

THE EFFECT OF MONOMERS FEEDING METHODS ON EMULSION COPOLYMERIZATION OF VINYLIDENE CHLORIDE AND ACRYLATES*

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ABSTRACT

The emulsion copolymerization of vinylidene chloride (VDC) with methyl-methacrylate (MMA) and acrylonitrile (AN) was carried out by batch, seeded batch and semicontinuous processes, respectively. Significant differences were found in the physical and mechanical properties of the latexes and films, depending on the methods of monomer feeding. The results both in theory and experiments demonstrated that the copolymer composition and the length of the VDC sequences in the copolymer could be controlled by the modes of monomer feeding process.

INTRODUCTION

Vinylidene chloride (VDC)-Acrylates (ACR) copolymer latexes have been received much attention as one kind of significant high barrier coating materials, for its low permeability against most gases and vapors^[1]. However, little has been published on the effect of monomer feeding methods on the copolymer latex properties in VDC-related copolymerization, especially for a multiple copolymerization system^[2,3].

In VDC copolymerization, compositional drifts should be controlled, because copolymer fractions containing long VDC sequences have a tendency to crystallize easily, resulting in poor film-forming ability in latexes, low thermal stability and color stability. It is the purpose of this paper to explore the control of copolymer composition by monomers feeding processes in the emulsion copolymerization of VDC-MMA-AN system.

EXPERIMENTAL

1. Materials

VDC was fractionally distilled under nitrogen at 31.2 °C, the freshly

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distilled fraction was immediately used for the experiments. MMA and AN were distilled under nitrogen in vacuum. These chemicals are all CP grade without further purification. Potassium persulfate ($K_2S_2O_8$), sodium bisulfite ($NaHSO_3$) were used as the oxidant and reductant respectively. sodium lauryl sulfate (SLS) and OP-10 were used as mixture emulsifier.

2. Emulsion polymerization

The recipes used in making the latexes by three processes are given as follows:

Monomer mixture 100g (VDC 88g, MMA 8g, AN 4g), $K_2S_2O_8$ 0.15g, $NaHSO_3$ 0.05g, SLS 25g, OP-10 1ml, distilled-deionized water 150g. Polymerization temperature 45°C.

The emulsion polymerization reactor was a 500ml four-necked flask immersed in a constant-temperature bath and equipped with stirrer magnetically.

For the batch polymerization, the total monomer mixture, emulsifier and initiators were added into the reactor at the beginning of the polymerization. For the seeded batch, 50 wt% of the total monomer mixture together with other agents was charged and the mixture was maintained under N atmosphere for 18h then the remaining of the reactants was fed into the reactor to proceed for an additional 18h to complete the reaction. For the semicontinuous polymerization, 20 wt% of the total monomer mixture with other agents was first added to form the seed emulsion, after 8h the remaining monomer mixture with other agents was dropwise fed into the reactor at a constant rate within 14h. After the monomer addition procedure was finished, the polymerization was allowed to proceed for an additional 10 h to complete the reaction.

3. Analytical

Emulsion viscosity was determined by using NDJ-1 rotational viscometer at 20°C. Coagulation ratio was measured gravimetrically from the gel weights based on the total amount of dry copolymer. Particle size of the latexes were determined by a Hitachi H-800 transmission electron microscope. IBASI/2 graphic instrument was used to determine the weight-average particle diameters, as well as the particle size distributions. Fourier-transform infrared spectroscopy (Nicolet 60 SXB) was employed to determine the crystallinity of the copolymers.

The thermo-gravimetric analysis of the copolymers were determined

using the Perkin-Elmer TGA. 10 to 20 mg specimens were scanned at a heating rate of 10°C/min in the range of 80–800°C.

Tensile measurements were made at room temperature using Instron — 1185 tester. The film specimens were cut to the size as described in ASTM D-1708.

RESULTS AND DISCUSSION

1. Sequence-distribution calculation by copolymerization theory

There have been reported that the poor thermal stability of VDC polymers results from the dehydrochlorination of VDC block sequences consisted of 5, or >5, units in polymer chains^[4]. Because of the significance of controlling VDC copolymer compositions, it seems worthwhile to estimate the sequence distribution of the copolymer. On the basis of the terminal-unit copolymerization model, it is possible to calculate two types of probability from initial monomer-feed composition and reactivity.

