigate the water solubility of AN in the VDC/AN/St suspension copolymerization system, its influences on polymerization, and ways to prevent polymerization in the aqueous phase. Unfortunately, research on these aspects is seldom reported, although the preparation of VDC/AN/St copolymer by suspension polymerization was previously reported in many patents.^{5,6}

In our investigation, AN phase partition in both monomer and aqueous phases was first studied at different conditions. Polymerization in the aqueous phase, transport of monomer molecule during polymerization, and the effect of different water-soluble inhibitors on preventing polymerization in the aqueous phase were investigated next.

EXPERIMENTAL

Polymerization

Monomer VDC, AN, and St were all of industrial polymerization-grade and distilled to remove inhibitors before use. Azobis(isobutyronitrile) (AIBN) and lauryl peroxide (LPO) were used as initiators and also refined before use. Deionized water was adopted as the polymerization medium. Hydropropyl methyl cellulose (HPMC) was used as the suspending agent. The polymerization between VDC, AN, and St can be expressed as follows:



Most of VDC/AN/St copolymerizations were carried out in a 5-L autoclave equipped with a jacket and a two-blade agitator. The polymerization temperature was well controlled by a connected water bath. To easily observe polymerization phenomena in the aqueous phase, some VDC/AN/St copolymerizations were carried out in

several closed glass bottles that could withstand low pressure. To conveniently separate the polymers produced in the monomer and aqueous phases in glass-bottle polymerization, a suspending agent was not used and agitation was not applied.

Measurement of AN Phase Partition

Abbe refractometry is the simplest method to measure AN phase partition. The AN concentration in water can be measured from the refractive index of either the oil phase⁷ or the aqueous phase.² However, the method cannot be applied successfully either to the oil phase, when it contains component(s) with low boiling point, or to the aqueous phase, when it contains suspending agent(s) or salt(s). For the VDC/AN/St suspension system, Abbe refractometry is not an effective method to determine the water solubility of AN because of the lower boiling point of VDC (31.8°C) and the presence of a suspending agent in water. The gas chromatographic (GC) method was adopted to determine the concentrations of AN in both the oil and the aqueous phases and then to obtain the phase partition of AN.

Type 103 gas chromatographic meter (Shanghai Analytical Apparatus Factory of China) was used. The columns were filled with GDX101 (crosslinked polystyrene) microspheres (Tianjing No. 2 Chemical Reagent Factory of China). Hydrogen with a flow rate of about 21 mL/min was used as the carrier gas in the experiments. The temperatures of the injection block, column, and detector assembly were set at about 160, 130, and 130°C, respectively. GC treatment analyzer was used to calculate the peak area. Determination of every AN aqueous solution was repeated three times and the average value was taken.

A calibration curve of AN concentration with measured AN percentage was first set up by measuring a series of aqueous solutions with known AN concentration. Thereafter, the AN percentage in the aqueous phase from the VDC/AN/St/water system was determined by GC, and the AN concentration in the aqueous phase could be obtained from the calibration curve. The AN content in the oil (VDC/St monomer) phase was then calculated by mass balance from the difference between the AN content in the feed and the AN concentration in the aqueous phase.

Characterization of VDC-AN-St Terpolymer

For various densities of monomer and water, the VDC/AN/St/water system in glass bottle appeared

in two layers. The water layer with low viscosity was first carefully removed and then the monomer phase was obtained. Thereafter, to remove the unreacted monomer and initiators, the monomer phase containing the formed polymer was dissolved in tetrahydrofuran (THF) and then deposited by pouring the THF solution into a large volume of ethanol. The precipitated polymer was filtered and dried at 60°C under vacuum to obtain the polymer in the monomer phase. The polymer in water was obtained by directly drying the aqueous phase at a higher temperature to evaporate water and unreacted monomer. Conversion was calculated by dividing the weight of obtained polymer (not including the polymer produced in the water phase) by the total weight of monomers charged.

