Room Temperature-Initiated and Self-Heating Copolymerization of Acrylonitrile with Vinyl Acetate

HANGQUAN LI,[1] ZHONGJIE DU,[1] ELI RUCKENSTEIN[2]

[1] School of Material Science and Engineering, Beijing University of Chemical Technology, Beijing, 100029 People's Republic of China

[2] Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260

ABSTRACT: A novel polymerization method [Ruckenstein and Li, *Polymer Bull.,* **37,** 43 (1996)]—room temperature-initiated, self-heating polymerization—was applied to both bulk and concentrated emulsion copolymerization of acrylonitrile (AN) with vinyl acetate (VAc). A redox system was employed as an initiator, with the oxidant dissolved in the monomers and the reductants (two reductants were employed) in the aqueous phase. In the bulk polymerization, the oxidant (cumene hydroperoxide) was dissolved in the mixture of monomers, and the two reductants (sodium metabisulfite and ferrous sulfate) were introduced as an aqueous solution. In the concentrated emulsion polymerization, a mixture of the monomers containing dissolved oxidant was first used as the dispersed phase of a concentrated emulsion in water, and the aqueous solution of reductants was subsequently added to the concentrated emulsion. In both cases, the polymerization started at room temperature, just after the reductants were introduced. Because the reactor was insulated, the heat generated by the reaction was mostly used to accelerate the polymerization, which reached a high conversion in 30 min. The effects of various parameters on the polymerization were investigated. Optimum values were found for the volume fraction of the dispersed phase, for the wt ratios of the two reductants and of the oxidant to reductants, and for the surfactant and reductant concentrations. One concludes that the concentrated emulsion polymerization method is particularly suitable for the room temperature-initiated, self-heating polymerization. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 999–1011, 1998

Key words: self-heating copolymerization; acrylonitrile; vinyl acetate

INTRODUCTION

Acrylonitrile (AN) based polymers constitute an important family of materials. They are widely used as plastics, rubbers, fibers, and in various composites. Emulsion polymerization is one of the major methods employed to synthesize AN-based homo- and copolymers. In recent decades, attempts have been made to obtain more stable AN-based emulsions[1–3] and to select new comonomers that can improve the properties of the AN-based polymers.[4–7] Few attempts were, however, made to improve the emulsion polymerization itself. The emulsion polymerization of AN, alone or with comonomers, requires either a high initial temperature (usually >90°C)[8,9] or a long polymerization time (>4 h).[10] To initiate polymerization, the system had to be heated to an elevated temperature, and, because of the highly exothermic nature of the polymerization of AN, the heat generated had to be removed. The initial heating and the subsequent cooling make its production highly energy consuming.

In a previous article,[11] a novel procedure for

the AN polymerization based on the concentrated emulsion method[12-14] was proposed. In that method, a redox system, consisting of a hydrophobic oxidant (cumene hydroperoxide, CHPO) dissolved in the monomer(s) that constitutes the dispersed phase and two hydrophilic reductants (sodium metabisulfite, SMBS, and ferrous sulfate, FS) introduced as an aqueous solution in the continuous phase (water), was employed as an initiator. The polymerization of the AN-based monomer mixture started at room temperature in an insulated reactor as soon as the aqueous solution of reductants was added to the concentrated emulsion of monomer(s) in water, and a high conversion achieved in less than 1 h, thus providing a fast and energy-saving method for the preparation of AN-based materials. To achieve this kind of polymerization, one needs: (1) a high monomer concentration, for the reaction heat not to be exceedingly used for the heating of the nonreactive continuous phase; (2) a high oil–water interfacial area per unit volume, because the oxidant is present in the oil phase and the reductants in the water phase, and hence, the polymerization is initiated at the interface between oil and water. The concentrated emulsion polymerization[12-14] method can meet these requirements.

A concentrated emulsion has the appearance of a paste, and differs from the conventional emulsion in that the volume fraction of the dispersed phase is greater than 0.74 (which represents the volume fraction of the most compact arrangement of spheres of the same size), and can be as high as 0.99. Both a high monomer concentration and a large oil–water interfacial area can be easily achieved in a concentrated emulsion. In a previous article,[11] the room temperature-initiated copolymerization of AN and vinylidene chloride (VDC) was successfully carried out in concentrated emulsions.

In this article, the novel method is applied to the AN/vinyl acetate (VAc) system. This system was selected because of its importance in the production of fibers. Because a concentrated emulsion is stable when one of its phases is highly hydrophilic and the other one highly hydrophobic,[14] and VAc is more hydrophilic than VDC, it is more difficult to ensure the stability of the AN/VAc–water emulsion than that of the AN/VDC–water emulsion.

The bulk polymerization, in which the monomer concentration is nearly 100%, is also expected to be suitable for the room temperature-initiated polymerization. The emphasis of this article is on the concentrated emulsion polymerization be-

cause it provides a much larger interfacial surface area between the two phases, and therefore, higher polymerization rates and higher 30-min conversions than its bulk counterpart. Furthermore, the concentrated emulsion polymerization provides a powder as the product, whereas the bulk polymerization, a bulk product only.

EXPERIMENTAL

Materials

Acrylonitrile (AN, Shanghai Reagent Manufacturer, China) and vinyl acetate (VAc, Tiantai Chemical Manufacturer, Tianjin, China) were filtered through an inhibitor removal column before use. Hexadecyltrimethylammonium bromide (CTAB, Beijing Chemical Reagent Co., China), cumene hydroperoxide (CHPO, tech, >70%, Zhongxin Chemical Manufacturer, Shanghai, China), ferrous sulfate ($FeSO_4 \cdot 7H_2O$, 99%, Beijing No. 3 Chemical Reagent Manufacturer, China), sodium metabisulfite (SMBS, 97%, Shanghai No. 4 Reagent Manufacturer, China), polyvinyl alcohol (80% hydrolyzed, Donghuan Chemical Manufacturer, Beijing, China), dimethyl formamide (DMF, 99%, Tianjin Chemical Reagent Manufacturer, China), and ethanol (99%, Beijing Chemical Manufacturer, China) were used as received.

