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High-rate polymerization of acrylonitrile and butyl acrylate based on a concentrated emulsion

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Abstract

A mixture of acrylonitrile and butyl acrylate was polymerized starting from a concentrated emulsion in water. The polymerization was initiated at room temperature by a redox system, consisting of reductants dissolved in the water phase and an oxidant dissolved in the dispersed phase. The initial polymerization was carried out adiabatically with self-heating until a temperature of about 70 °C was reached; this was followed by additional heating in a water bath at a higher temperature, up to a total polymerization time of 30 min. The conversion thus achieved was higher than that obtained via the adiabatic process alone. An optimum temperature during the additional heating was observed. Because of the gel effect, the molecular weight of the product increased with time and the reaction rate became affected by diffusion. The additional heating enhanced the mobility of the species in the system, thus ensuring a final product with a composition near that of the feed. © 2002 Published by Elsevier Science Ltd.

Keywords: Acrylonitrile; Butyl acrylate; Concentrated emulsion

1. Introduction

The acrylonitrile (AN) homopolymer could not be used as a plastic because it softens only slightly below its decomposition temperature of about 300 °C. In addition, it does not dissolve in its monomer and hence cannot be shaped by bulk casting. However, the copolymers of AN with a number of comonomers could be used as plastics or rubbers. The copolymers with vinylidene chloride have been used for years to prepare films of low gas permeability, often as coatings on various materials [1]. Styrene–acrylonitrile (SAN) with styrene as the predominant unit has also been available for a long time [2]. More recently, many plastics containing high proportions of AN, the balance being an acrylate or a methacrylate, have been developed. About 95% of the materials produced are used for packaging and refrigerator liners, because their barrier capabilities are superior to those of more conventional plastics, such as ABS (acrylonitrile/butadiene/styrene ternary copolymer) and SAN. The copolymers of AN and butyl acrylate (BA) combine superior mechanical properties with a low gas permeability. However, they have been prepared by graft copolymerization, which often last for more than 6 h [3]. The radiation-induced emulsion polymerization of AN and BA was also explored [4]; however, little was applied industrially because of the complexity of the equipment. The purpose of this paper is to suggest an alternate preparative methodology, which can shorten tremendously the time of synthesis.

A high rate polymerization method based on a concentrated emulsion [5–7] was proposed by this group. A concentrated emulsion [8] is an emulsion whose volume fraction of the dispersed phase is higher than 74%, which corresponds to the close packing of spheres of the same size. At high volume fractions, the concentrated emulsions are composed of polyhedral cells, separated by thin films of continuous phase. This kind of structure of the concentrated emulsion provides, because of its large interfacial area, high rates of initiation and interfacial reaction. In the high rate polymerization, the initiation occurred at the interface between the droplets and the continuous phase. Redox initiators, consisting of reductants and an oxidant soluble in the continuous and dispersed phases, respectively, were employed and the polymerization was carried out under adiabatic conditions. Since the concentration of droplets is high, the heat generated during the reaction could be efficiently used to accelerate the polymerization, and in less

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than 1 h a high conversion, above 80 wt%, was reached. This procedure was employed to polymerize AN and a comonomer, the high reaction rate of the former being responsible for the high rate of polymerization. The comonomers studied included vinylidene chloride [5] and vinyl acetate [6,7]. It was found that the reaction heat could maintain a high polymerization rate for less than about 15 min, after which the rate has slowed down.

In this paper, an initial adiabatic self-heating was followed by an external heating to achieve a high rate of polymerization of AN with BA. The initial step was performed under adiabatic conditions until a temperature of 70 °C was reached, whereas the latter one was carried out in a water bath. The adiabatic self-heating followed by the external heating ensured a higher conversion than the adiabatic process alone. The effect of various reaction conditions on the rate of the concentrated emulsion polymerization of AN/BA system was investigated, and a comparison was made between the adiabatic alone and the combined procedures.

