

Studies on Synthesis of Acrylic Water Borne Polymer

—Synthesis of Poly(vinyl acetate) and Poly(vinyl acetate-co-2-ethylhexyl acrylate)—

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Acrylic Water Borne Polymer의 합성 연구

—Poly(vinyl acetate)와 poly(vinyl acetate-co-2-ethylhexyl acrylate)의 합성 연구—

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요 약

Poly(vinyl acetate)와 poly(vinyl acetate-co-2-ethylhexyl acrylate)를 여러 조건에서 semicontinuous emulsion 중합으로 합성하였다. Overall conversion, emulsion 입자크기, pH, 점도 등을 합성한 두 emulsion polymer에 대해 측정하였다. Vinyl acetate monomer에 2-ethylhexyl acrylate를 도입함으로써 emulsion 입도, 점도, 중합 속도, 유리 전이 속도가 감소함을 확인하였다.

I. Introduction

Water-borne systems are now being viewed as a potential major new technology for industrial coatings.^{1, 2)}

Industry's need for new coatings technologies has been a result of many influences, including increased attention to environmental pollution and occupational health and safety. There is also an advantage in cleanup operations, since water or water-based agents can be used instead of solvent-type cleaners.³⁾

Latex-based coatings can increase productivity. High-solids latex systems can provide good sealing and filling properties with one-coat, one-pass application. Because they are dispersions rather than solutions, latexes also provide fast

water release for quick set and dry.^{4, 5)}

The two main types of copolymer latexes are vinyl acetate-acrylic and styrene-acrylic. In each type, hardness is provided by the vinyl acetate or styrene component, with acrylic acetate incorporated at varying levels to control hardness and increase flexibility.

The vinyl acrylic latexes are characterized by outstanding ultraviolet stability and tint retention on weathering.

D. Donescu et al. had studied the emulsion polymerization of vinyl acetate(VAc) in the presence of macromolecular protective colloids of poly(vinyl alcohol)(PVA), ethylene oxide-propylene oxide-copolymers, and hydroxyethyl cellulose. The result pointed out that during emulsion polymerization, graft copolymer of poly(vinyl acetate)-protective colloid were obtained.^{6, 7)}

In the present paper, attempts were made to observe the overall polymerization features of poly(vinyl acetate)(PVAc) and poly(vinyl acetate-co-2-ethylhexyl acrylate)[Copolymer (VAc/2-EHA)] emulsion systems, particle size, viscosity, and thermal behavior of emulsion systems.

II. Experimental

1. Materials

Vinyl acetate and 2-ethylhexyl acrylate were purified by inhibitor removal column. Poly(vinyl alcohol) was used without further purification. The number average molecular weight of Poly(vinyl alcohol) were 35,000 and 120,000.

Sodium acetate, ammonium persulfate, nonyl phenol(12moles of ethylene oxide), sodium dodecylbenzene sulfonate, ammonium acetate were used as supplied.

2. Polymerizations

1) Preparation of a vinyl acetate homopolymer latex stabilized with polyvinyl Alcohol.

The semicontinuous emulsion polymerization was carried out using the formula given in Table 1.

2.36g polyvinyl alcohol was stirred into 66.3g of deionized water in a 250mL polymerization flask. The solution was heated to 90°C with stirring and held at that temperature for 30 minutes before cooling at 30°C.

Table 1. Formula 1 in emulsion polymerization of PVAc

Composition	Parts by weight
Polyvinyl alcohol (120,000 88% Hydrolysis)	1.57
Water	44.22
Vinyl acetate	54.05
Sodium acetate	0.1
Ammonium persulfate	0.06

8.1g of vinyl acetate, 0.15g Sodium acetate and 0.09g ammonium persulfate were added and the whole heated slowly to 70°C. At 67~68°C reflux started with severe foaming. It may be necessary to remove the water bath for few minutes to prevent foam shooting out through the condenser.

The temperature was raised to 75°C and the addition of 72.98g vinyl acetate was started. This was timed to take 90 minutes. At the end of monomer addition the bath temperature was raised to 98°C and the reaction temperature increased to 92~93°C in 15 minutes. After holding for 10 minutes at this temperature product was cooled.

2) Preparation of a poly(vinyl acetate) and poly(vinyl acetate-co-2-ethylhexyl acetate) by pre-emulsion method.

The polymerization was carried out using the formula in Table 2.

Pre-emulsion mixture were prepared using ultrasonicator at room temperature. After charging reactor, reaction mixture was stirred and heated to 75°C, 10% of pre-emulsion mixture was charged to the reactor, and the remained pre-emulsion mixture was gradually added to the reactor over 1.5 hour.

After finishing the addition product was cooled.

3. Analysis

Sample were withdrawn during the polymerization, and the polymerization was stopped with hydroquinone. The overall conversion was determined gravimetrically. The particle size was measured by dynamic light scattering.

The viscosity of final latex was measured with Brook-field viscometer(DV II+) using spindle no. 34 at 3r.p.m. for PVAc by the recipe in Table 1 and 30rpm for PVAc and poly(vinyl acetate-co-2-ethylhexyl acrylate) by the recipe as shown