Bulk Polymerization

A mixture of acrylonitrile (AN) and vinyl acetate (VAc) was first placed in a 30-mL test tube and the tube sealed with a rubber septum and insulated. A certain amount of oxidant (cumene hydroperoxide, CHPO) was added with a syringe and allowed to dissolve in the mixture. Subsequently, an aqueous solution of reductants [sodium metabisulfite (SMBS) and ferrous sulfate (FS) of various concentrations (reductant/water) and various (SMBS/FS) ratios] was introduced with a syringe. As soon as the reductant solution was added, the test tube was shaken vigorously by hand to uniformly mix the components. After a few seconds the color of the system in the tube became first dark and subsequently white, which is an indication that the reaction started. At the moment the system became white, a glass thermometer was inserted through the rubber septum into the system to measure its temperature, which was recorded at various times during a total polymerization time of 30 min. The product

Table I   Typical Recipes for the Bulk and the Concentrated Emulsion Polymerizations

Bulk polymerization
   Monomer mixture: 5 ml (AN/VAc wt ratio = 9/1, 8/2, 7/3, ...) containing 0.2 g of oxidant
   Reductants: SMBS: 0.045 g, FS: 0.090 g
   Concentration of reductant solution: 0.5 g/g water

Concentrated emulsion polymerization
   Continuous phase—2 mL water containing 0.15 g CTAB and 0.018 g PVA
   Dispersed phase—mixture of monomers: 8 mL (AN/VAc wt ratio = 9/1, 8/2, 7/3, . . .) containing 0.263 g of
      oxidant
   Reductants: SMBS: 0.057 g, FS: 0.114 g
   Concentration of reductant solution: 0.167 g/g water

was washed and dried, and the weight ratio of the product to the monomers before polymerization taken as the monomer conversion. Because the polymerization was stopped after 30 min, the conversion will be denoted as a 30-min conversion. Table I provides typical recipes employed.

Concentrated Emulsion Polymerization

An aqueous solution of hexadecyltrimethylammonium bromide (CTAB, in various concentrations) and a very small amount of an aqueous solution of polyvinyl alcohol (PVA, 0.009 g/g water) were first placed in a 50-mL flask provided with a magnetic stirrer. The flask was sealed with a rubber septum and insulated. The monomer mixture of AN and VAc containing the oxidant, cumene hydroperoxide, was added dropwise with a syringe to the flask with vigorous stirring, until the volume fraction of the aqueous solution became a selected value (usually 0.2). The whole addition process lasted about 5 min, and took place at room temperature. A concentrated emulsion was thus generated. Subsequently, an aqueous solution of the reductants (sodium metabisulfite and ferrous sulfate) was introduced with a syringe. As soon as the reductant solution was uniformly dispersed in the concentrated emulsion (evaluated on the basis of color), the stirring was stopped. The remaining operations were as for the bulk polymerization. Table I provides typical recipes employed.

As already noted, the polymerization was carried out for only 30 min. In the preliminary work it was found that one can attain a conversion of about 80–95 wt % in 1 h. However, most of the conversion (70–85 wt %) occurred in half an hour, and after 30 min the temperature of the system became by about 30°C lower than the maximum temperature and the rate greatly slowed down.

The behavior in the first 30 min is, therefore, sufficient to describe the entire polymerization.

Product Characterization

The copolymer product was washed with ethanol to remove the small molecule impurities and subsequently with chloroform to remove the VAc homopolymers (if any). The samples thus obtained were tested with an IR-420 Fourier transform infrared spectrometer. The glass transition of the products was determined by differential scanning calorimetry, with a Perkin−Elmer DSC-2C instrument. The molecular weight was determined from the intrinsic viscosity, using the relation: $[\eta] = KM^a$, in which, because the constants K and a are not available for the copolymers, a set of constants for the AN homopolymer $K = 52 \times 10^{-3}$ and $a = 0.69$[15] were used.

RESULTS AND DISCUSSION

Temperature–Time Curves

Some typical temperature–time curves are presented in Figure 1. Additional cases are presented throughout the article. One can see that most temperature–time curves have a common shape: the temperature of the system increases first sharply, passes through a maximum, and subsequently decreases slowly. The temperature after 30 min will be denoted as T_{30}. Because the reaction is exothermic and the reactor (flask) was insulated, the temperature–time curve is actually a description of the polymerization kinetics.

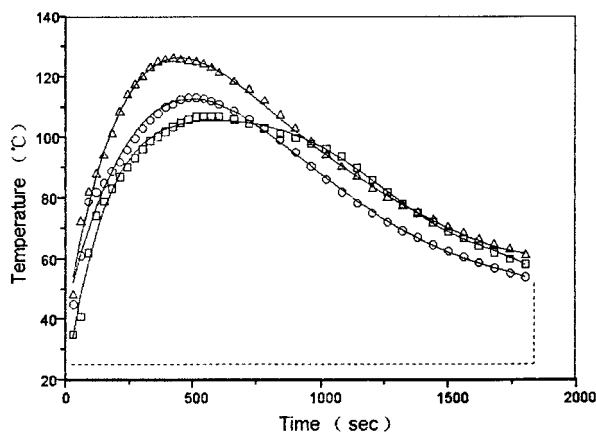Three parameters on the temperature–time curve should be noted.

Figure 1 Examples of temperature–time curves for bulk polymerization. Curve 1: square, curve 2: triangle, curve 3: circle. AN: 5 mL. Oxidant (CHPO): 0.15 g. Oxidant/reductant wt ratio = (1) 1/0.45; (2) 1/0.67; (3) 1/0.89; reductant SMBS/FS wt ratio = 2/1; concentration of reductants: 0.5 g/g water.

Temperature Maximum

Each temperature–time curve exhibits a maximum. If two polymerizations have the same temperature maximum, the one with the maximum at a later time will have usually a higher 30-min conversion, because the polymerization at the lower concentrations of the monomers was carried out at elevated temperatures.

Temperature at 30 Min (T_{30})

The value of T_{30} is an indication for the potential to continue the polymerization after 30 min. As already noted, the 30-min conversion is by about 10% smaller than the final one. Obviously, the higher the T_{30}, the higher the extent of polymerization that can be carried out after 30 min. If two polymerizations have the same 30-min conversion, the one with the higher T_{30} can be considered the better one.

