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Acrylonitrile-*co*-vinyl acetate with uniform composition via adiabatic, self-heating copolymerization in a concentrated emulsion

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Abstract

A copolymer of acrylonitrile and vinyl acetate was prepared via the room temperature-initiated, self-heating polymerization of a concentrated emulsion. A mixture of the monomers containing an oxidant was first dispersed in an aqueous solution of surfactants to generate a concentrated emulsion with a volume fraction of 0.8 of the dispersed phase. An aqueous solution of reductants was subsequently introduced into the concentrated emulsion to initiate polymerization together with the oxidant. Since the container was properly insulated, the system self-heated because of the energy released from polymerization, and achieved a high conversion in 30 min. The molecular weight distribution was determined using the gel permeation chromatography (GPC), and the composition of the product was determined via elemental analysis. The GPC traces indicated that the molecular weight was a function of time. The longer the polymerization time, the greater the molecular weight. During polymerization, the composition remained almost unchanged. These two results differ from those of the traditional radical polymerization. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Acrylonitrile-*co*-vinyl acetate; Concentrated emulsion; Self-heating

1. Introduction

Acrylonitrile (AN)-based polymers have been widely used as plastics, rubbers, fibers, and in composites. Because the flow temperature of the AN homopolymer is higher than its decomposition temperature, AN in most cases is copolymerized with one or two comonomers, such as acrylates, methacrylates, styrene, and particularly, vinyl acetate (VAc). The copolymer of AN and VAc can be used either as a plastic (VAc > 15 wt%) or as fibers (VAc < 15 wt%). The copolymerization of AN/VAc was commonly carried out via the aqueous precipitation polymerization, which has the merit of simple operation and easy control of the quality of the product. The kinetics and the relationship between the properties and the reaction conditions of the aqueous precipitation polymerization were widely examined [1–3]. However, the procedure has also the shortcomings of a long reaction time and low conversion. For this reason, other approaches have been tried. The emulsion polymerization was one of them [4,5]. However, in order to increase the conversion in the copolymerization of AN-based systems via emulsion polymerization, long reaction times or high reaction temperatures had to be employed and, for these reasons, the emulsion polymerization was rarely employed in industry.

Recently, a new approach based on the methodology of concentrated emulsion [6,7], which provided a high rate and which saved energy, was proposed for the copolymerization of AN/VAc [8,9]. The concentrated emulsion is characterized by a high volume fraction of the dispersed phase, higher than 74% for globules of equal size; it can be as high as 99%. The high concentration of dispersed droplets can lead to a high productivity and a high polymerization rate. The mixture of AN and VAc was first dispersed in an aqueous solution of surfactants to generate a concentrated emulsion, and the polymerization was initiated at room temperature and occurred under adiabatic conditions. In less than 1 h, a high conversion of above 80 wt% was reached. In the reported papers, the emphasis was on the polymerization rate and its effect on conversion. Because of self-heating, the temperature changed, and this had a major effect on the polymerization rate and the resulted molecular weight and its distribution. To clarify this effect, special attentions will be paid in this paper to the molecular weight distributions (MWDs).

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2. Experimental

2.1. Materials

AN (CP 99%) was provided by Shanghai No. 3 Reagent Manufacturer, and the VAc (AR 99.5%) by the Tianjin Tiantai Reagent Manufacturer. The two monomers 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. The water was distilled and deioned.

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 a small drop of an aqueous solution of PVA (0.009 g/g H_2O) were first introduced. Then, with stirring, a mixture containing AN, VAc and an oxidant (CHPO) was added dropwise with a syringe that penetrated the rubber septum, which was sealing the flask, until the volume fraction of the dispersed phase became 0.8. The addition lasted 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 (SMBS + FS) was added with stirring using a syringe. The reductants together with the oxidant (CHPO) constitute a redox initiator. After the solution of reductants was uniformly dispersed, the stirring could not be continued, because the rapid polymerization that occurred increased tremendously the viscosity. The temperature of the system, which changed during polymerization, was determined using a thermometer inserted into the system through the rubber septum. After 30 min of polymerization, the system was taken out from the flask, washed with methanol and dried in a vacuum oven. The weight ratio of the dried product and of the initial reactants represents the conversion (in wt%).