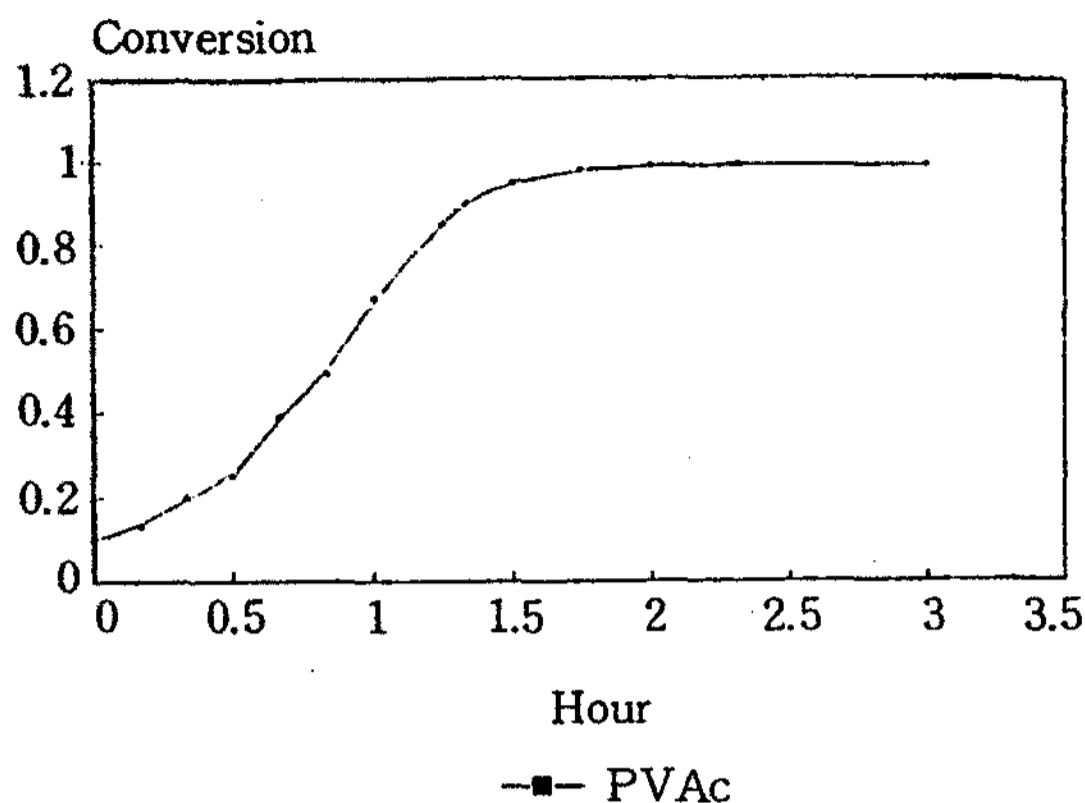


Fig. 1. Time evolution of conversion for PVAc.

in Table 2. The DSC and TGA Data were obtained by TA DSC 2010. and TGA 2050.

III. Results and Discussion

Poly(vinyl acetate) was polymerized by the formula in Table 1. Figure 1 presents the time evolution of fractional conversion for the poly(vi-

nyl acetate). The fractional conversion is defined as the weight fraction of the monomers already fed into the reactor that has been converted into polymer. For all the reactions, the first point corresponds to the end of the batch pre-period. The conversion reached 1.0 within 1.5 hour. The properties of obtained emulsion are shown in Table 3.

Polymerization probably decreases intermolecular hydrogen bonding in the vinyl alcohol; increased cooking leads to higher emulsion viscosity and to greater grafting of vinyl acetate onto the polyvinyl alcohol.

Polymer particle size at various time were measured during polymerization. Polymer particle sizes are shown in Table 4.

During the final heating period, the reaction mixture had a sharp rise in particle size and then a small decrease to the value of $0.725\mu\text{m}$. The final decrease is probably due to a smoothing out of the coagulated particle. The particle agglom-

Table 2. Formula 2 by pre-emulsion

Composition	PVAc	VAc /2-EHA Copolymer
1. Pre-emulsion tank charge		
Poly(vinyl alcohol)	1.935	1.935
(Mn=35,000, 88% hydrolysis)	0.96	0.96
Nonyl-phenol+12 E. O.	80.58	64.47
Vinyl acetate	—	16.11
2-EHA	0.195	0.195
Sodium dodecyl-benzene sulfonate	59.08	59.08
D. I. water		
2. Reactor charge		
D. I. water	7.0	7.0
Ammonium acetate	0.08	0.08
Ammonium persulfate	0.161	0.161

Table 3. Properties of PVAc emulsion

pH	Non-volatile content	Viscosity at 25°C	Particle size
4.5	53%	10000 cps (0.84s^{-1})	$0.725\mu\text{m}$

Table 4. Polymer particle size at various time

Reaction time(hr)	0.25	0.5	0.75	1.0	1.5	1.75	2.00
Particle size(μm)	0.158	0.180	0.345	0.588	0.657	0.953	0.725

eration process is reproducible and characteristic of polyvinyl alcohol grades. The rapid reaction of 105 minutes compared with the 3-5 hours for solution polymerization is a major advantage of the emulsion method.

The crude emulsion contains small quantities of ungrafted colloid, graft copolymer with a very small amount of poly(vinyl acetate), graft polymer with high content of poly(vinyl acetate), ungrafted poly(vinyl acetate), and poly(vinyl acetate) crosslinked with poly(vinyl alcohol). The glass transition temperature of crude emulsion was around 28°C (Figure 2).