If we assume that A, B and C represent VDC, MMA and AN monomer units respectively, $[A]$, $[B]$, and $[C]$ represent the mole fractions of monomers A, B, and C in the polymerization mixture, the conditional probability that a growing A radical adds to an A monomer expressions can be derived^[5].

$$P_{(A/A)} = \frac{1}{1 + [B]/r_{AB} * [A] + [C]/r_{AC} * [A]} \quad (1)$$

Here r_{AB} and r_{AC} are the reactivity ratios.

With a knowledge of the probability one can predict the number distribution of A sequence consisted of n units N. D. $[A_n]$:

$$\text{N. D. } [A_n] = p_{(A/A)}^{n-1} [1 - p_{(A/A)}] \quad (2)$$

and the number average length of A unit N_A :

$$N_A = (1 - p_{(A/A)})^{-1} \quad (3)$$

If r_{AB} and r_{AC} are taken to be 0.09 and 0.49 respectively from the literature^[6], we can obtain that the fraction distribution of block VDC units is 0.026, and the number average length of VDC unit is 1.89 in polymer of the present polymerization system from equations (1) to (3). It is evident that there would have been shorter VDC units and less five block VDC units in the present copolymer. However, it should be pointed out that the calculations above are adequate only for polymers prepared under conditions where the ratios of monomers in the monomer mixture remain constant. It is therefore possible to keep the ratios of monomers constant so as to control

the VDC sequence in VDC copolymers by using suitable methods of monomers feeding.

Table 1 shows the effect of feeding processes on the properties of latexes. It could be seen from Table 1 that the latex prepared by semicontinuous process has lower emulsion viscosity and higher emulsion stability than that of others. Copolymer latex which has high VDC content can not be obtained by batch process. The reason is that the copolymerizing monomers whose reactivity ratios are much larger than that of VDC would be first consumed; VDC will subsequently homopolymerize to form crystallizable VDC homopolymer, which will produce emulsion coagulating or even breaking.

Fig. 1 shows the result of average particle diameters and its distribution of VDC-MMA-AN copolymer latexes determined by TEM. The latex prepared by conventional batch polymerization showed a smaller average particle size and narrow size distribution, indicating the latex prepared by batch

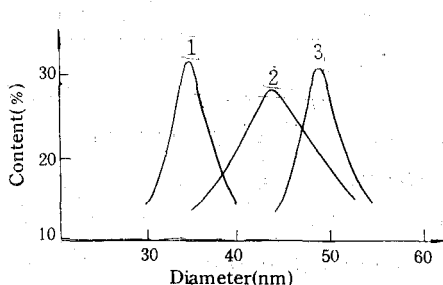


Fig. 1 The average particle diameters and size distribution of VDC-MMA-AN copolymer latexes

1. batch, 2. seeded batch, 3. semicontinuous

process has a larger number of nuclei than those of latexes by seeded process. The copolymer latex prepared by seeded batch polymerization showed an increase of average particle diameters and size distribution. These results indicate that the secondary particle nucleation took place after the seeding process. The copolymer latex prepared by semicontinuous polymerization showed a further increase of average particle diameters and almost the same narrow size distribution as those of the batch polymerization. These seem to be an indication that no secondary nucleation took place after the seeding process. The monomer mixture, dropping into the reactor after seeding process in the semicontinuous polymerization, was in a starved state so that the secondary generation of new particles would be avoided.

Table 2 shows the results of molecular weight analysis of copolymers prepared by seeded batch and semicontinuous processes respectively.

Table 1 The effect of feeding processes on properties of latexes

Properties	Batch	Seeded batch	Semicontinuous
Emulsion viscosity(cps)	65.4	52.8	27.5
Coagulation ratio (%)	12.5	0.89	0.12
Storage stability	emulsion breaking after 1 mon.	no precipitation after 3 mon.	no precipitation after 6 mon.

Table 2 The effect of two feeding processes on copolymer molecular weight

	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_w / \bar{M}_n$	$\bar{M}_z / \bar{M}_n$	$\bar{M}_z / \bar{M}_w$
Seeded batch	1.685×10^4	1.225×10^5	3.827×10^5	7.27	22.7	3.12
Semicontinuous	9.739×10^4	2.468×10^5	8.334×10^5	2.53	8.56	3.37

As illustrated in Table 2, the copolymer prepared by semicontinuous polymerization has higher molecular weight and much narrow molecular weight distribution than those of seeded batch polymerization, indicating again that the copolymers prepared by semicontinuous polymerization shows much more homogeneous than their counterparts by the seed batch polymerization.

