

# Preparation of an Acrylic-Grafted Polyester and Its Aqueous Dispersion—Effect of the Molecular Structures of the Grafted Polyesters on Viscosity and Rheology of Dispersion

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**ABSTRACT:** An investigation was undertaken to develop a new class of water-borne polyesters that have various viscosity and various rheological profiles. We discussed the effect of the grafting condition on the molecular weights of the acrylic segments in the acrylic-grafted polyester. The molecular weights of the acrylic segments could be changed by an initiator concentration, a chain transfer agent concentration, and a monomer concentration. We discussed the viscosity and the rheology of the dispersions obtained from the above-grafted polyesters. The viscosity of the dispersion decreased as the molecular weights of the acrylic segments decreased. It was considered that the interaction between the particles of the dispersions decreased with a decrease in the thickness of the shell layer. The viscosity of the dispersions also decreased as the solubility of the acrylic segments in water decreased. It was considered that the interaction between the particle of dispersion decreased with the shrinkage of the shell layer. The rheological profile of dispersion was changed not by the molecular weights but the composition of the acrylic segments. The dispersions having various rheological profiles could be obtained by the control of the molecular weights or the composition of the acrylic segments in the grafted polyesters. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 350–356, 2000

**Key words:** grafted polyester; acrylics; aqueous dispersion; viscosity; rheology

## INTRODUCTION

The reduction of volatile organic compounds and CO<sub>2</sub> has been acquiring intensive attention, and the reduction of the solvent emission from organic coatings such as paints and adhesives has been considered for about 20 years.<sup>1</sup> High-solids coatings, powder coatings, and water-borne coatings have been developed to replace conventional solvent-borne coatings; however, these coatings involved several problems,<sup>2</sup> for example, high-solids coatings still contain some solvents, powder coating systems need a breakthrough in the control of

the film thickness, and even water-borne coating systems have some problems. Among these coatings, water-borne coatings are most preferable because of the compatibility of conventional coating systems. However, water-borne coatings have some problems, for examples, flow control, viscosity stability, and improved drying rates.<sup>3</sup> Especially, the establishment of the viscosity control is very important because the suitable viscosity is different in each application method. A lot of studies on the viscosity and rheology of the aqueous dispersions have been carried out for 50 years.<sup>4</sup> These studies were carried out using the acrylic emulsions, so that the polymer composition on the surfaces of polymer particles could not be controlled freely because of limitation of the emulsion polymerization.

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In previous articles, we reported the grafting of hydrophilic acrylics to hydrophobic unsaturated polyesters<sup>5</sup> and the grafted polyesters formed the particles having "core-shell" structures.<sup>6</sup> By use of this method, the dispersion of the particles that have a predetermined surface can be prepared. In this article, we report the dispersion viscosity and rheology of the predetermined particles and discuss the relationships between the molecular structures of grafted polyester and these characteristics.

## EXPERIMENTAL

### Materials

Dimethyl terephthalate (DMT), dimethyl isophthalate (DMI), ethylene glycol (EG), and neopentyl glycol (NPG) were of commercial grade. Other reagents were of reagent grade. All reagents were used without further purification.

### Preparation of Polyester

DMT (466.0 g), DMI (466.0 g), EG (443.0 g), NPG (401.0 g) and *t-n*-butyl titanate (0.52 g) were charged in a stainless steel autoclave equipped with a stirrer, a thermometer, and a refluxing condenser. Transesterification was carried out between 160 and 220°C for 4 h. After the reaction mixture was cooled to 200°C, fumaric acid (FA, 23.0 g) was added to this reaction mixture. Temperature was elevated from 200 to 220°C over 1 h for esterification. Finally, the temperature was raised to 255°C, and the pressure was gradually released over 1.5 h to 0.2 mmHg. The polyester obtained was pale yellow and transparent. It was used without further purification. The results are shown in Table I.

### Preparation of Grafted Polyester and Its Aqueous Dispersion

A polyester (60.0 g), methyl ethyl ketone (MEK, 45.0 g), and isopropyl alcohol (IPA, 15.0 g) were charged in a reaction vessel equipped with a stirrer, a thermometer, a refluxing device, and an inlet device. The mixture was stirred under reflux (at 75°C) to dissolve the polyester. After complete dissolution of the polyester, a mixture of acrylic monomers (20.0 g), azobisisobutyronitrile (1.2 g), and octyl mercaptane (1.0 g) in MEK (15.0 g) and IPA (5.0 g) were dropwise added over 1.5 h. The reaction mixture was further reacted for 3 h to

**Table I** Composition of Polyester

	Unit	
DMT	(g)	460.8
DMI	(g)	460.8
FA	(g)	29.0
EG	(g)	443.3
NPG	(g)	400.4
Content of		
Unsaturated Unit	(mol %)	5
$M_n$	(-)	6400
$M_w$	(-)	37,500

obtain a solution of the grafted reaction product. To the solution of the grafted reaction product, triethylamine (20.2 g) was added to neutralize to it. Deionized water (160.0 g) was added to the neutralized mixture and stirred for 30 min. Then the remaining solvents and the excess of triethylamine removed by distillation to obtain an aqueous dispersion. Table II shows the composition of the grafted polyesters and the grafting conditions. These dispersion concentrations were adjusted to 30% using deionized water.