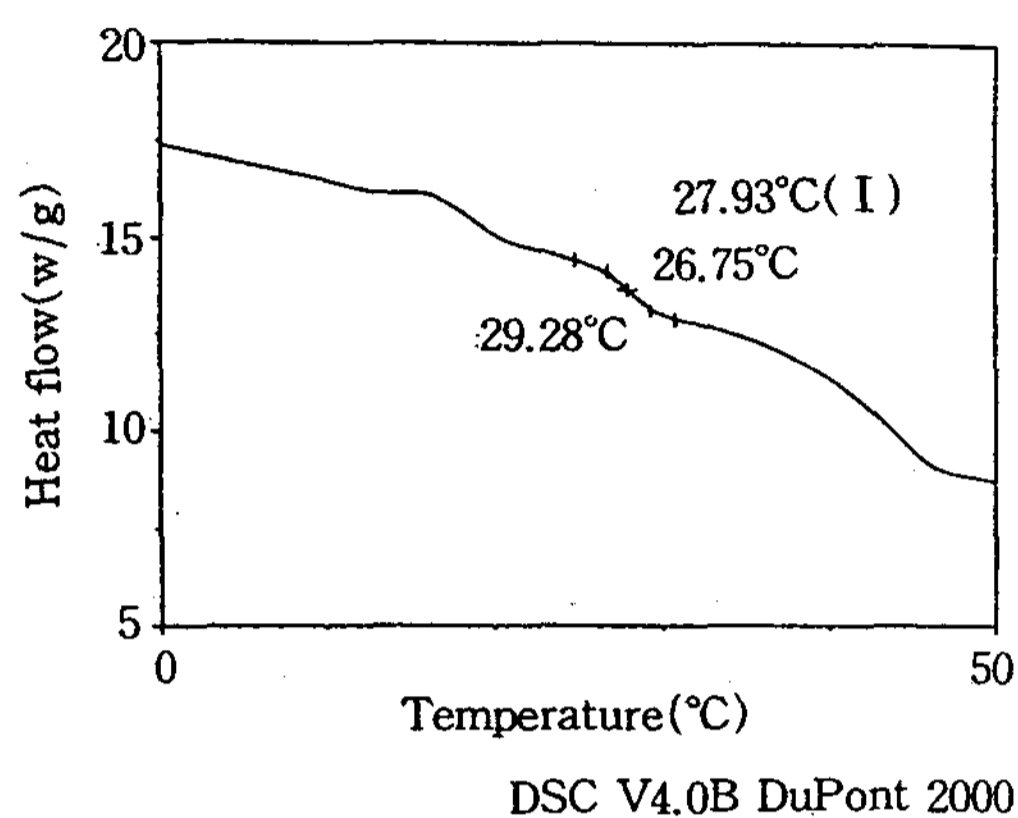


Fig. 2. Glass transition temperature of PVAc.

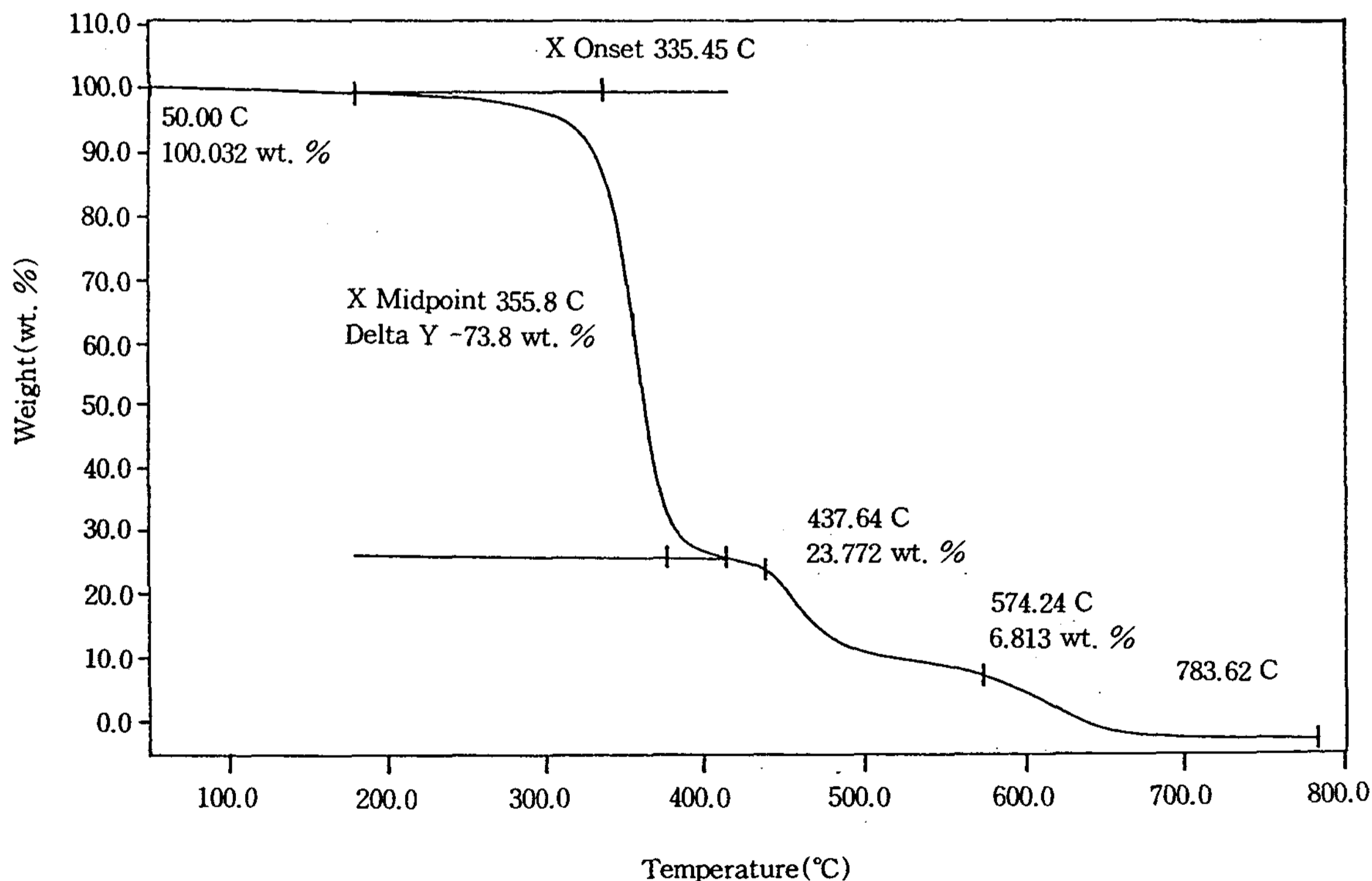


Fig. 3. TGA of PVAc.