A significant difference was also found in tensile properties of these latex films. Table 3 shows the results of the tensile measurements. The latex films prepared by semicontinuous polymerization have higher tensile strength and larger elongation to break, which might be contributed to both high molecular weight and homogeneous monomer compositions in copolymers.

Table 3 The tensile properties of the latex films

	Tensile strength (Mpa)				Elongation to break (%)			
	1	2	3	av.	1	2	3	av.
Seeded batch	23.79	17.65	23.62	21.69	230	180	220	210
Semicontinuous	38.33	32.57	36.45	35.78	304	254	286	281

Table 4 The effect of feeding processes on the thermal stability of the copolymers

	Batch	Seeded batch	Semicontinuous
Baking in 150°C for 2h	Changing to black	changing to brownish	no changing

Fig. 2 shows the curves of loss in heating determined by thermo-gravimetric analysis for the copolymers prepared by various feeding methods. It can be seen from Fig. 2 that the start temperature of thermal decomposition for the batch, seeded batch, and semicontinuous polymerization processes was 80, 210, and 215°C respectively. The difference in thermal decomposition temperature might be due to the difference in sequence compositions in the copolymers. In the semicontinuous polymerization, the corresponding compositions were more homogeneous, the VDC sequences were shorter, resulting in copolymers having higher thermal stability. These also can be illustrated by the results in Table 4.

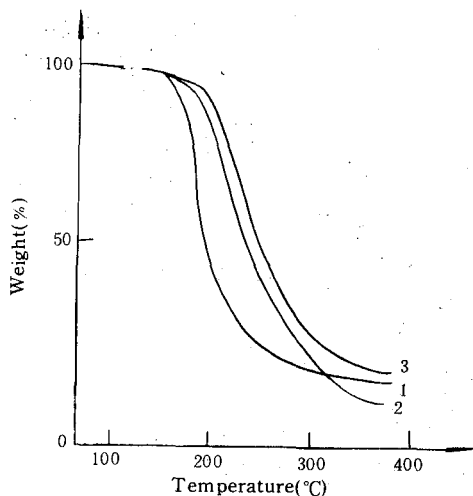


Fig. 2 The curves of thermo-gravimetric analysis for the copolymers
1. batch, 2. seeded batch, 3. semi-continuous

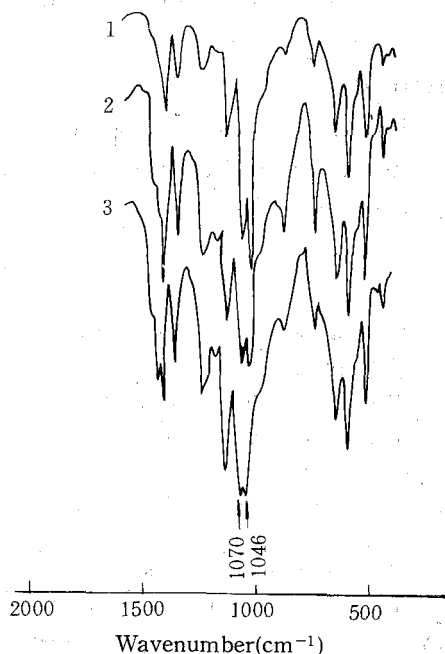


Fig. 3 Infrared spectra of the copolymer latex films
1. batch, 2. seeded batch, 3. semi-continuous

Fig. 3 shows the infrared spectra of the copolymer latex films prepared by three monomer addition models. It is known that the doublet at 1046 and 1070 cm^{-1} are designated as the characteristic crystallinity peaks of VDC copolymers^[17]. The copolymer latex film prepared by batch polymerization shows the sharpest doublet at 1046 and 1070 cm^{-1} in Fig. 3, indicating that the copolymer film has high degree of crystallinity. As only VDC units can

crystallize, this result indicate that in the batch process, the copolymer composition drifted with conversion, resulting in copolymers having a fraction of chains containing long, say 5 or more, VDC sequences.

CONCLUSIONS

The method of monomer feeding is found to have a remarkable effect on the physical and mechanical properties of VDC — MMA — AN emulsion copolymerization. The copolymer latex films prepared by semicontinuous polymerization, in general, were much more homogeneous in composition and amorphous in character. The copolymer composition and the length of the VDC sequences in the copolymer could be controlled by the mode of monomer addition.

Keywords:

Vinylidene chloride, Methyl methacrylate; Acrylonitrile; Emulsion polymerization; Feeding modes; Sequence distribution of copolymers composition

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