2. Experimental

2.1. Materials

Acrylonitrile (AN, CP, 99%) and butyl acrylate (BA, AR, 99.5%) were provided by Shanghai No. 3 Reagent Manufacturer; they were distilled before use to remove the inhibitors. Azobisisobutyronitrile (AIBN, CP) was provided by Shanghai No. 4 Reagent Manufacturer, and was recrystallized from methanol before use. Cumene hydroperoxide (CHPO, CP, >70%) and sodium metabissulfite (SMBS, CP, 90%) were purchased from the Shanghai Zhongxin Chemical Manufacturer, hexadecyltrimethylammonium bromide (HTAB) from Beijing Chemical Reagent Co., poly(vinyl alcohol) (PVA, grade 124) from Beijing Donghuan Chemical Manufacturer, ferrous sulfate (FS, AR, 99%) from Beijing Chemical Reagent Manufacturer, *N*,*N*-dimethylformamide (DMF) and ethyl acetate (EA) from Beijing Yili Chemical Co. The water was distilled and deionized.

2.2. Concentrated emulsion polymerization

Into a 50 ml flask equipped with a magnetic stirrer, 3 ml of an aqueous solution of HTAB (0.3 g/g H_2O) and about 0.04 ml of an aqueous solution of PVA (0.009 g/g H_2O) were first introduced. Then, with stirring, a mixture containing AN and BA and an oxidant (CHPO) was added dropwise with a syringe, which penetrated the rubber septum sealing the flask, until the volume fraction of the dispersed phase became 0.8. The addition lasted for about 20–30 min, and a paste-like concentrated emulsion was thus generated. After the flask containing the concentrated emulsion was properly insulated, an aqueous solution of reductants (0.167 g/g H_2O) was added with stirring using a syringe. After the solution of reductants was uniformly dispersed, the stirring could no longer be continued, because the rapid adiabatic polymerization that occurred increased tremendously the viscosity. A thermometer that penetrated the rubber septum to the center of the concentrated emulsion was employed to measure the temperature. As soon as the system attained a temperature of about 70 °C, external heating was provided. After a total of 30 min of polymerization (adiabatic plus monadiabatic), the system was taken out from the flask, washed with methanol and dried in a vacuum oven. The weight ratio of the dried product to the initial reactants represents the conversion (in wt%).

2.3. Elemental analysis

The elemental analysis was carried out using an Elemental Analyzer (Carloerba 1106, Italy).

2.4. Intrinsic viscosity measurements

The intrinsic viscosity was used as a measure of the molecular weight. It was determined using an Ubbelhode viscometer with DMF as solvent. The samples were dissolved in DMF at a concentration of 20 mg/10 ml. The testing temperature was 30 °C.

3. Results and discussion

3.1. Conversion at 30 min

The polymerization was carried out for only 30 min. In a preliminary work [6] it was found that during adiabatic polymerization one could attain a conversion of about 80–95 wt% in 1 h. However, most of the conversion (70–85 wt%) occurred in 30 min, after which the temperature of the system decreased slowly due to heat losses. The behavior in the first 30 min is, therefore, sufficient to describe the entire polymerization. In this paper, unless otherwise mentioned, the term 'conversion' denotes exclusively the conversion after 30 min of reaction.

The conversion and some polymerization parameters of AN and BA for various wt ratios of AN and BA are listed in Table 1. One can note that the fraction of AN in the mixture played an important role in the conversion: the greater the fraction of AN, the higher was the conversion. The temperature of the adiabatic systems is plotted against time in Fig. 1, which shows that the greater the fraction of AN, the higher the temperature achieved. It is obvious that the *high* temperature was responsible for the high polymerization rate. The heat of reaction for the homopolymerizations of AN and BA are 77.5 and 78 kcal/mol [9], respectively, hence the polymerization of both monomers is exothermic. However, the propagation constants for AN and BA are 28,000 and 2100 [10,11], respectively,

Table 1
Conversion (wt%) at 30 min of the concentrated emulsion

	AN/BA wt ratio		
	8/2	7/3	6/4
Adiabatic system			
Maximum temperature (°C)	91	86	71
Temperature at 30 min (°C)	73	69	62
Conversion (wt%)	80.7	76.7	61.3
Additionally heated system			
Temperature of water bath (°C)	Conversion (wt%)		
70	86.9	84.9	70.1
80	87.4	86.0	75.0
90	83.7	77.8	73.8