The thermal behavior of crude emulsion film was examined by TGA(Figure 3). It show 3-step degradations. At 437°C it was decomposed up to 73wt%. The scanning-electron micrograph was obtained on Jeol SEM(Figure 4). Small degrees of particle agglomeration were observed in PVAc emulsion.

Poly(vinyl acetate-co-2-ethylhexyl acrylate) was polymerized by using the recipe as shown in Tabel 2. In this case, 2-ethylhexyl acrylate is the internal plasticising comonomer. Mixed surfactants (anionic and non-ionic), buffer and colloid are present.

Figure 5 shows time evolution of conversion for poly(vinyl acetate) and poly(vinyl acetate-co-2-

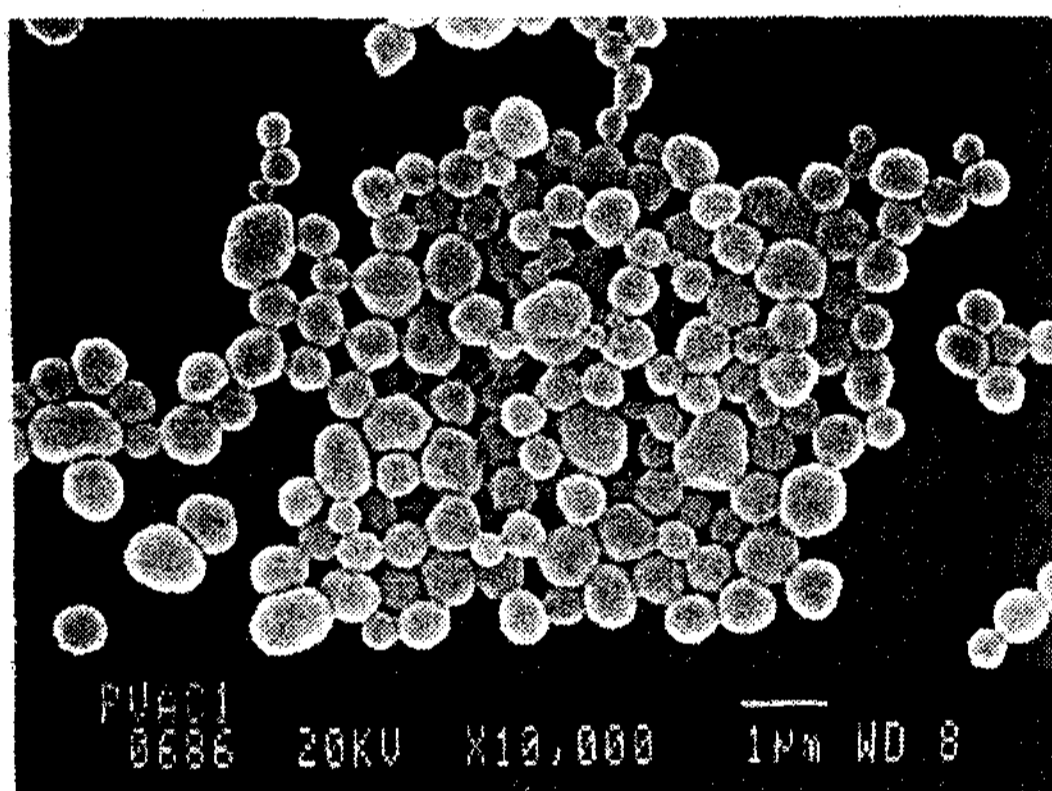


Fig. 4. SEM of PVAc.

ethylhexyl acrylate). By introducing 2-ethylhexyl acrylate comonomer, the polymerization rate was decreased.

Although the reactivity ratio of 2-EHA is large compared with that of vinyl acetate(Table 5), it shows slow rate due to low solubility of 2-EHA in water. In this case pre-emulsion by ultrasonification was used. The properties of crude emulsions are tabulated in Table 6.

The use of anionic surfactant was required to assist the incorporation of 2-EHA and result in a slight reduction in particle size.