The size and distribution of particles of VDC–AN–St polymer were determined by LS 230 particle size analyzer (Coulter, Miami, FL). The IR spectrum of VDC copolymer was obtained using Nicolet-M560 (Nicolet Instruments, Madison, WI) Fourier transform infrared spectroscopy.

The chlorine (Cl) content of VDC–AN–St terpolymer was determined by combustion of polymer in a glass bottle filled with oxygen and titration with mercury nitrate $[\text{Hg}(\text{NO}_3)_2]^8$; the VDC content was then calculated from the Cl content. Carlo Erba 1106 element analyzer was employed to determine the nitrogen (N) content in terpolymer, after which the AN content was calculated from the N content. Besides the content of VDC and AN in copolymer, the residual content was considered as St.

RESULTS AND DISCUSSION

AN Phase Partition between Oil Phase and Aqueous Phase

AN phase partitions between the oil phases (consisting of different VDC/St monomer ratios) and aqueous phases at a temperature of 30°C are shown in Figure 1. The water solubility of AN increases with the increase of AN content in the oil phase. The increase of VDC/St ratio in the monomer recipe has no obvious effects on AN phase partition. Results from other studies of AN phase partition in both VDC/water and St/water systems determined by the refractive index method are also plotted in Figure 1. It can be seen that AN phase partitions in various systems are nearly the same.

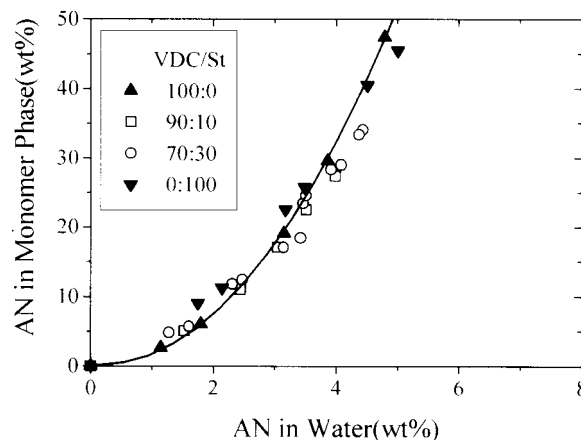


Figure 1 AN phase partition between monomer and aqueous phases at lower temperature. ■, ○: this work, 30°C; ▲: Ref. 3 (determined by refractive index method); ▼: Ref. 7 (determined by refractive index method), 26°C; solid line: calculated by eq. (1).

Marker et al.³ proposed the following relationship

$$\begin{aligned} [(A_m/m)/(A_w/w)][0.075 - A_w/w] \\ = 0.060 + 7.6A_w/w \quad (1) \end{aligned}$$

to quantitatively describe AN phase partition between VDC and water phases. Here, A_m and A_w are the weights of AN in the oil and water phases; m and w are the weights of VDC and water, respectively. Figure 1 also shows that eq. (1) can be used to predict all the AN phase partitions between the monomer phase (with different VDC/St ratios) and the aqueous phase at 30°C.

In fact, suspending agents have to be used in the suspension polymerization. The influence of the suspending agent HPMC on AN phase partition was studied and the results are presented in Table I, showing that HPMC has no obvious influence on the water solubility of AN, which is quite different from the emulsifier.⁹ Therefore, the influence of HPMC on the water solubility of AN can be neglected in the following study.