Total weight of the monomers: 12 g, volume fraction of the dispersed phase: 0.8, HTAB: 0.09 g, PVA: 0.04 ml of its aqueous solution (0.009 g/g H_2O), oxidant: 0.4 g, reductants: 0.257 g, (SMBS/FS = 1.5/1 w/w). The reductants were introduced as an aqueous solution (0.167 g/g H_2O).

hence the reaction rate of AN is by an order of magnitude higher than that of BA. For this reason, the polymerization of AN is much more exothermic per unit time. As a result, the polymerization was maintained mainly by AN. In fact, experiments indicated that when the fraction of AN was lower than 50 wt%, the polymerization could hardly be initiated at room temperature.

Fig. 1 shows that during the adiabatic polymerization, the temperature inside the flask increased first rapidly, reached a maximum in less than 15 min, after which the polymerization rate slowed down and the temperature decreased slowly because of some heat losses. In order to enhance the conversion, an additional external heating was employed. However, Table 2 indicates that when an external heating was employed from the beginning of the polymerization, the conversion has decreased instead of being enhanced. This may be attributed to the rate of decomposition of the organic initiator, which was larger at higher temperatures. When the polymerization was carried out under adiabatic conditions, the decomposition rate of the oxidant was enhanced slowly as the temperature increased, and thus the system could be provided steadily with fresh radicals. When, however, the system was subjected to a high temperature from the beginning, the initial decomposition rate of the organic oxidant became too high, and little organic oxidant remained available for further initiation. For these reasons, lower conversions were reached.

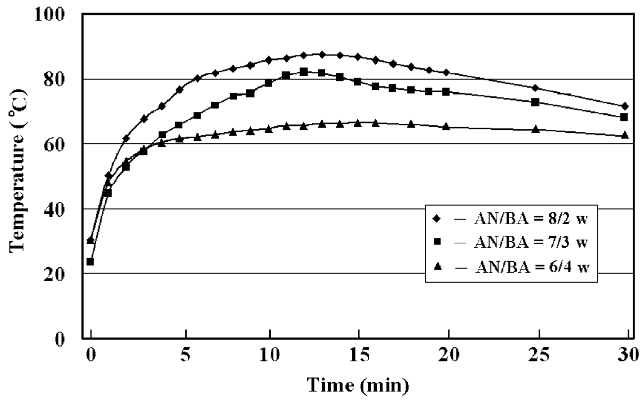

Fig. 1. Temperature–time plots for adiabatic systems of various AN/BA wt ratios. The other polymerization conditions are as for Table 1.

Table 2
Conversion in systems additionally heated from the beginning of polymerization

	Temperature of the water bath (°C)				
	50	60	70	80	90
Conversion (wt%)	68.6	72.9	60.8	55.5	70.7

AN/BA = 7/3 (wt); the other polymerization conditions are as for Table 1.

Another mechanism, involving the temperature enhancement of the reaction rate between the organic oxidant and reductants is, however, also possible. During the adiabatic polymerization, the rate of formation of the radicals is more uniform because, while the temperature gradually increases, the concentrations of the initiators decrease, and the system was provided continuously with radicals. In contrast, when the system was subjected to a high temperature from the beginning, a large number of radicals were formed initially and much fewer later, and the competition among the initial radicals decreased the conversion.

In order to avoid the above behavior, the concentrated emulsion was first subjected to an adiabatic polymerization (for about 9 min) until the temperature reached a value of about 70 °C, after which the flask was introduced into a water bath at a temperature equal or higher than 70 °C, the total polymerization time being 30 min. Table 1 shows that higher conversions were thus achieved than via the adiabatic polymerization alone. The enhancement of the conversion was dependent on the AN/BA wt ratio and on the temperature of the water bath. The lower the fraction of AN, the greater the increment of the conversion, because a smaller AN content made the adiabatic reaction less exothermic and the external heating had a greater effect. In addition, Table 1 shows that the change in temperature should not be too sharp. The conversion attained in a water bath of 90 °C was, for reasons already noted, less than that at 80 °C, and, in some cases, even below than at 70 °C. One can conclude that 80 °C represents an optimum temperature.