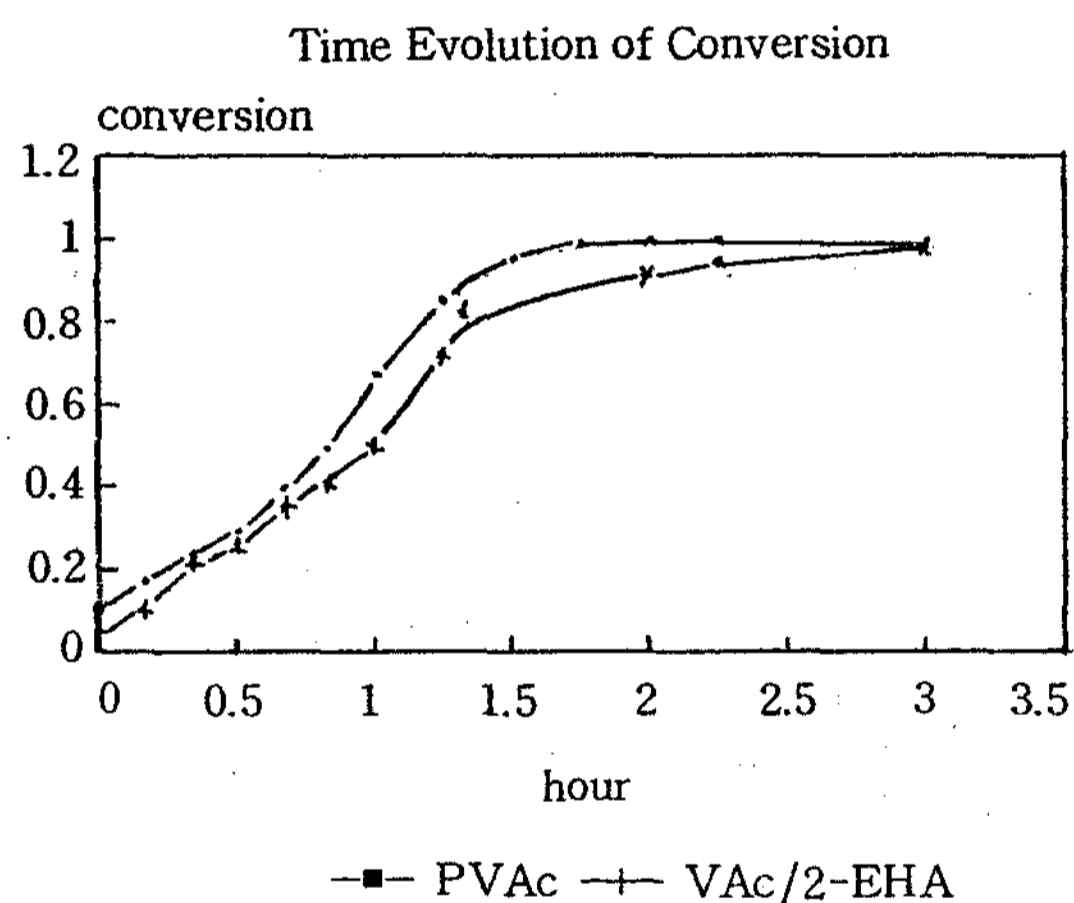


Fig. 5. Time evolution of conversion for PVAc and VAc/2-EHA copolymer.

Table 5. Copolymerization reactivity ratios(determined by the Q and e method)

	r ₁	r ₂
VAc /2-EHA	0.02 (Q ₁ =0.026, e ₁ =-0.88)	10.87 (Q ₂ =0.37, e ₂ =0.24)

Table 6. Properties of crude emulsions

	PVAc	Copolymer of VAc and 2-EHA
pH	4.5	4.3
Non volatile content	53%	50%
Viscosity at 25°C(3.4 s ⁻¹)	260	210
Particle size(µm)	0.72	0.65

From Figure 6 and 7 the glass transition temperatures of PVAc and copolymer of VAc and 2-EHA are 29°C and 13°C, respectively. Figure 8 shows TGA thermogram of PVAc by

pre-emulsion. There is no difference compared with PVAc polymerized by the recipe of Table 1. In the case of VAc/2-EHA copolymer, it shows 2-step degradation. After 1-st degradation, the

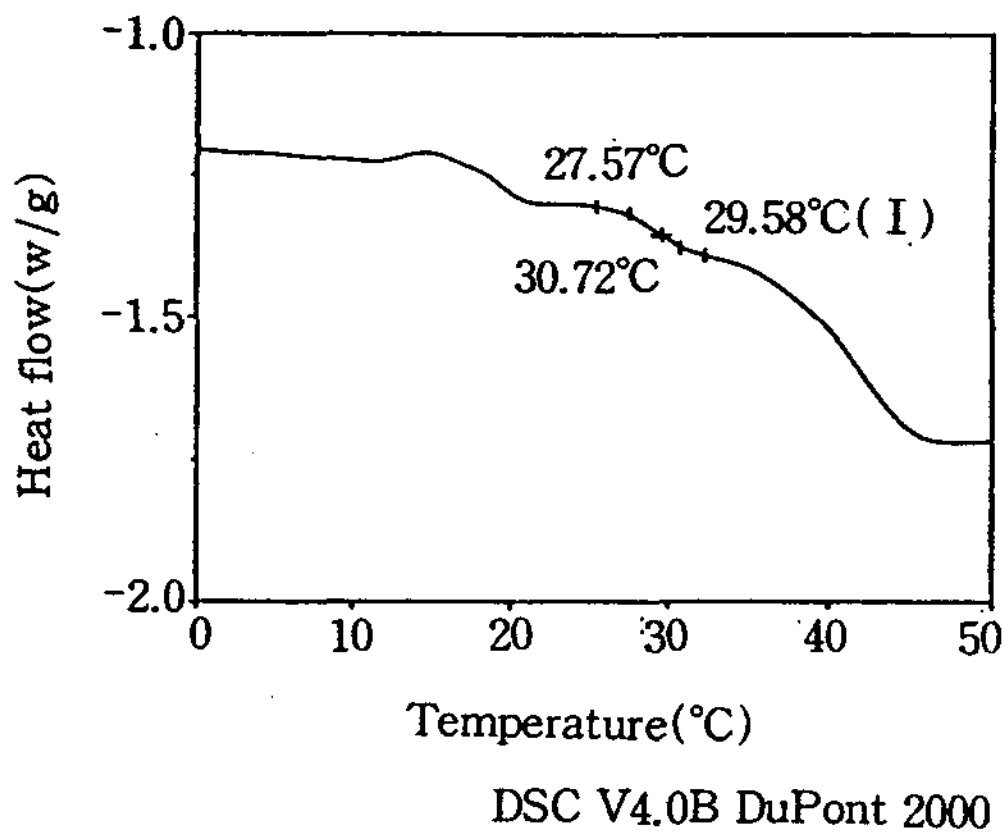


Fig. 6. Glass transition temperature of PVAc by pre-emulsion.