Area under the Curve

The extent of reaction can be estimated from the area under the temperature–time curve above the horizontal line (dashed line in Fig. 1 that stands for the room temperature). Such an area, which we denote as "heat area," can be used as a measure of the conversion. A plot of 30-min conversion (in wt %) vs. the heat area is presented in Figure 2, which shows that the "heat area" is linearly related to the 30-min conversion.

BULK POLYMERIZATION

Effect of the Copolymerization Ratio (AN/VAc wt Ratio)

Table 2 shows that the incorporation of the comonomer VAc retards the polymerization and thus reduces the 30-min conversion. Figure 3 also shows that the maximum temperature decreases with increasing VAc content. This occurs because the polymerization of AN is much more exothermic than that of VAc. Indeed, when the homopolymerization of VAc was carried out, no polymerization took place because the heat generated by the VAc polymerization is negligible. One can conclude that the copolymerization is maintained by the heat generated by AN alone. Figure 3 shows that, for AN/VAc wt ratios of 9/1, 8/2, 7/3, and 6/4 the T_{30} are 66, 60, 55, and 38°C, respectively. At the low temperature of 38°C, the polymerization is nearly absent. These experiments indicate that for an AN/VAc wt ratio lower than 7/3, the room temperature-initiated copolymerization can hardly be employed.

Effect of SMBS/FS wt Ratio (S/F wt Ratio)

Two reductants (SMBS and FS) had to be employed. When only SMBS was used, the polymerization could be initiated, but the 30-min conversion was low (36%) (see Table II). When FS was used alone, the polymerization could not even be started. The wt ratio S/F has an effect on the 30-min conversion and the molecular weight. As the S/F wt ratio increases, the 30-min conversion passes through a maximum. The location of the maximum depends, unexpectedly, on the AN/VAc wt
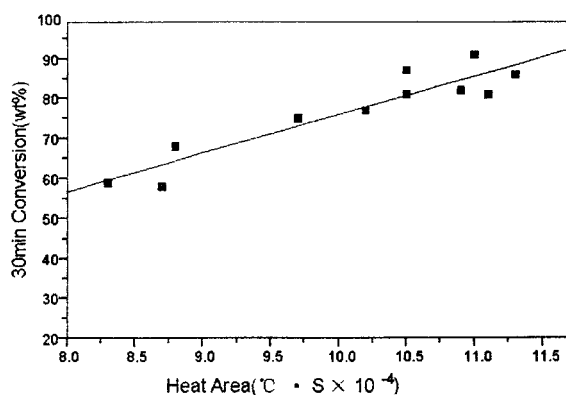

Figure 2 Relationship between the "heat area" and the 30-min. conversion (samples prepared by bulk polymerization and for various compositions).

Table II   Effect of SMBS/FS wt Ratio and Copolymerization Ratio on Bulk Polymerization

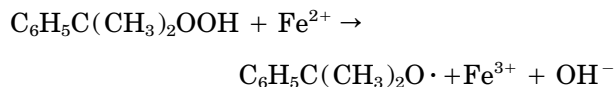| SMBS/FS Wt Ratio	AN/VAc wt Ratio	30-min conversion (wt %)	$MW \times 10^{-5}$
pure SMBS	8/2	36	1.04
6/1	8/2	40	1.18
3/1	10/0	75	—
	9/1	63	—
	8/2	60	1.15
	7/3	59	—
	6/4	43	—
2/1	8/2	61	1.34
1/1	10/0	81	—
	9/1	66	—
	8/2	63	1.59
	7/3	60	—
	6/4	42	—
1/2	10/0	91	—
	9/1	80	—
	8/2	76	2.90
	7/3	39	—
	6/4	31	—
1/3	8/2	71	2.14
1/6	8/2	69	1.85

Polymerization conditions: total volume of monomers: 5 mL.
Oxidant (CHPO): 0.15 g.
Total weight of reductants: 0.1 g, concentration of reductants: 0.5 g/g water.

ratio. When AN/VAc $\geq$ 8/2, the maximum is located at an S/F wt ratio of about 1/2; when the AN/VAc $\leq$ 7/3, the maximum is located between 3/1 and 1/1. The shift of the maximum 30-min conversion with the AN/VAc wt ratio may be due to the mixing process of the aqueous solution with

Figure 3 Temperature–time curves for various AN/ VAc wt ratios and bulk polymerization. AN/VAc wt ratio = (1) 10/0; (2) 9/1; (3) 8/2; (4) 7/3; (5) 6/4; volume of monomers: 5 mL, oxidant (CHPO): 0.2 g, SMBS: 0.045 g, FS: 0.090 g; concentration of reductants: 0.5 g/g water.

the mixture of monomers and/or to the participation of the monomers in the initiation step. The maximum can be explained by the synergism caused by the cooperation between the two reductants. Indeed, the following reaction between CHPO and FS:

$$C_6H_5C(CH_3)_2OOH + Fe^{2+} \rightarrow$$

$$C_6H_5C(CH_3)_2O \cdot + Fe^{3+} + OH^-$$

leads to a radical and Fe^{3+}, and SMBS reduces Fe^{3+} to Fe^{2+}, thus stimulating the activity of FS.

The temperature–time curves of Figure 4 show that the four curves for the higher SMBS contents exhibit higher initial slopes and earlier temperature maxima; the other four curves for lower SMBS contents exhibit lower initial slopes but later temperature maxima.