It should be pointed out that the polymerization in a water bath at a constant temperature is not necessarily an isothermal process. Indeed, the concentrated emulsion acquired a high viscosity and became a semi-solid for a conversion of about 20 wt%. At this conversion, stirring could no longer be employed. Under such conditions, the heat exchange with the water bath occurred only near the wall of the flask and the polymerization in the central region of the flask was still driven mostly by the self-heating due to

Table 3
Effect of the wt ratio of the reductants under adiabatic conditions

	SMBS/FS (w/w)				
	2/1	1.5/1	1/1	1/1.5	1/2
Maximum temperature (°C)	84	86	78	65	58
Temperature at 30 min (°C)	79	80	77	65	58
30 min conversion (wt%)	68.3	71.5	66.4	36.0	30.8
Intrinsic viscosity (dl/g)	85.7	124.4	115.2	97.1	67.0

AN/BA wt ratio = 7/3, other polymerization parameters are as for Table 1.

Table 4
Intrinsic viscosity (dl/g) of the concentrated emulsion with external heating

Temperature of water bath (°C)	AN/BA wt ratio		
	8/2	7/3	6/4
70	165.2	134.3	123.7
80	181.6	159.4	125.6
90	163.6	131.2	116.9
Adiabatic system	154.4	124.4	102.8

The polymerization conditions are as for Table 1. For the additional heating, the flask was introduced into a water bath when the temperature inside became about 70 °C.

the reaction. Therefore, the external heating accelerated only the region near the wall of the polymerization system.

Besides the monomer wt ratio and the external heating, the wt ratio between the two reductants also affected the conversion. Two reductants (SMBS and FS) were employed to initiate the polymerization of the concentrated emulsion. When SMBS or FS was used alone, the polymerization could hardly be initiated. Table 3 shows that the highest conversion was attained when the SMBS/FS wt ratio was 1.5/1. For higher or lower SMBS/FS wt ratios, the conversions were lower. The temperature–time curves in Fig. 2 show that for an SMBS/FS wt ratio of 1.5/1 the temperature was always higher than for the other systems. For this reason the SMBS/FS ratio of 1.5/1 constitutes an optimum ratio. This optimum was explained in a previous paper [6], as being a result of the synergism caused by the cooperative reactions of the two reductants. The reaction between the oxidant CHPO and the reductant FS is as follows

$$C_6H_5C(CH_3)_2OOH + Fe^{2+} \rightarrow C_6H_5C(CH_3)_2O^{\cdot} + Fe^{3+} + OH$$

and leads to a radical and Fe^{3+}. Further, SMBS reduces Fe^{3+} to Fe^{2+}, thus stimulating the activity of FS. In addition, we found that the SMBS/FS wt ratio affected the stability of the concentrated emulsion. When the SMBS/FS wt ratio was 1/1.5, the concentrated emulsion was partially segregated, and became less stable as the fraction of FS increased. Because the valencies of Fe^{2+} and SO_4^{2-} are two, the doubling of the concentration of FS increased four times the ionic strength. The high ionic strength was responsible for the instability of the concentrated emulsion, because of the shielding of the repulsive double layer force. A stable concentrated emulsion possesses a large surface area of the interface between the dispersed and the continuous phases where the initiation can occur; as a consequence, a higher initiation rate and thus a higher polymerization rate can be achieved.

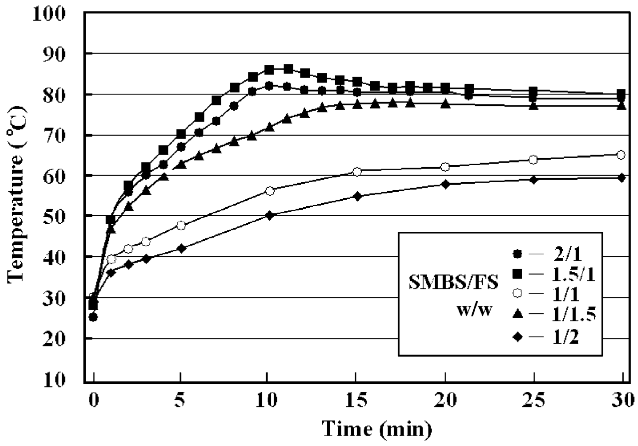

Fig. 2. Temperature–time plots for adiabatic systems of various reductant wt ratios. The other polymerization conditions are as for Table 1.