VDC/AN/St suspension polymerization is usually carried out at temperatures higher than the boiling point of VDC monomer (31.8°C). It is necessary to investigate the effect of temperature on AN phase partition. Figure 2 shows the experimental results for the oil phase with a constant VDC/St (70 : 30) ratio. It shows that the water solubility of AN increases slightly with the increase of temperature. A similar result was ob-

Table I Effects of Suspending Agent on the Water Solubility of AN

HPMC Concentration [$\times 10^{-3}$ (g/gH ₂ O)]	AN Concentration in Monomer Phase [c_v (%)]	AN Concentration in Water Phase [c_w (%)]	Phase Partition Coefficient (c_v/c_w)
0.0	2.49	10.67	4.28
2.042	2.40	9.56	3.97
4.407	2.29	9.72	4.24
5.996	2.40	9.77	4.06

Polymerization conditions: VDC/AN/St/H₂O = 60 : 15 : 25 : 200, 30°C.

served for the AN phase partition between styrene and water phases.⁷ By using the same form of eq. (1), eq. (2) is obtained by the nonlinear fitting method for AN phase partition at 60°C.

$$\begin{aligned} [(A_m/m)/(A_w/w)][0.22 - A_w/w] \\ = 0.15 + 29.15A_w/w \quad (2) \end{aligned}$$

Because St has little effect on AN phase partition, eq. (2) can be approximately used to predict the water solubility of AN for all VDC/AN/St/water systems at 60°C. It should be noted that a calculation error will be made by using the solubility value of water in the oil phase when the oil phase is rich in AN.

Evidence of Polymerization in Water

In VDC/AN/St suspension polymerization, a majority of polymer particles precipitated out immediately after stirring was stopped, although some polymer particles remained suspended in water for a long time, indicating that quite a number of

small polymer particles were formed in the suspension process. Two factors have been attributed to the formation of small particles: (1) the polymerization of some very fine monomer droplets formed under the intensive agitation and ample protection by the suspending agent, and (2) the polymerization in the water phase. To prove which factor has a greater possibility of occurrence, the AN content in polymer particles of differing diameters was measured by elemental analysis, which shows polymer particles with weight-average diameters of 10 and 90 μm , respectively, and particle size distributions (shown in Fig. 3) of 15.74 and 12.67 wt %, respectively. Elemental analysis also shows that the terpolymer compositions are different for polymer particles of various diameters. Thus, polymerization in the aqueous phase is more likely the result of the formation of small polymer particles.

To further demonstrate the presence of polymerization in water, a series of polymerizations was carried out, only without suspending agent and agitation. It was found that the water phase becomes feculent only 0.5 h later when AIBN

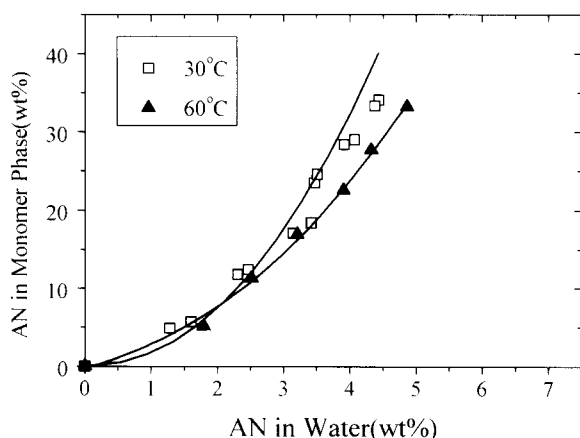


Figure 2 AN phase partition at different temperatures for VDC/St = 70 : 30 (wt %) system.

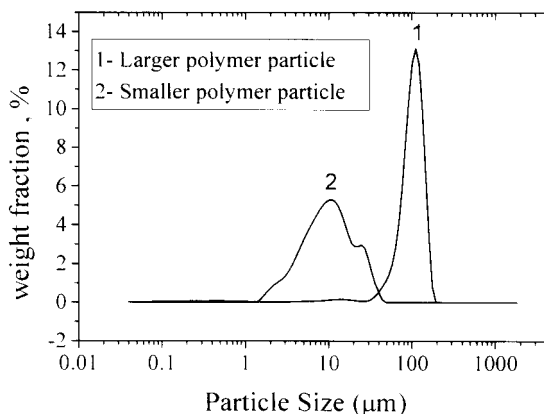


Figure 3 Particle size and distribution of larger and smaller polymer particles.