It is interesting to note that the MW of the product also exhibits a maximum that coincides with that for the 30-min conversion. In other words, the conditions that favor a high 30-min conversion also favor a high MW. Consequently, controlling the maximum 30-min conversion, one can control the molecular weight. Obviously, the 30-min conversion is dependent on the position
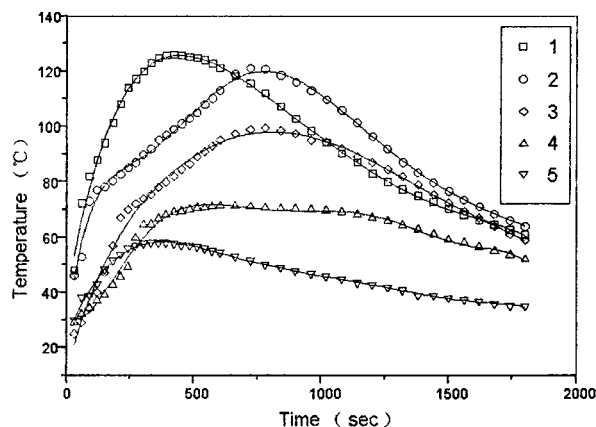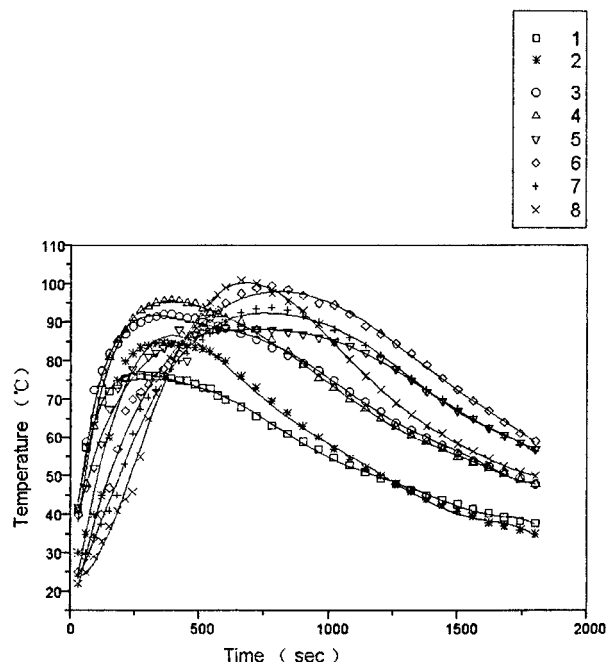
Figure 4 Temperature–time curves for various SMBS/FS wt ratios and bulk polymerization. (1) Pure SMBS, SMBS/FS wt ratio = (2) 6/1; (3) 1; (4) 2/1; (5) 1/1; (6) 1/2; (7) 1/3; (8) 1/6; volume of monomers: 5 mL, AN/VAc wt ratio = 8/2; oxidant (CHPO): 0.15 g; total weight of reductants: 0.10 g; concentration of reductants: 0.5 g/g water.

Table III Effect of Oxidant/Reductant wt Ratio on Bulk Polymerization

Oxidant/Reductant wt Ratio	30 min. Conversion (wt %)
1/0.45	52
1/0.56	61
1/0.67	60
1/0.89	56

Polymerization conditions: total volume of monomers: 5 mL, AN/VAc wt ratio = 8/2.
Oxidant (CHPO): 0.15 g, reductant SMBS/FS wt ratio = 2/1.
Concentration of reductants: 0.5 g/g water.

sequently, a higher final conversion is expected for the O/R wt ratio of 1/0.67.

The Effect of the Amount of Initiator

The effect of the amount of initiator was investigated for the fixed weight ratios CHPO/SMBS/FS = 2/0.45/0.9. The results are presented in Table IV and Figure 6. Table III shows that the effect of the amount of initiator on the 30-min conversion depends on the AN/VAc wt ratio.
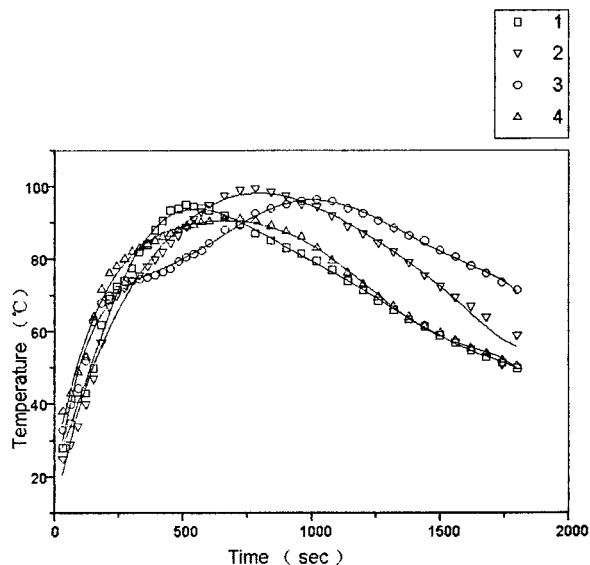
of the maximum temperature. If the maximum temperature is sufficiently late in time, the viscosity of the system can remain moderate during a large time interval and the reaction rate sufficiently high even at not too large concentrations of the monomers.

The Effect of Oxidant/Reductant wt Ratio (O/R wt Ratio)

The effect of O/R wt ratio is examined in Table III and Figure 5. Table II indicates that there is an optimum O/R wt ratio between 1/0.67–1/0.56. Higher or lower O/R wt ratios decrease the 30-min conversion. This occurs because when the proportion of reductant is low, not enough free radicals can be produced to maintain a high polymerization rate; if the amount of reductant is, however, too large, the excess reductant will react with and deactivate the radical. The curves of Figure 5 show that the O/R wt ratio of 1/0.67 should be preferred to the 1/0.56 ratio because, while the 30-min conversions are near to one another, a higher T_{30} is attained for the 1/0.67 ratio. Con-

Figure 5 Temperature–time curves for various oxidant/reductant wt ratios and bulk polymerization. Oxidant/reductant wt ratio = (1) 1/0.45; (2) 1/0.56; (3) 1/0.67; (4) 1/0.75; volume of monomers: 5 mL, AN/VAc wt ratio = 8/2; oxidant (CHPO): 0.15 g, reductant SMBS/FS wt ratio = 2/1; concentration of reductants: 0.5 g/g water.