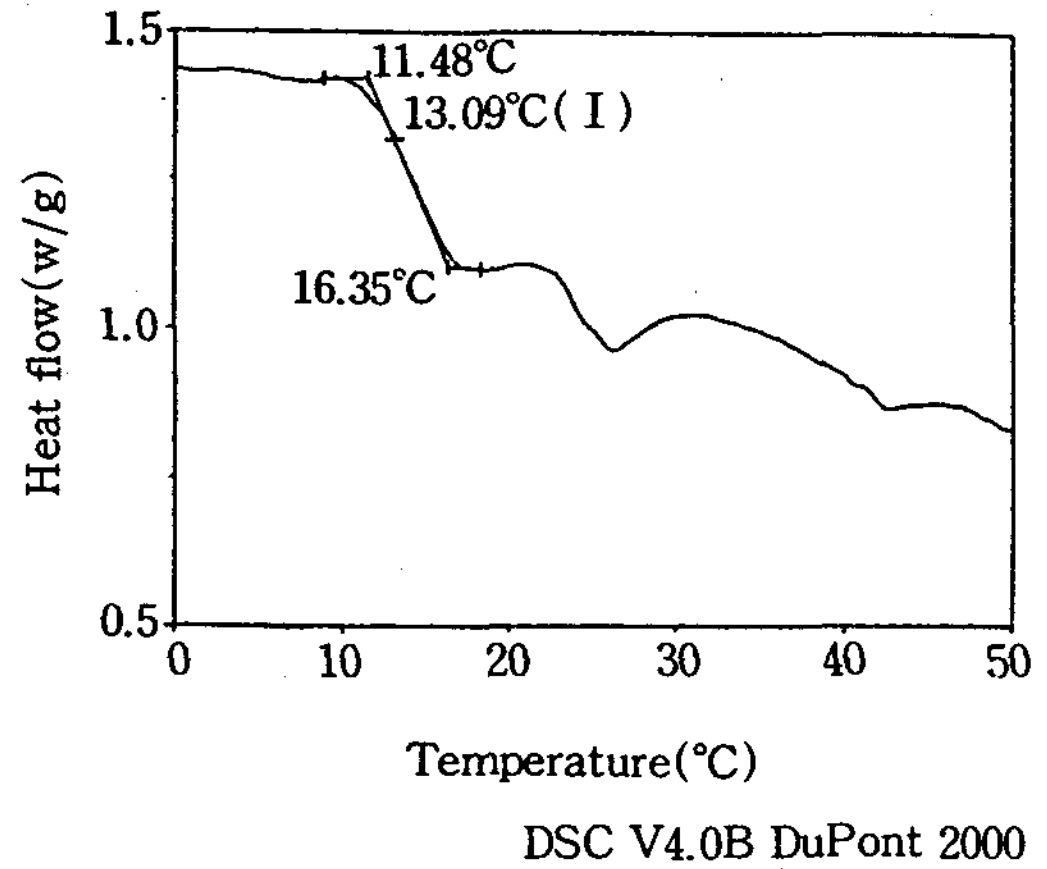


Fig. 7. Glass transition temperature of VAc/2-EHA by pre-emulsion.

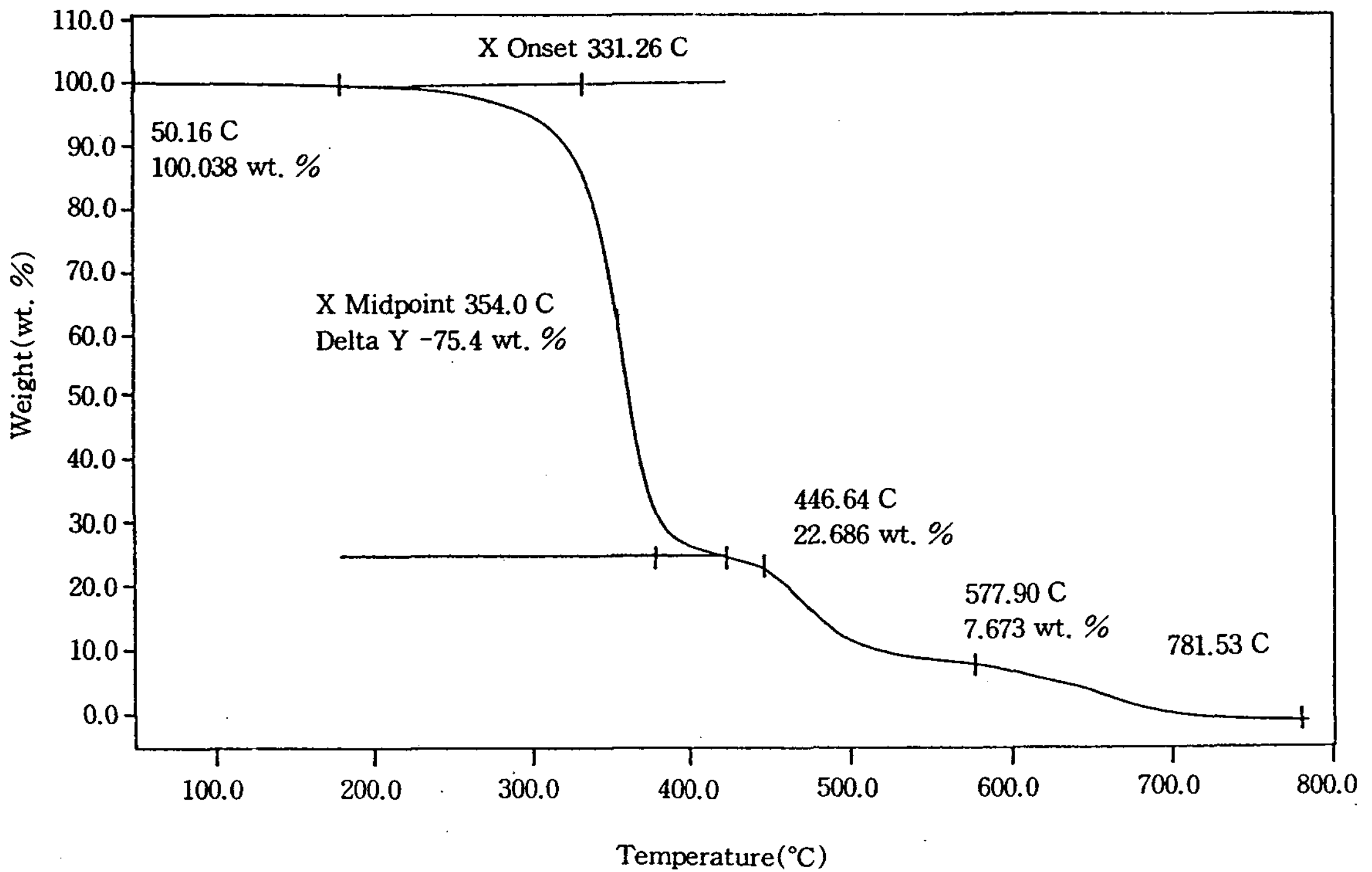


Fig. 8. TGA of PVAc by pre-emulsion.