Table II Amounts of Polymer Produced in Monomer and Water Phases Using Different Initiators

Recipe			Reaction Time (h)	Polymer Formed	
Monomer (g)	Water (g)	Initiator (g)		In Monomer Phase (g)	In Water Phase (g)
10.0710	20.5254	0.1510 AIBN	6.38	6.5526	0.7218
9.0275	20.4545	0.1576 AIBN	7.25	7.6649	0.0721
9.7368	20.2127	0.3454 LPO	6.38	6.0604	0.0096
10.5946	20.4724	0.3518 LPO	7.43	9.2619	0.0049

Polymerization conditions: VDC/AN/St = 60 : 15 : 25, 70°C.

initiator was used, which caused polymerization in the water phase and formation of primary particles, as polymer chains reached a limit length and precipitated out from the water. To research the effects of initiator on the polymerization in water, LPO was also used. Table II lists the amounts of polymer produced in both the monomer and the water phases using different initiators.

Table II shows that a considerable amount of polymer is formed in the water phase when AIBN is used as initiator. Although AIBN is regarded as an oil-soluble initiator, its solubility in water is reportedly up to 1×10^{-3} mol/L in the presence of AN in water.¹⁰ The formation of polymer in the water phase must be the initiation result of AIBN in water. The polymer in the water phase reduces at 7.25 h as a result of coagulation of polymer particles and adhesion to the viscous monomer phase, without the protection of a suspending agent. This agglomeration is clearly observed

from the transparent glass bottle reactor. Because of the very low solubility of LPO in water, the amounts of polymer formed in water are negligible compared with those formed by using AIBN as initiator, although the appearance of the water phase is still cloudy. Thus, polymerization in the water phase certainly occurs in the VDC/AN/St suspension polymerization and occurs even more extensively if the water solubility of the initiator used increases.

To further understand polymerization in water, polymerization kinetics was investigated for the case with AIBN as initiator. The amounts of polymer formed at different times are plotted in Figure 4, which shows that the polymer formed in water also increases with time. Therefore, transport of monomer may occur in that case.

Transport of Monomer between Monomer and Water Phases

Transport of VDC Monomer

The VDC content in polymer is shown in Figure 5, where it can be seen that the percentage of VDC in polymer formed in the water phase is higher than that in polymer formed in the monomer phase. Figure 6 shows the IR spectra of polymer formed in both the monomer and the water phases. The absorbency peaks at frequencies of about 2240, 1500–1480, and 1355 cm^{-1} , which represent AN, St, and VDC units, respectively, occur in both IR spectra, confirming that polymers formed in both monomer and aqueous phases contain VDC, AN, and St monomer units. A comparison of the ratio of peak area at 2240 to 1494 cm^{-1} reveals that the amount of polymer formed in the aqueous phase is 15-fold larger than that of polymer formed in the monomer phase. It also indicates that the St content in polymer produced in the water phase is very low

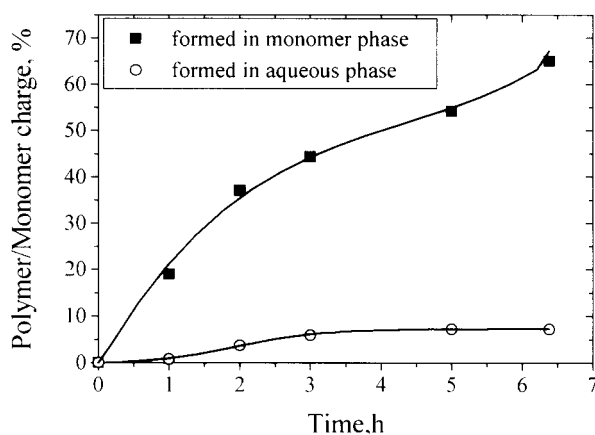


Figure 4 Variation of polymer produced in monomer and water phases with time. Polymerization conditions: VDC/AN/St/ H_2O = 60 : 15 : 25 : 200, 1.5% AIBN as initiator, 70°C.