Table IV Effect of Initiator Amount on Bulk Polymerization

Total Amount of Initiator (g/mL Monomer)	AN/VAc wt Ratio	30-min Conversion (wt %)	MW $\times$ 10^{-5}
0.025	7/3	39	—
	6/4	29	—
0.033	10/0	75	—
	9/1	71	—
	8/2	64	3.0
	7/3	64	—
	6/4	59	—
0.050	10/0	91	—
	9/1	79	—
	8/2	76	2.9
	7/3	39	—
	6/4	20	—
0.067	10/0	80	—
	9/1	79	—
	8/2	77	2.2
	7/3	51	—
	6/4	31	—
0.084	10/0	86	—
	9/1	83	—
	8/2	78	1.2
	7/3	20	—

Polymerization conditions: volume of monomers: 5 mL.
Oxidant/reductant wt ratio = 1/0.67.
SMBS/FS wt ratio = 1/2.
Concentration of reductants: 0.5 g/g water.

AN/VAc $\geq$ 8/2

In this case, the higher the amount of initiator, the higher the 30-min conversion. However, when the amount becomes greater than 0.05 g/mL, the increase of the 30-min conversion becomes moderate. Additional information is provided by the temperature–time curves of Figure 6. Curves 1, 2, and 3 are for the amounts of 0.033, 0.050, and 0.067 g/mL, respectively. The maximum temperatures are almost the same, but the times at which they are reached are 550, 750, and 1050 s, and the T_{30}s are 50, 58, and 69°C, respectively. One can conclude that, in the range 0.033–0.067 g/mL, the higher the initiator amount, the higher the conversion. However, when the initiator amount becomes too high, say 0.084 g/mL, both the maximum temperature and the T_{30} become smaller. This indicates that a value near 0.067 g/mL constitutes the optimum amount. Of course, a greater initiator amount will produce initially a larger number of free radicals, thus achieving a high initial polymerization rate. However, when an excess of initiator is present, the reductant will deactivate the free radicals, thus lowering the polymerization rate.
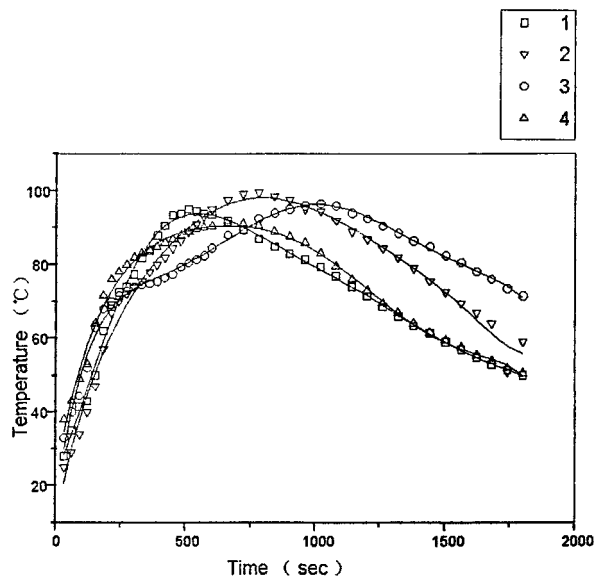

Figure 6 Temperature–time curves for various initiator amounts and bulk polymerization. Volume of monomers: 5 mL, AN/VAc wt ratio = 8/2; total amount of initiators (g/g monomers) = (1) 0.033; (2) 0.050; (3) 0.067; (4) 0.084; oxidant/reductant wt ratio = 1/0.67; SMBS/FS wt ratio = 1/2; concentration of reductants: 0.5 g/g water.

Table V Effect of the Volume Fraction (ϕ) of the Dispersed Phase in the Concentrated Emulsion

Volume Fraction (ϕ)	30-min Conversion (wt %)
66.7	54
72.7	73
76.2	79
80.0	87
84.2	78

Polymerization conditions: total volume of monomers: 8 mL, AN/VAc wt ratio = 8/2.

Oxidant (CHPO): 0.263 g, reductants: SMBS: 0.057 g, FS: 0.114 g.

Concentration of reductants: 0.167 g/g water.

Concentration of CTAB: 0.075 g/g water.

AN/VAc ≤ 7/3

In this case, the 30-min conversion has an optimum for an initiator amount of 0.033 g/mL.

CONCENTRATED EMULSION POLYMERIZATION

The Effect of the Volume Fraction ϕ of the Dispersed Phase

When ϕ changes, the reaction is affected in two opposite directions: first, because the reaction in
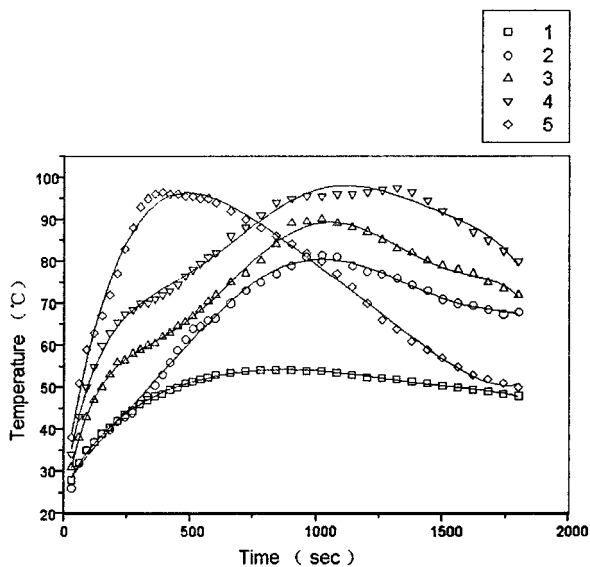

Figure 7 Temperature–time curves for various volume fractions of the dispersed phase (ϕ) in the concentrated emulsion polymerization. Φ = (1) 66.7%; (2) 74.2%; (3) 76.2%; (4) 80.0%; (5) 84.2%; volume of monomers: 8 mL, AN/VAc wt ratio = 8/2; oxidant (CHPO): 0.263 g; reductants: SMBS: 0.057 g; FS: 0.114 g; concentration of reductants: 0.167 g/g water.