2.3. Bulk polymerization of AN and VAc

A mixture containing AN, VAc and an initiator (AIBN) was introduced into a test-tube sealed with a rubber septum. The test-tube was placed into a water bath at 65 °C to carry out polymerization for 12 h.

2.4. Elemental analysis

The elemental analysis was carried out using the Elemental Analiser (Carloerba 1106, Italy).

2.5. Dynamic mechanical analysis

The dynamic mechanical analysis (DMA) was conducted using a Rheology Science V (USA) instrument; the frequency was 1 Hz and the heating rate 10 °C/min.

2.6. Molecular weight distribution

MWD was determined with a gel permeation chromatography (GPC) instrument (Waters 150C, USA). The samples were dissolved in DMF at a concentration of (20 mg/10 ml). The testing temperature was 45 °C. Since no calibration parameters for the AN/VAc copolymer in DMF at 45 °C were available, the data were calibrated using the parameters for polystyrene in DMF at 25 °C.

2.7. Fractionation of the products

A sample powder was washed with a solvent mixture of DMF and EA in an extractor at 80 °C for 10 h. The extracted sample was precipitated with methanol.

3. Results and discussion

The GPC traces of the products for various polymerization times and for a particular system are presented in Fig. 1. The conversion, molecular weight and its distribution as well as other parameters are listed in Table 1. All traces

Table 1
Parameters for the products at various polymerization times

Polymerization time (min)	5	10	15	20	25	30
Conversion (wt%)	16	20.6	27.4	54.2	68.1	80
CN content (wt%)	74	73.6	74.8	74	73.9	74.6
10^{-3} M_w	323	171	185	186	211	219
M_w/M_n	16.48	9.32	6.16	5.06	6.02	7.78
10^{-3} Molecular weight of peak I	410	308	323	344	353	409
Area fraction of peak I (%)	49	41.2	44.1	49.3	48	52
10^{-3} Molecular weight of peak II	86	88	91	98	104	129
Area fraction of peak II (%)	29.3	38.7	37.4	36.6	34	36.9
10^{-3} Molecular weight of peak III	114	116	117	138	139	150
Area fraction of peak III (%)	21.7	20.1	18.5	18	14.1	11.1