3.2. Molecular weight

The molecular weight in this paper was characterized by the intrinsic viscosity. Table 3 shows that under adiabatic conditions, as the SMBS/FS wt ratio increases, the molecular weight of the product passes through a maximum that coincides with that for the conversion. This indicates that there is a relationship between the polymerization rate and the molecular weight. Table 4 provides the intrinsic viscosities of the copolymers for various AN/BA wt ratios and temperatures of the water bath. It shows that high molecular weights are always associated with high polymerization rates. One can therefore conclude that the heat supply affected both the polymerization rate and the molecular weight. The greater the heat supply, the higher the polymerization rate and the molecular weight. Under adiabatic conditions, the only source of heat was the reaction heat. During the initial stage of polymerization, the higher the initiation rate, the higher was the polymerization rate, and an optimum wt ratio of the reductants provided a maximum polymerization rate. Using the same wt ratio of reductants, the larger the amount of AN, the greater was the heat generated. When additional heating was employed, an optimum temperature was found which provided a maximum polymerization rate. The gel effect was responsible for the high polymerization rate and the high molecular weight. Indeed, the higher the polymerization rate, the more rapid was the increase in the viscosity of the system. As the reaction mixture became more viscous, the radical ends of the polymer chains had an increasing difficulty in diffusing

Table 5
The conversion and intrinsic viscosity of the product at various polymerization time

		Time (min)								
		0.5	2.5	5	7.5	10	15	20	25	30
Conversion (wt%)	Adiabatic	4.1	11.8	19.4	34.8	57.1	62.9	61.9	67.5	77.8
	Water bath					60.4	65.2	72.4	82.2	88.2
Intrinsic viscosity (dl/g)	Adiabatic	28.7	93.7	102.7	105.6	108.1	110.0	116.3	122.0	124.4
	Water bath					114.8	125.2	136.9	149.3	159.4
Content of AN (wt%)	Adiabatic	54.5	54.7	55.0	56.5	62.6	61.3	62.6	63.3	64.6
	Water bath					65.5	64.4	66.7	66.8	69.8

AN/BA wt ratio = 7/3. For additional heating, the flask was introduced into a water bath of 80 °C after about 8 min when the temperature inside became about 70 °C. The other polymerization conditions are as for Table 1.

towards each other to terminate their growth. On the other hand, the smaller monomer molecules had lesser difficulty in diffusing so that the propagation reaction could be continued. The decrease in the termination rate constant increased both the overall rate and molecular weight. In systems with high initiation and polymerization rates, the gel effect occurs earlier, and higher molecular weights can be achieved. Particularly, when the polymer is insoluble in its monomer, the radical end becomes entrapped in the coiled chains and the termination reaction rate becomes slower. Because the AN/BA copolymer is insoluble in either AN or BA, the gel effect became very active and lasted during almost the entire process of polymerization.

The conversion and molecular weight at various times for a particular system are presented in Table 5, which indicates an abrupt increase in molecular weight at about 2.5 min, for a conversion of about 12 wt%. This behavior was most likely caused by the starting of the gel effect. Afterwards the molecular weight increased with increasing conversion, hence, the gel effect continued to be significant. Comparing the results of the adiabatic and additionally heated systems one can note that after the system was introduced into the water bath, the molecular weight kept still increasing rapidly with time, whereas in the adiabatic system it increased only moderately. This occurred because in the later stages of polymerization, the system became a semi-solid and the species needed a higher temperature to polymerize at a high rate. While the self-heating alone could not provide such conditions, the external heating could provide them and hence could maintain a high polymerization rate and achieve a high molecular weight.

Table 6
AN content of the products of adiabatic polymerization of different AN/BA wt ratios

	AN/BA wt ratio in the feed			
	9/1	8/2	7/3	6/4
AN fraction in the product (wt%)	84.3	75.1	64.6	57.5

The polymerization conditions are as for Table 1.