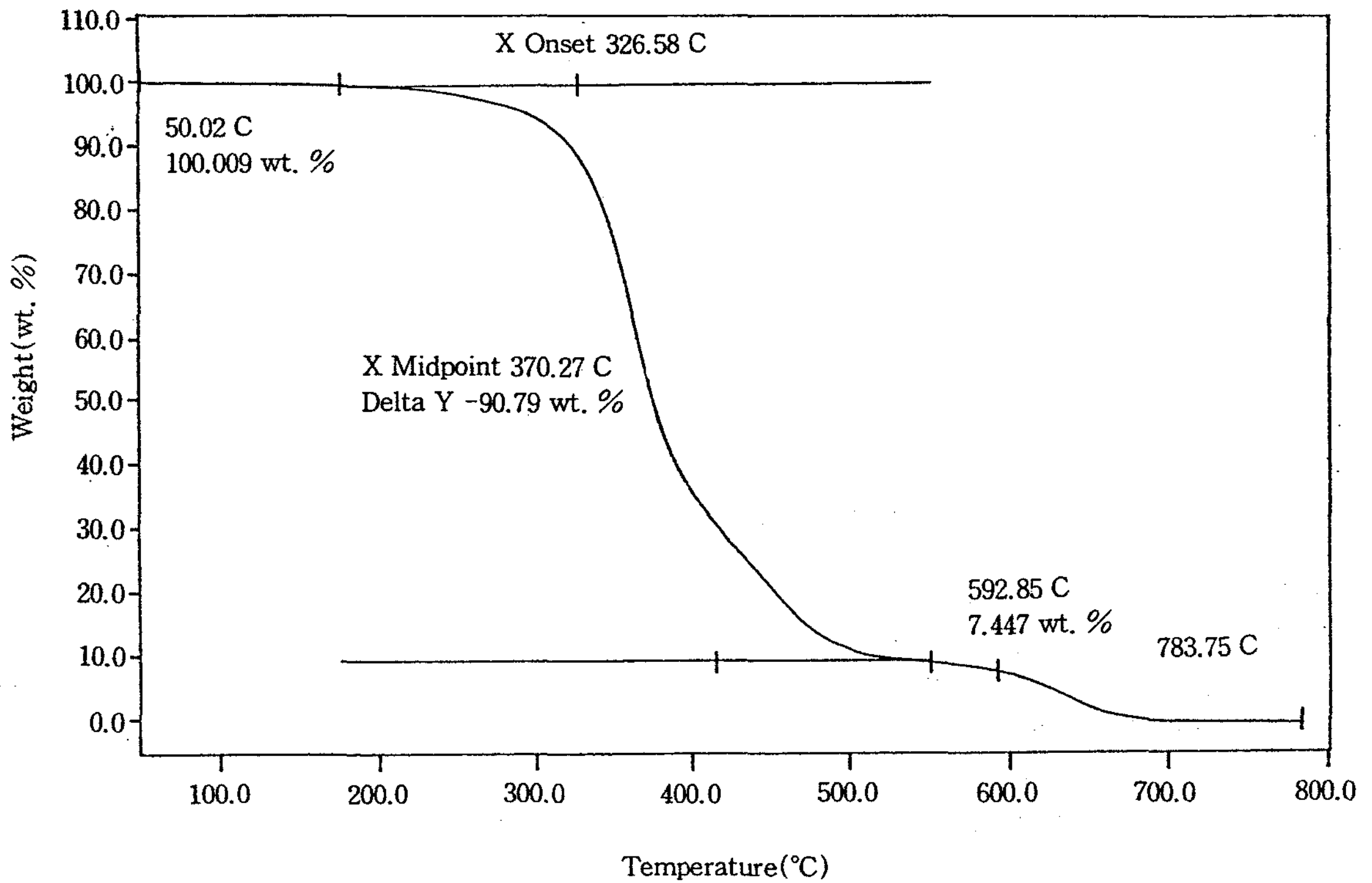


Fig. 9. TGA of VAc/2-EHA copolymer.