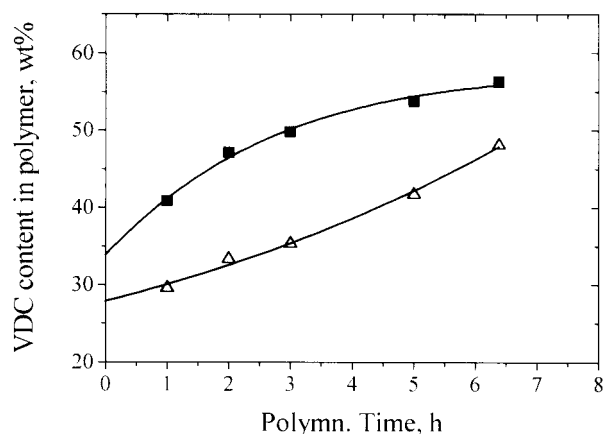


Figure 5 Variation of VDC composition in polymer with polymerization time. ■: polymer in water phase; △: polymer in monomer phase; polymerization conditions are the same as in Figure 4.

and thus negligible, which is reasonable because the water solubility of styrene (0.0271 wt %¹¹) is 10-fold lower than that of VDC (0.25 wt %¹²). Therefore, the monomer phase can be regarded as

a VDC/AN/St terpolymerization system and the water phase as a VDC/AN copolymerization system. VDC monomer is easier to add to polymer chains for VDC/AN copolymerization than for VDC/AN/St copolymerization, known from its reactivity ratios.¹³ But the water solubility of VDC is so low that it can nearly not be determined by the GC method. Thus the VDC monomer concentration in the water phase is much lower than that in the monomer phase. How is the high VDC content in polymer realized? It must be that the VDC monomer has a higher reactivity than AN in water media. To compensate the deficiency of VDC in water solution, VDC monomer has to transfer from the monomer phase to the water phase as polymerization proceeds.

The transport of VDC is a thermodynamically favored process because VDC concentration in the monomer phase increases with the increase of polymerization conversion. It found that the VDC/AN/St/water system reached equilibrium only 0.5 h later at room temperature determined by Abbe refractometer. The quick phase equilibrium of small molecules between the monomer