this article is nearly adiabatic, the heat generated by the reaction is partially used for polymerization and partially consumed for the heating of the continuous phase, water, which does not participate in the reaction. For this reason a higher ϕ should favor the reaction and should provide a high conversion. However, when ϕ becomes too large, much larger than 0.74, (which represents the volume fraction of the most compact arrangements of spheres of the same size), the thin films between the droplets may rupture, and the concentrated emulsion becomes unstable. The higher ϕ, the more unstable the concentrated emulsion, which will segregate, thus decreasing the surface area of the interface between the continuous and dispersed phases. Because the initiation takes place at the interface, a decrease of the interfacial area will decrease the 30-min conversion. The two opposite effects lead to an optimum ϕ. Indeed, Table V and Figure 7 show that there is an optimum for ϕ = 0.8. In Figure 7 the curve based on ϕ = 0.8 possesses the highest temperature maximum and the highest T_{30}, which means that the system provides not only an optimum 30-min conversion but also possesses the highest polymerization potential after 30 min. If ϕ becomes too large (curve 5), the system exhibits a high initial polymerization rate, which, however, decreases quickly, because the emulsion becomes unstable. If ϕ is too low (curve 1), the system can hardly polymerize effectively. In conclusion, the room initiated polymerization should not be combined with the conventional emulsion polymerization, since ϕ is in the latter case much lower than 0.74.

Effect of the Surfactant

Changing the type and amount of surfactant affects directly the stability of the concentrated

Table VI Effect of the Concentration of CTAB Aqueous Solution

Concentration of CTAB (g/g Water)	30-min Conversion (wt %)
0.005	72
0.01	82
0.03	83
0.05	73
0.08	28

Polymerization conditions: total volume of monomers: 8 mL, AN/VAc wt ratio = 8/2.

Oxidant (CHPO): 0.263 g, reductants: SMBS: 0.057 g, FS: 0.114 g.

Concentration of reductants: 0.167 g/g water.

Volume fraction of the dispersed phase: 0.8.

Table VII   Effect of the Concentration of Reductants on the Concentrated Emulsion Polymerization

Concentration of Reductants (g/g water)	30-min Conversion (wt %)
0.125	64
0.167	75
0.250	73
0.333	75
0.500	42

Polymerization conditions: total volume of monomers: 8 mL, AN/VAc wt ratio = 7/3.

Oxidant (CHPO): 0.263 g, reductants: SMBS: 0.057 g, FS: 0.114 g.

Concentration of CTAB: 0.075 g/g water.

Volume fraction of the dispersed phase: 0.8.

emulsion, which in turn affects the conversion. Hexadecyltrimethylammonium bromide (CTAB), which is a cationic surfactant, was selected as the surfactant and poly(vinyl alcohol) (PVA) as co-surfactant. Anionic and nonionic surfactants such as sodium dodecylsulfate (SDS) and Tween 20 were also tried. Stable concentrated emulsions could be obtained with the latter surfactants in the presence of PVA. However, the concentrated emulsions broke as soon as the aqueous solution of reductants was introduced, and no polymerization could be initiated. Therefore, CTAB became the only choice for the room-initiated polymerization method. The amount of surfactant introduced strongly affected the stability of the emulsion. When the amount of surfactant was too small, the droplets were large and the interfacial area between the two phases relatively small. When the concentration of surfactant was too high, the ionic strength in the water became high and this weakened the double-layer repulsive force between the droplets, resulting again in a relatively small surface area. Table VI shows that as the surfactant concentration increases, the 30-min conversion exhibits a maximum. The optimum concentration is located between 0.01–0.03 (g/g water).

Effect of the Concentration of the Reductant Solution

In this article, the two reductants are introduced as an aqueous solution. The concentration of the

Table VIII   Effect of SMBS/FS wt Ratio and Copolymerization Ratio on the Concentrated Emulsion Polmerization

SMBS/FS wt Ratio	AN/VAc wt Ratio	30-min Conversion (wt %)	MW $\times 10^{-5}$	Stability of the Concentrated Emulsion
Pure SMBS	7/3	35	0.73	
6/1	8/2	63	—	
	7/3	48	0.76	
3/1	10/0	91	—	
	9/1	85	—	
	8/2	83	—	
	7/3	70	0.77	stable
	6/4	68	—	
2/1	8/2	82	—	
	7/3	77	0.81	
	6/4	71	—	
1/2	8/2	85	—	
	7/3	75	0.84	
	6/4	69	—	
1/3	7/3	61	0.72	partial segregation
1/6	7/3	38	0.66	complete segregation

Polymerization conditions: total volume of monomers: 8 mL.

Oxidant (CHPO): 0.263 g, total weight of reductants: 0.171 g.

Concentration of reductants = 0.167 g/g water.

Volume fraction of the dispersed phase: 0.8.
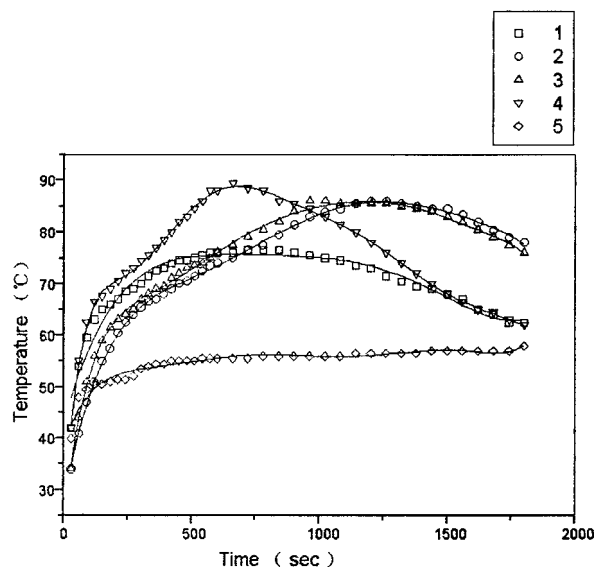
Concentration of CTAB: 0.075 g/g water.