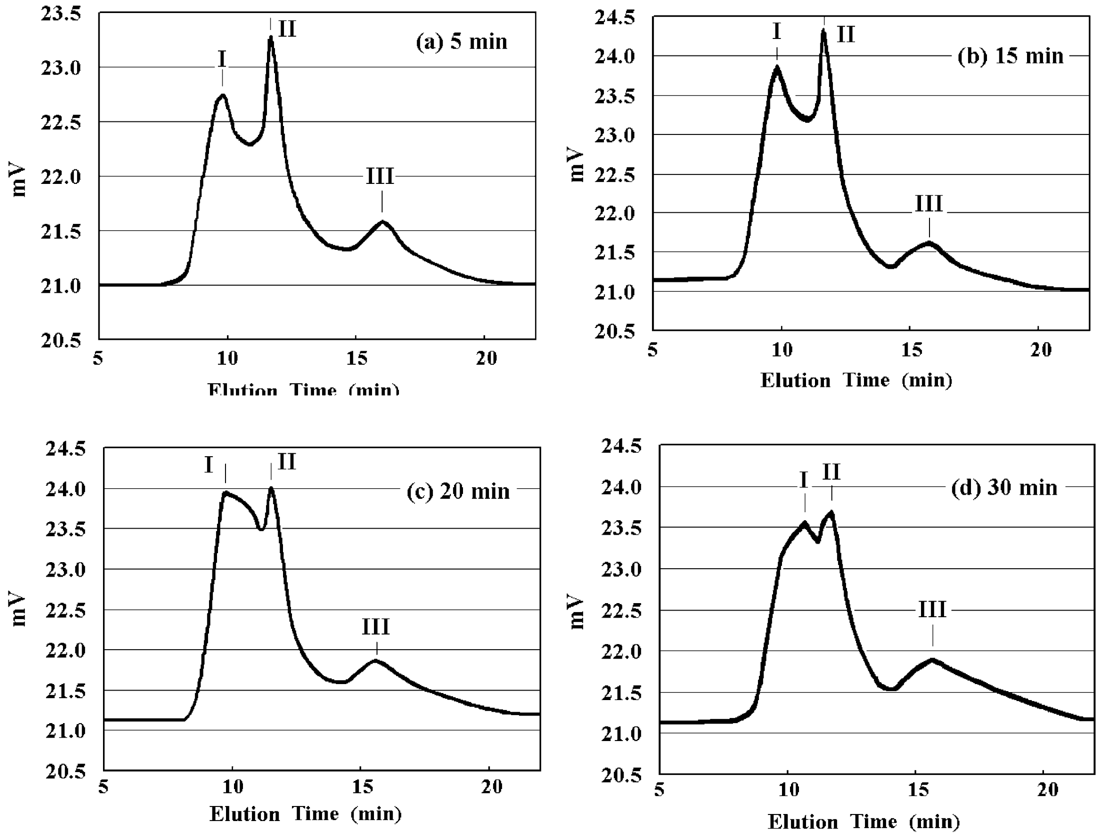

Fig. 1. GPC traces of the products at various polymerization times. Amount of monomers: 12 g; AN/VAc = 7/3 (w/w); oxidant: 0.4 g; reductant: 0.257 g; SMBS/FS = 1/2 (w/w).

have a similar shape and exhibit three peaks, two sharp ones located at higher molecular weights and a small broad one in the lower molecular range; they are denoted as I, II and III, respectively. Table 1 reveals two general trends: (i) with one exception for peak I, the molecular weight of each of the peaks increases with the polymerization time, and (ii) the area fraction of peak I increases and that of peak III decreases with the polymerization time. This indicates that the molecular weight is a function of time. This is a result of the increasing gel effect. In the radical polymerization, the average molecular weight would slowly decrease over time because the concentration of monomer decreases with time. However, because the viscosity kept increasing in each of the droplets of the concentrated emulsion during the 30 min of reaction, the coupling termination was actually weakened, and as a result, the molecular weight increased with time.

It is also worth noting that, in spite of different molecular weights, there is almost no difference in the composition of the product obtained at various times (the composition was determined via elemental analysis of nitrogen). As explained later, this is a noticeable characteristic of the concentrated emulsion polymerization.

The copolymerization parameters for AN and VAc are 4.2 and 0.05, respectively. Consequently, the copolymer should contain a much larger fraction of AN than in the monomer mixture. For comparison purposes, a bulk polymerization was carried out using the same recipe as for the concentrated emulsion polymerization. Because the reductants employed in the concentrated emulsion were soluble in water but insoluble in the hydrophobic monomers, a hydrophobic initiator (AIBN) had to be employed. The composition of the products obtained during the bulk polymerization is listed in Table 2. It is obvious that the AN content in each sample was much higher than in the initial monomer mixture, and that it changed with time. In contrast, the AN content in the product of the concentrated emulsion polymerization was only a little higher than in the initial one and remained almost unchanged during polymerization.

Two possible reasons for the uniformity of composition, which remained near that of the initial mixture of monomers, are as follows:

Table 2
Composition of the products for various reaction times of bulk polymerization (amount of monomers: 12 g; AN/VAc: 7/3 w/w; AIBN: 0.12 g; temperature: 65 °C)

Time	15 min	30 min	1 h	2.5 h	6 h	12 h
AN content (wt%)	88.8	87.4	86.6	82.3	80.5	79.7