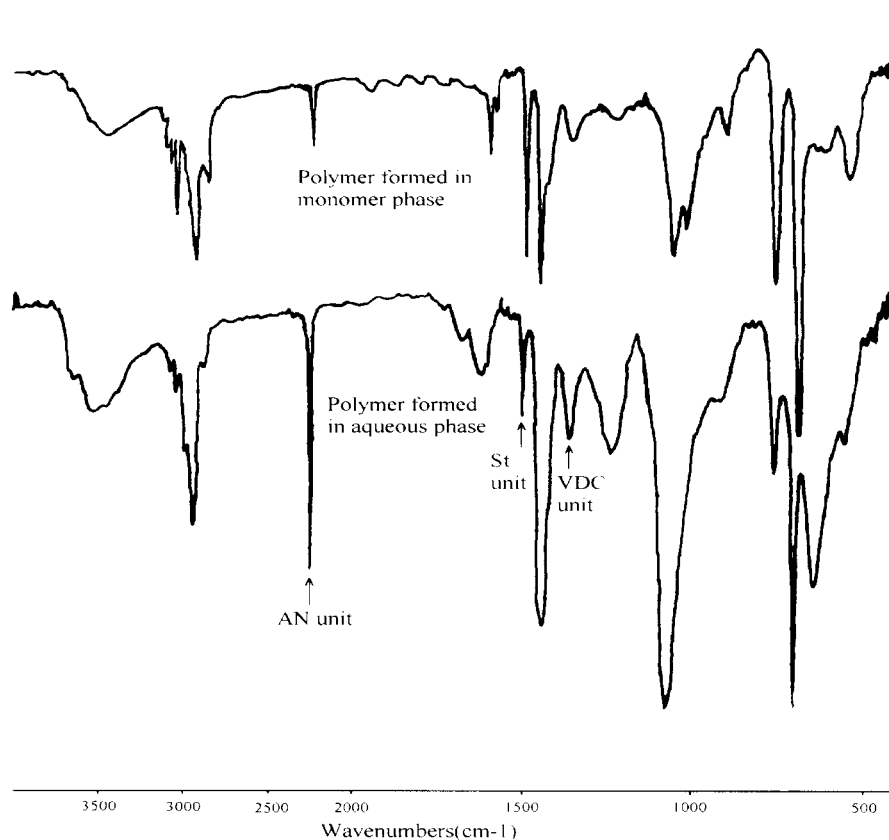


Figure 6 IR spectrum of polymer in monomer and aqueous phases.

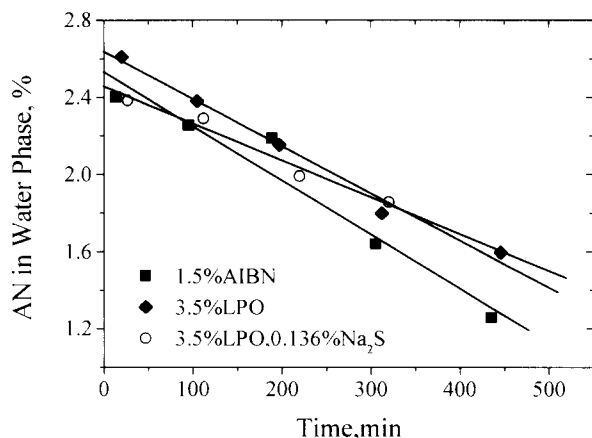


Figure 7 AN concentration in water phase against time during polymerization.

and aqueous phases was also observed by Smith⁷ and Zhang and Ray.⁴ At higher temperatures, phase equilibrium is expected to set up even more quickly, which indicates that mass-transfer resistance is small, at least at the initial polymerization stage. Thus, transport of VDC from the monomer phase to the water phase is thermodynamically and kinetically favored.

Transport of AN Monomer

Figure 7 shows the variation of AN concentration in the water phase with time during polymerization. It can be seen that AN concentration in water decreases with the increase of polymerization time for polymerization initiated by either AIBN or LPO. Polymerization, in both the monomer and the water phases for polymerization initiated by AIBN, impedes AN transport between the monomer and water phases. The theoretically calculated variations of AN concentration in water with conversion are shown in Figure 8 for two cases: (1) there was no AN transfer during polymerization and (2) AN dynamic equilibrium, by eq. (2), during polymerization was always reached. A comparison of the two curves in Figure 8 shows that the thermodynamic mass-transfer direction is from the monomer phase to the water phase. Based on the same kinetic factor of VDC transport, transport of AN from the monomer phase to the water phase encounters only slight mass-transfer resistance. For the polymerization system initiated with LPO and with/without Na₂S (water inhibitor), polymerization in water is very sparse and can be neglected; thus, the decrease of AN concentration in water is caused by

the transport of AN from the water phase to the monomer phase as polymerization in the monomer phase proceeds.

Because of the poor solubility of St in water, transport of St between the water and the monomer phases is negligible.

In a real VDC suspension system, the monomer phase was dispersed into small liquid droplets (about 100 μm). The surface per unit mass is larger and thus transport of monomer is easier than in the static polymerization system investigated in this study.

Inhibition of Polymerization in the Water Phase

Polymerization in the water phase is undesirable in suspension polymerization. From the preceding study, we know that polymerization in the water phase influences not only the composition distribution of polymer but also the polymer particle size and its distribution, and also makes posttreatment of polymer particles more difficult. To eliminate polymerization in water, two methods can be selected. One method is to use an initiator, such as LPO, that is insoluble in water. Because of the low polymerization rate of the VDC/AN/St system, great quantities of LPO have to be used in the polymerization recipe. The other method is to add water-soluble inhibitor. Table III lists the polymers formed in both the monomer and the water phases after the addition of water-soluble inhibitors.