3.3. Composition

The change in the AN content of the product with time during the adiabatic polymerization is presented in Table 6, which shows that for each AN/BA wt ratio the AN fraction was lower than in the initial feed. The reactivity ratios reported for the copolymerization of AN and BA are comparable: 1.08 and 0.82 [12] (or 1.00 and 1.20 [13]). Consequently, the difference between the compositions of the product and the initial feed cannot be a result of their reactivity ratios alone. The AN contents for various polymerization times of a typical system are listed in Table 5, which shows that during the initial stages of polymerization the fraction of AN was much lower than that of the initial feed, but as the polymerization proceeded it increased with the conversion. In the additionally heated system, the AN fraction reached finally a value approximately equal to that in the initial mixture. However, during the adiabatic polymerization, the increase of the AN fraction was slower, being after 30 min by about 5 wt% lower than in the initial feed. The apparent higher reactivity of BA can be attributed to the gel effect, which became active a few minutes after the starting of the polymerization, when the viscosity of the droplets reached a sufficiently high level. The high molecular weight chains lost their mobility almost completely, whereas the monomers could still diffuse with some difficulty. To be incorporated into the copolymer chains, the monomers had to diffuse to become available to the radical ends. Under such circumstances, the reaction was no longer controlled by the reactivity alone, but was also affected by diffusion. Because the AN homopolymer is not soluble in either monomer, but the BA homopolymer is soluble in its monomer, BA had a higher affinity for the BA sequences. As a result, BA acquired a higher access to the polymer chains than AN and had a higher chance to be incorporated. In addition, because AN is polar and BA is nonpolar, the former molecule has stronger interactions with the polar chain and had, therefore a lower mobility than the latter molecule. As the polymerization proceeded, the fraction of AN increased, and this enhanced its incorporation rate. More importantly, as the viscosity further increased, the system became semi-solid. The movement of all the species became slower and the polymerization had to occur in an in situ way. As a result, the AN content increased with time. Because the external heating enhanced the mobility, at the end of 30 min a product with the composition of the feed was obtained. However, for adiabatic conditions, the polymerization rate was lower because of the lower temperature, and the increase in the AN fraction was more moderate. A longer reaction time would have led to an AN composition in the product comparable to that in the feed.

4. Conclusion

The effect of an additional heating that followed an adiabatic one on the high rate of polymerization of AN/BA in a concentrated emulsion was investigated. It was found that the two steps in succession achieved a conversion higher than 80 wt% within 30 min. An optimum heating temperature was found. The high rate of polymerization was caused by the gel effect and by the additional heating. The latter enhanced the mobility of the species in the semi-solid system generated during the adiabatic polymerization. The two effects ensured the generation of a high molecular weight product with a composition near that of the initial feed.

References

[1] Kodani T, Sakai H, Takayama A, Nomura M. J Appl Polym Sci 1998;69:573.
[2] Schneider M, Pith T, Lambla M. Polym Adv Technol 1996;7:577.
[3] Capek I, Juranicova V, Barton J. Eur Polym J 1999;35:691.
[4] Duflot VR, Dobrov IV, Lukhovitskii VI. High Energy Chem 2001;35:23.
[5] Ruckenstein E, Li HQ. Polym Bull 1996;37:43.
[6] Li HQ, Du ZJ, Ruckenstein E. J Appl Polym Sci 1998;68:999.
[7] Zhang C, Du ZJ, Li HQ, Ruckenstein E. Polymer 2002;43:2945.
[8] Ruckenstein E. Adv Polym Sci 1997;127:1.
[9] Brandrup J, Immergut EH. Polymer handbook, 3rd ed. New York: Wiley; 1989.
[10] Bengough WJ, Melville HW. Proc R Soc (London) A 1959;249:455.
[11] Dainton FS. J Polym Sci 1959;39:313.
[12] Tamikado T, Iwakura Y. J Polym Sci 1959;36:529.
[13] Tatemichi H, Suzuki S. Kogyo Kagaku Zassi 1960;63:1843.