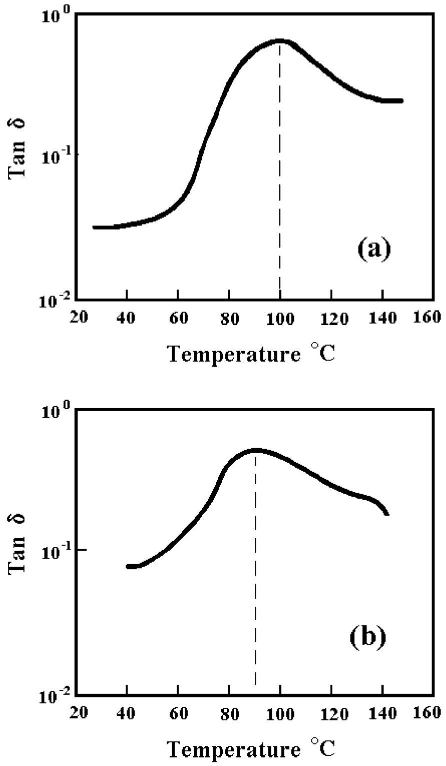

Fig. 2. DMA curves of the samples. Amount of monomers: 12 g, AN/VAc: (a) 8/2, (b) 7/3 (w/w); oxidant: 0.4 g; reductants: 0.257 g; SMBS/FS = 1/2; polymerization time: 30 min.

(a) In the copolymerization of AN and VAc, the living center prefers AN to VAc. However, the AN monomers have to diffuse rapidly to become available to the living center. Because of the high initiation rate, in a short time after the start of the polymerization, of the order of a few seconds, each of the droplets acquired such a high viscosity that stirring could no longer be performed. As a consequence, the diffusion of the monomers was greatly decreased inside the droplets, and the copolymerization occurred in an in situ way. As a result, the composition of the product remained almost the same as that of the feed.

(b) A concentrated emulsion contains many small reactors (the droplets), of the order of 1 μm. Consequently, the reaction in each of them can be completely finished in a very short time. The reaction continued for about 30 min probably because the reductant must be adsorbed on the surface of the globules to form together with the oxidant contained in the droplets a redox initiator for the reaction in the globules to take place. This process was, however, slowed down by the tremendous increase in the viscosity of the system just at the beginning of the polymerization (after a few seconds). In other words, the diffusion followed by the adsorption of the reductants constitutes the rate-determining step of the process; only the cells that acquired enough reductant molecules reacted completely, almost instantaneously in a time shorter than the times of diffusion of the monomers inside the droplets. The diffusion times of the monomers inside the droplets were actually increased because of the increasing viscosity.

Both explanations involve the slow down of the diffusion of the monomers inside the droplets (the gel effect). Explanation (b) involves, in addition, the slow down of the diffusion of the reductants in the continuous phase.

Fig. 2 presents the DMA curves of tangent of loss angle against temperature for samples prepared with wt ratios AN/VAc of monomers of 8/2 and 7/3. Both curves exhibit only one peak, which represents the glass transition temperature. As expected, the higher the initial AN content, the higher the glass transition of the final product. The single glass transition temperature provides evidence for a uniform composition in the product.

In order to bring additional evidence regarding the narrow dispersion in the composition of the product, two samples with an initial AN/VAc wt ratios = 7/3 and 9/1 were fractionated via consecutive extraction. A solvent mixture with the lowest polarity (lowest DMF/EA volume ratio) was first used to extract the species with a high content of VAc. The volume ratio of DMF was increased successively several times, in order to remove the species with higher AN content, until the entire sample was dissolved. The AN content, determined by elemental analysis, is listed in Tables 3 and 4, respectively, which show that indeed the wt% content of AN changed very little. Because the VAc homopolymer is soluble in both DMF and EA, Tables 3 and 4 reveal that this homopolymer is not present in the product. In addition, because the AN content is almost constant, no AN homopolymer is likely to be present in the product. The three peaks of the GPC traces cannot be therefore assigned to different species, but belong to chains of different molecular weights.