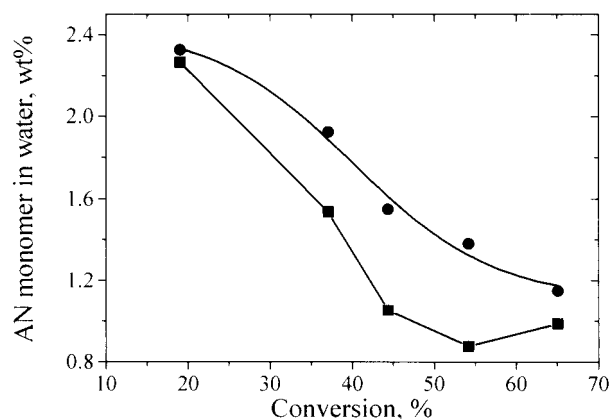


Figure 8 Variation of the calculated AN concentration in water with conversion. ●: AN concentration in water with AN dynamic equilibrium considered; ■: AN concentration in water without any AN transport between water and monomer phase during polymerization.

Table III Quantities of Polymer Formed Using Different Water-Soluble Inhibitors

Monomer (g)	Water (g)	Water-Soluble Inhibitor (g)	Polymer Formed	
			In Monomer Phase (g)	In Water Phase (g)
10.0123	20.0283	0.0102 NaNO ₂	5.6788	0.032
10.0050	20.0030	0.0204 NaNO ₂	5.7915	0.045
10.0252	20.0122	0.0305 NaNO ₂	5.4232	0.0782
10.0039	20.0118	0.0403 NaNO ₂	5.6049	0.0852
10.0024	20.0006	0.0109 Na ₂ S	5.6386	0.4922
10.0005	20.0174	0.0208 Na ₂ S	5.0576	0.4623
10.0115	20.0077	0.0302 Na ₂ S	4.2345	0.4003
10.0240	20.0011	0.0415 Na ₂ S	4.3316	0.6452

Polymerization conditions: VDC/AN/St = 60 : 15 : 25, 1.5% AIBN (based on monomer), 70°C, 5 h.

The polymer produced in the water phase substantially decreased after sodium nitrite (NaNO₂) was used, whereas the polymer produced in the monomer phase did not change with an increase of NaNO₂ usage, thus indicating that NaNO₂ exerts no inhibitory role in polymerization in the monomer phase. When sodium sulfide (Na₂S) was used, the polymer produced in the water phase is still considerable, whereas the polymer in the monomer phase decreased with increased Na₂S usage, the reason for which may be that part of Na₂S can dissolve in the monomer phase and play a role on the inhibition of polymerization in the monomer phase. Thus, Na₂S is not a good water-soluble inhibitor for the VDC/AN/St suspension copolymerization system.

CONCLUSIONS

Because of the water solubility of AN, AN phase partition between the monomer phase and the water phase takes place in the VDC/AN/St suspension polymerization system. The water solubility of AN is not affected either by the VDC/St ratio or by the presence of a suspending agent, and increases as temperature increases. When AIBN is used as the initiator, polymerization in the water phase occurs as a result of the considerable water solubility of AIBN, which is caused by the existence of AN in water. Both VDC and AN monomer transfer from the monomer phase to the water phase during polymerization. Although polymerization in water also occurs when LPO is

used as initiator, it is negligible because the quantities of polymer formed in the water phase are much less than those when using AIBN as initiator. Polymerization in water is not welcomed in VDC/AN/St suspension polymerization. It can be effectively inhibited by the water-soluble inhibitor NaNO₂, which exerts less influence on polymerization in the monomer phase.

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