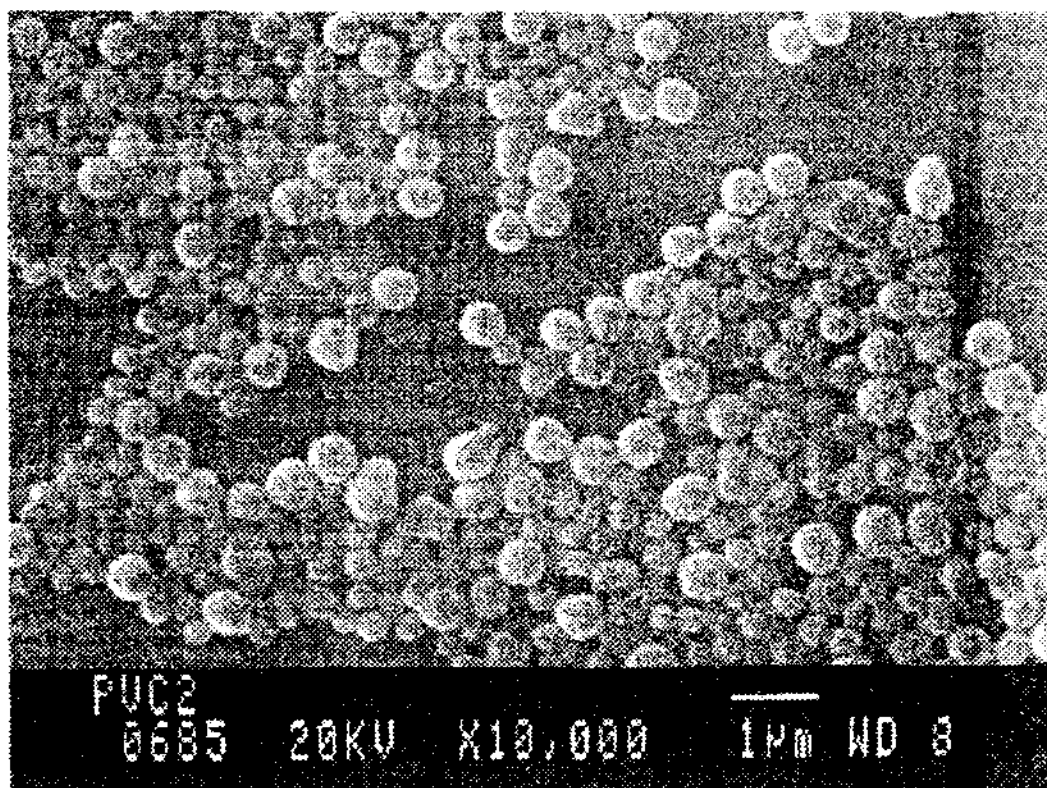


Fig. 10. SEM of PVAc by pre-emulsion.

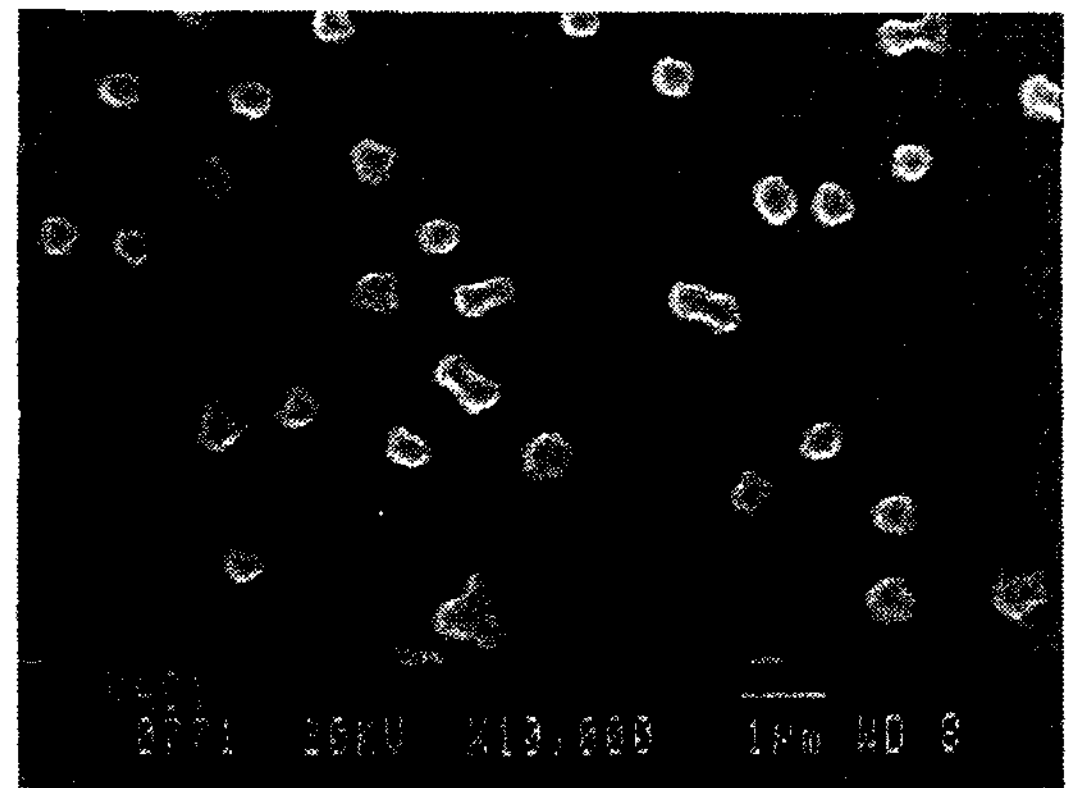


Fig. 11. SEM of VAc/2-EHA copolymer.

residual wt. % is 6.3(Figure 9).

Figure 10 and 11 show the mophologies of PVAc emulsion and VAc/2-EHA copolymer emulsion. The particle size of PVAc by pre-emulsion was reduced compared with that of

PVAc by recipe 1. By introducing 2-EHA comonomer, the particle shape was changed from spherical one to dumbbell-shaped or angular one. Obviously the particle size was slightly reduced to 0.07µm.

IV. Conclusion

Poly(vinyl acetate) was polymerized by using poly(vinyl alcohol). Polymerization decreases intermolecular hydrogen bonding in poly(vinyl alcohol). This leads to higher emulsion viscosity and to greater grafting of vinyl acetate onto poly(vinyl alcohol).

During the final heating period, the reaction mixture had a sharp rise in particle size and then a small decrease to the value of $0.725\mu\text{m}$. The final decrease was probably due to a smoothing out of the coagulated particle.

By introducing 2-EHA comonomer, overall reaction was retarded, and particle size and viscosity were reduced slightly.

V. Acknowledgment

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