The effect of time on the proportions of the three kinds of chains is examined in Table 1. As already mentioned, the area fraction of peak I increases and that of peak III decreases with the polymerization time. The only exception is provided by peak I at 5 min. This happened because in the first 5 min the temperature of the system increased dramatically. The change in temperature is plotted in Fig. 3, which

Table 3
Results of the fractionation of a sample of AN/VAc = 7/3 (initial monomer wt ratio: AN/VAc = 7/3; AN content in the product: 74.3 wt%; extraction temperature: 80 °C; sample fractionated: 1.462 g)

Volume ratio of the solvents: DMF/EA	< 4/6	4/6	5/5	6/4	7/3	8/2
Wt% of the fraction	0	49.1	26.0	10.5	6.2	8.2
AN content in the fraction (wt%)	–	72.9	74.3	75.9	76.5	77.0

Table 4
Results of the fractionation of a sample of AN/VAc = 9/1 (initial monomer wt ratio: AN/VAc = 9/1; AN content in the product: 92.71 wt%; extraction temperature: 80 °C; sample fractionated: 2.152 g)

Vol ratio of the solvents: DMF/EA	< 5/5	5/5	52.5/47.5	55/45	57.5/42.5	60/40	62.5/37.5
Wt% of the fraction	0	14.03	0.71	28.49	33.69	17.84	4.83
AN content in the fraction (wt%)	–	89.95	90.47	91.87	94.44	94.64	94.81

Table 5
Polymerization parameters for various amounts of initiator (the polymerization conditions are as for Fig. 3)

Sample number	1	2	3
Amount of initiators	[a]	1.2[a]	1.5[a]
30 min conversion (wt%)	71.7	81.1	79.4
10^{-3} M_w	151	152	210
M_w/M_n	7.27	7.23	9.17
10^{-3} Molecular weight of peak I	189	198	383
Area fraction of peak I (%)	39.7	44.8	42.3
10^{-3} Molecular weight of peak II	93	119	97
Area fraction of peak II (%)	36.2	42.0	34.1
10^{-3} Molecular weight of peak III	139	148	141
Area fraction of peak III (%)	24.1	13.2	23.6

[a] Oxidant: 0.4 g, reductants: 0.257 g, wt ratio of reductants: SMBS/FS = 1/2.

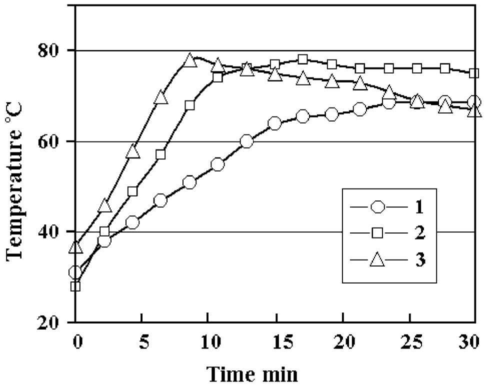

Fig. 3. Temperature–time curves for various amounts of initiators. Amount of monomers: 12 g; AN/VAc = 6/4 (w/w). Amount of initiators: oxidant: (1) 0.4 g; reductants: 0.257 g; wt ratio of reductants: SMBS/FS = 1/2; (2) (1) × 1.2; (3) (1) × 1.5.

shows that in the initial stages of polymerization, it increased rapidly and reached a maximum. A large amount of heat was generated during the early stages. As a result, the living centers could propagate rapidly, and a large fraction of high molecular weight species could be formed. Later on, the heat available decreased and the propagation of the chains was slowed down.

Fig. 3 examines the effect of the amount of initiators on the polymerization rate, which affected the molecular weights of the different types of chains present in the system. The study was carried out for CHPO/SMBS/FS = 0.4/0.086/0.171 g. The GPC traces of the products are presented in Fig. 4, and the values of various parameters are listed in Table 5. One can see that the larger the amounts of initiators, the higher the molecular weight of the whole sample and of peak I. Table 4 shows that the molecular weight of peak I of sample 3 is much higher than those of samples 1 and 2. However, the molecular weights of peaks II and III of the three samples are comparable, those of sample 2 being somewhat larger. This suggests that the effect of the amount of initiators is more important in the early stages of polymerization. Indeed, because the initiation has taken place at the interface of the droplets of the concentrated emulsion, the greater the amounts of initiators, the higher the rate of initiation. However, the viscosity of each micro-reactors increased rapidly, the motion of all the kinds of species was inhibited, and thus the termination by coupling was depressed. In addition, at high amounts of initiators, the competition between them decreased the conversion. Indeed, Table 5 shows that the conversion of sample 3 was somewhat lower than that of sample 2. As a result, high amounts of initiators are not expected to affect the polymerization rate in a major way.