Figure 8 Temperature–time curves for various concentrations of the aqueous solution of the reductants in the concentrated emulsion polymerization. Concentration of the reductants (g/g water) = (1) 0.125; (2) 0.167; (3) 0.250; (4) 0.333; (5) 0.500; volume of monomers: 8 mL, AN/VAc wt ratio = 7/3; oxidant (CHPO): 0.263 g; reductants: SMBS: 0.057 g, FS: 0.114 g; concentration of CTAB: 0.075 g/g water; volume fraction of the dispersed phase: 0.8.

solution plays an important role in the concentrated emulsion polymerization, even though it played a much less important role in the bulk polymerization. Table VII indicates an optimum concentration range between 0.167 and 0.333 (g/g water). Outside this range the 30-min conversion falls sharply. Figure 8 further narrows this optimum range to between 0.167 and 0.250 (g/g water). One can see that the temperature–time curve for the concentration of 0.333 g/g has a T_{30} of 62°C, whereas those for the concentrations of 0.167 and 0.250 have a T_{30} of 75°C. The optimum range is again a result of two competing factors. First, if the concentration of the reductant solution introduced is too high, the ionic concentration will be high, and this will tremendously decrease the repulsive force between droplets, making the concentrated emulsion unstable. For this reason a lower solution concentration will favor the stability of the concentrated emulsion, and hence, the polymerization. On the other hand, if the concentration of the reductant solution is too low, too much water will be introduced in the system, which will consume a part of the heat generated by the reaction, resulting in a lower polymerization rate. In addition, the low concentration itself reduces the rate. Combining the above factors, an

optimum reductant concentration is indeed obtained.

Effect of the Initiator System

Effect of SMBS/FS wt Ratio (S/F wt Ratio)

One can see from Table VIII that there is a wide range of S/F wt ratios between 3/1 and 1/2, for which, high, comparable 30-min conversions are obtained. Outside this range, i.e., for too high or too low values of the S/F ratio, the 30-min conversion is low. Among the temperature–time curves of Figure 9, that for an S/F wt ratio of 1/2 exhibits the highest T_{30}. For this reason the S/F ratio of 1/2 may be considered as the optimum one; it coincides to that for the bulk polymerization. Besides the 30-min conversion, the stability of the concentrated emulsion is also dependent on the S/F ratio. As shown in Table VIII, when the S/F ratio ≥ 1/3, the concentrated emulsion is partially or completely segregated. Because the valence of Fe^{2+} and SO_4^{2-} is two, doubling the concentration of FS will increase four times the ionic strength.
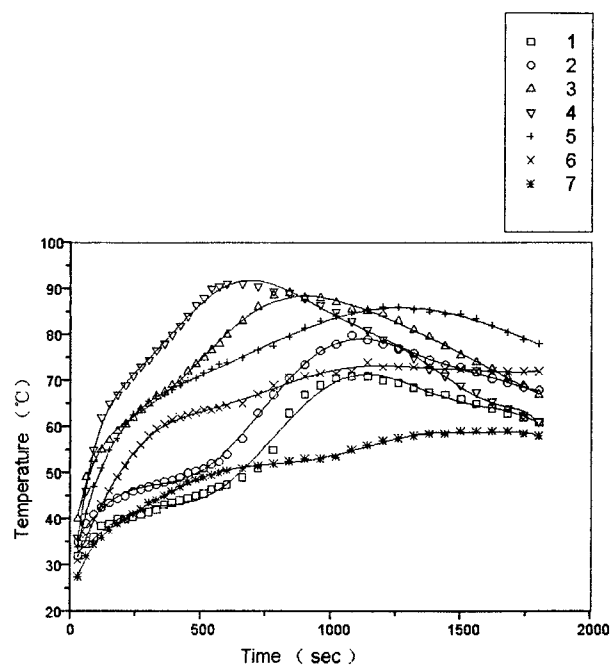

Figure 9 Temperature–time curves based on various SMBS/FS wt ratios in the concentrated emulsion polymerization. (1) pure SMBS, SMBS/FS wt ratio = (2) 6/1; (3) 3/1; (4) 2/1; (5) 1/2; (6) 1/3; (7) 1/6; volume of monomers: 8 mL, AN/VAc wt ratio = 7/3; oxidant (CHPO): 0.263 g, total weight of reductants: 0.171 g; concentration of the reductants = 0.167 g/g water; concentration of CTAB: 0.075 g/g water; volume fraction of the dispersed phase: 0.8.

Table IX Effect of Initiator Amount on the Concentrated Emulsion Polymerization

Total Amount of Initiator (g/mL monomer)	AN/VAc wt Ratio	30-min Conversion (wt %)	MW $\times 10^{-5}$
0.027	8/2	53	1.56
	7/3	34	—
	6/4	32	—
0.040	8/2	78	—
	7/3	71	1.21
	6/4	55	—
0.054	10/0	91	—
	9/1	85	—
	8/2	83	1.07
	7/3	70	—
	6/4	68	—
0.080	8/2	83	0.43
	7/3	79	—
	6/4	68	—
0.108	8/2	90	0.39
	7/3	80	—
	6/4	65	—

Polymerization conditions: total volume of monomers: 8 mL.
  Oxidant/reductant wt ratio = 1/0.65.
  SMBS/FS wt ratio = 1/3.
  Concentration of the reductants = 0.167 g/g water.
  Concentration of CTAB: 0.075 g/g water.
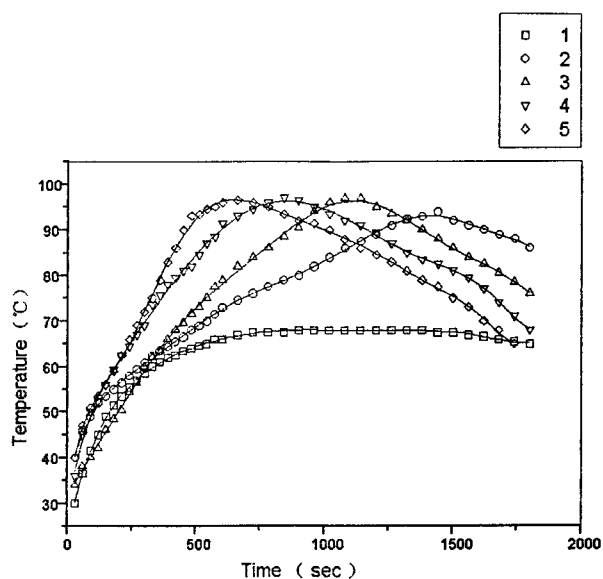 Volume fraction of the dispersed phase: 0.8.