The GPC traces of the products from various monomer wt ratios are presented in Fig. 5, and the values of the parameters for various monomer wt ratios are listed in Table 6. The latter table shows that the greater the fraction

Table 6
Polymerization parameters for various monomer wt ratio (amount of monomers: 12 g; AN/VAc = (1) 9/1, (2) 8/2, (3) 7/3, (4) 6/4; oxidant: 0.4 g; reductants: 0.257 g; wt ratio of the reductants: SMBS/FS = 1/2)

Wt ratio of AN/VAc	9/1	8/2	7/3	6/4	5/5
30 min conversion (wt%)	83.25	80.0	73.6	71.7	33.7
10^{-3} M_w	310	265	219	150	–
M_w/M_n	6.15	6.88	7.78	7.27	–
10^{-3} Molecular weight of peak I	423	411	409	189	–
Area fraction of peak I (%)	90.4	78.6	52.0	39.7	–
10^{-3} Molecular weight of peak II	324	192	129	93	–
Area fraction of peak II (%)	2.62	12.1	36.9	36.2	–
10^{-3} Molecular weight of peak III	168	159	150	139	–
Area fraction of peak III (%)	6.94	9.3	11.1	24.1	–

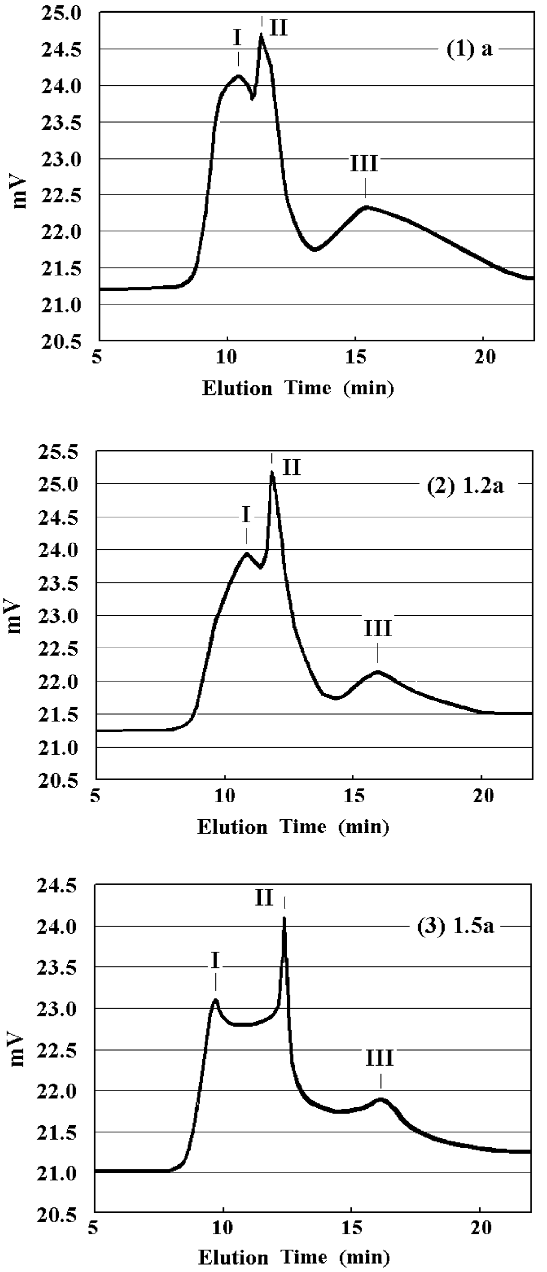

Fig. 4. GPC traces of products for various amounts of initiator. Conditions are as in Fig. 3.

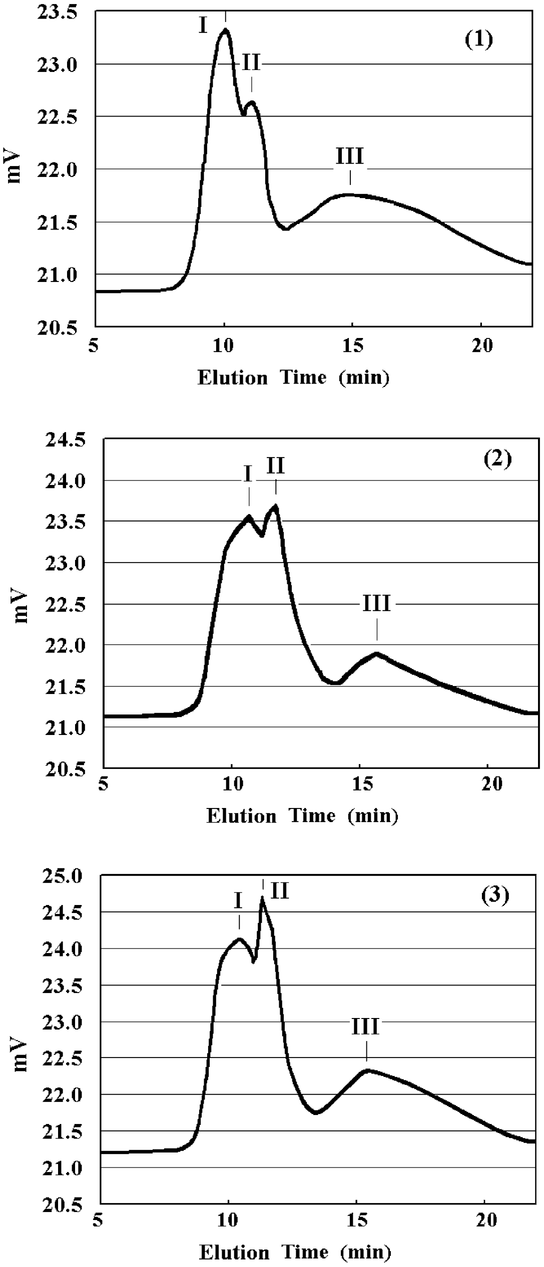

Fig. 5. GPC traces of products for various wt ratio of monomers. Amount of the monomers: 12 g; AN/VAc: (1) 8/2, (2) 7/3, (3) 6/4; oxidant: 0.4 g; reductants: 0.257 g; wt ratio of the reductants: SMBS/FS = 1/2.

of AN in the initial monomer mixture, the higher the conversion achieved within 30 min. When the weight ratio of AN/VAc was lower than 5/5, the polymerization could hardly be initiated. This can be attributed to the much larger propagation constant of AN than that of VAc (23 000–32 500 vs. 1000–1100 l/mol s). Indeed, while the heat of polymerization is somewhat higher for VAc (86 kJ/mol) than for AN (77 kJ/mol), the greater the fraction of AN, the greater the amount of heat generated per unit time through polymerization. The reaction heat is expected to affect the polymerization rate and the molecular weight. One can note that the sample based on the highest AN fraction gave rise to the highest molecular weights for all the peaks, the largest area fraction of peak I, and the highest conversion. Consequently, the heat constitutes an important factor because it accelerates the polymerization rate and also increases the molecular weight in the concentrated emulsion polymerization.

4. Conclusion

In the room temperature-initiated, self-heating copolymerization of AN and VAc via the concentrated emulsion method, the molecular weight of the products is a function of the polymerization time. The longer the reaction time is, the greater is the molecular weight. In spite of the great difference in the values of the copolymerization parameters of the two monomers (4.2/0.05), the composition of the products remained almost constant with time and conversion. The molecular weight also depends on the heat generated in the system particularly through the reaction involving the AN. High fractions of AN and high amounts of initiators favor the formation of high molecular weight species.

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