Figure 10 Temperature–time curves for various amounts of initiators in the concentrated emulsion polymerization. Total amount of initiators (g/g monomers) = (1) 0.027; (2) 0.040; (3) 0.054; (4) 0.081; (5) 0.108; oxidant/reductant wt ratio = 1/0.65; SMBS/FS wt ratio = 1/3; concentration of the reductants = 0.167 g/g water; volume of monomers: 8 mL, AN/VAc wt ratio = 7/3; concentration of CTAB: 0.075 g/g water; volume fraction of the dispersed phase: 0.8.

The high ionic strength is responsible for the instability of the concentrated emulsion.

Effect of the Amount of Redox System

As in the bulk polymerization, the investigation was carried out at the constant wt ratios CHPO/SMBS/FS of 0.26/0.13/0.04. The effect of the amount of initiator is examined in Table IX and Figure 10. When the amount of initiator is low (0.027 g/mL monomer), the 30-min conversion is

Table X Effect of Oxidant/Reductant wt Ratio on the Concentrated Emulsion Polymerization

Oxidant/Reductant wt Ratio	30-min Conversion (wt %)
1/0.49	63
1/0.65	87
1/0.81	80
1/0.98	73

Polymerization conditions: total volume of monomers: 8 mL, AN/VAc wt Ratio = 8/2.
  Reductants: SMBS: 0.057 g; FS: 0.114 g.
  Concentration of the reductants = 0.167 g/g water.
  Concentration of CTAB: 0.075 g/g water.
  Volume fraction of the dispersed phase: 0.8.

Figure 11 Effect of the VAc content on the T_g of the copolymers. Total volume of monomers: 8 mL; AN/VAc wt ratio = (1) 10/0; (2) 9/1; (3) 8/2; (4) 7/3; (5) 6/4; oxidant (CHPO): 0.263 g; reductants: SMBS: 0.057 g, FS: 0.114 g; concentration of the reductants = 0.167 g/g water; concentration of CTAB: 0.075 g/g water; volume fraction of the dispersed phase: 0.8.
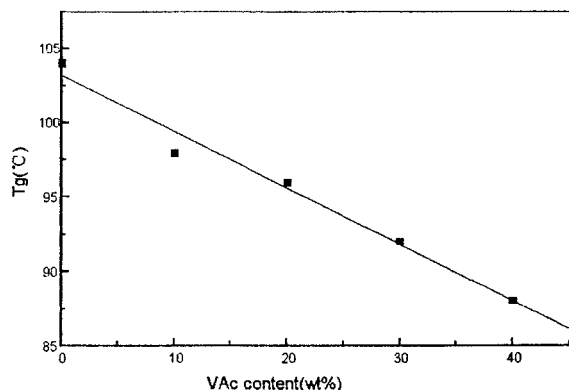
very low for obvious reasons. However, when the amount ≥ 0.04 g/mL, the 30-min conversions are high and comparable, and the amount seems to have no appreciable effect. Nevertheless, Figure 10 shows that for the four curves with initiator amounts between 0.04 and 0.108 g/mL (curves 2–5), the lower the initiator amount, the later the temperature maximum and the higher the T_{30}. One can therefore conclude that the initiator amount of 0.04 g/mL constitutes an optimum. One can also note that the MW decreases rapidly with the increase in the initiator amount. One can therefore control the MW of the product by simply adjusting the initiator amount.

Effect of Oxidant/Reductant wt Ratio (O/R wt Ratio)

Table X shows that an optimum O/R wt ratio in the range 1/0.67–1/0.87 exists, which is somewhat higher than that for the bulk polymerization (1/0.56–1/0.67).

The above experiments indicate that the VAc and AN monomers can be readily copolymerized. Because the reactivity of AN is much higher than that of VAc, a certain degree of blockiness is expected, however, to occur. In the conventional copolymerization, a third component is usually added to adjust the difference in reactivities. This issue will be explored in future work.

DSC and IR Characterization

The T_gs of a series of copolymer products are plotted against the VAc monomer content in Figure 11. Because the T_gs of AN and VAc homopolymers are 104 and 28°C, respectively, the T_g of the copolymer should decrease with increasing number of VAc units in the copolymer chains. Figure 11 indeed shows such a tendency.

The IR spectra contain the characteristic peaks of the AN and VAc units at 2242 and 1738 cm^{-1}, respectively. The relative proportion of the two units on the copolymer chains can be determined from the ratio of the heights of the two peaks. The results are listed in Table XI. One may note that the fraction of VAc units in the copolymer molecules increases with the initial monomer fraction.

CONCLUSION

The copolymerization of acrylonitrile (AN) with vinyl acetate (VAc) can be readily initiated by

Table XI Characteristics Peaks in the IR Spectra

AN/VAc wt Ratio	Location of the Peak (cm^{-1})	Height of the Peak (cm)	h_{1738}/h_{2242}
9/1	1738	2.42	0.69
	2242	3.53	
8/2	1738	3.25	1.23
	2242	2.65	
7/3	1738	2.75	1.45
	2242	1.90	
6/4	1738	2.55	1.53
	2242	1.70	

Polymerization conditions: total volume of monomers: 8 mL.
Oxidant (CHPO): 0.263 g, reductants: SMBS: 0.057 g, FS: 0.114 g.
Concentration of reductants = 0.167 g/g water.
Concentration of CTAB: 0.075 g/g water.
Volume fraction of the dispersed phase: 0.8.

a redox system formed of one oxidant and two reductants at room temperature, in bulk and concentrated emulsion polymerizations and continued on the basis of the self heating by the reaction heat. The low heat of the reaction of VAc limits its amount in the system; the room temperature initiation, self-heating polymerization is suitable only when the AN/VAc wt ratio $\geq 7/3$. Optimum values for the parameters were identified for both bulk and concentrated emulsion polymerization. For the concentrated emulsion polymerization, optimum values for the volume fraction of the dispersed phase, surfactant concentration and reductant concentration were found. They ensure a high polymerization rate and a good control of the molecular weight of the product.

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