### Molecular Weight

The number-average molecular weight ( $M_n$ ) and weight-average molecular weight ( $M_w$ ) of polymers was determined by GPC apparatus (Shimadzu Seisakusho. Inc., 6A series) using the column (Showa Denko Inc., KF80M 8 mm i.d.  $\times$  30 cm  $\times$  1, KF801 8 mm i.d.  $\times$  30 cm  $\times$  1, KF802 8 mm i.d.  $\times$  30 cm  $\times$  1). Measurement was carried out using a refractive index detector and tetrahydrofuran as a solvent. The column was calibrated using polystyrene standard samples of defined molecular weights.

### Particle Size

The particle concentration in the dispersion was adjusted to 0.1%, using deionized water. The particle size was measured with a laser light-scattering particle size distributor (Coulter Inc., model N4) at 20°C.

### Conversion of Acrylic Monomers

The conversion of acrylic monomers was calculated from the amount of residual monomers determined by the use of a gas chromatography

**Table II** Composition of the Grafted Polyesters

		GP1	GP2	GP3	GP4	GP5	GP6	GP7	GP8	GP9	GP10	GP11	GP12
Polyester	(g)	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0	60.0
AA	(g)	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	12.0	8.0	11.0	18.0
EA	(g)	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	8.0	12.0	9.0	2.0
AIBN	(g)	1.2	2.0	2.4	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
OcM	(g)	1.0	1.0	1.0	0	0.2	0.6	1.0	1.4	0.2	0.2	0.2	0.2
MEK	(g)	60.0	60.0	60.0	96.0	96.0	96.0	96.0	96.0	150.0	96.0	96.0	96.0
IPA	(g)	20.0	20.0	20.0	24.0	24.0	24.0	24.0	24.0	30.0	24.0	24.0	24.0
TEA	(g)	20.2	20.2	20.2	20.2	20.2	20.2	20.2	20.2	20.2	12.6	18.5	30.3
Viscosity	(poise)	1.4	0.8	0.5	35.0	4.6	1.2	0.2	0.2	0.6	1.0	1.2	5.0
Diameter	(nm)	80	80	80	50	60	80	100	100	120	150	110	100
$M_w$													
Grafting product	(-)	60,000	58,000	58,000	65,000	63,000	61,000	59,000	57,000	59,000	63,000	61,000	60,000
Side chain	(-)	12,000	8000	7000	25,000	20,000	13,000	9000	9000	9000	18,000	20,000	20,000

		GP13	GP14	GP15	GP16	GP17
Polyester	(g)	64.0	53.0	40.0	60.0	72.0
AA	(g)	12.0	12.0	12.0	4.0	4.0
EA	(g)	4.0	15.0	28.0	16.0	4.0
AIBN	(g)	1.0	1.6	2.4	1.2	0.5
OcM	(g)	0.5	1.4	2.0	0.2	0.0
MEK	(g)	96.0	96.0	96.0	96.0	60.0
IPA	(g)	24.0	24.0	24.0	24.0	20.0
TEA	(g)	20.2	20.2	20.2	6.7	6.7
Viscosity	(poise)	3.0	0.9	1.0	0.5	0.2
Diameter	(nm)	100	80	40	150	350
$M_w$						
Grafting product	(-)	55,000	47,000	48,000	59,000	45,000
Side chain	(-)	12,000	9000	12,000	17,000	12,000

AA: acrylic acid; EA: ethyl acrylate; AIBN: 2,2-azobisisobutyronitrile; OcM: octyl mercaptane; MEK: methyl ethyl ketone; IPA: isopropyl alcohol; TEA: triethylamine.

apparatus (Shimadzu Seisakusho Inc., GC-7A series) with a column (GL Sciences Inc., Gaskuropak 56).

### Water-Soluble Component

The concentration of the dispersion was adjusted to 10.0% using a deionized water, and the dispersion was centrifuged by an ultracentrifuge (Hitachi Koki Inc., Automatic preparative ultracentrifuge model 55P-72) with a rotor (Hitachi Koki Inc., RP50T-2). Centrifugation was carried out under an average centrifugation at  $82,000 \times g$  for 2 h. After centrifugation, the supernatant fraction was dried at 120°C for 2 h. The solid concentration of the supernatant fraction was calculated gravimetrically. The amount of the water-soluble components was calculated from the concentration of the supernatant fraction.

### Number of the Carboxyl Groups (CN)

CN was determined by titrating the 1.0% of polymer solution in dimethylformamide with 0.1 N potassium ethoxide.

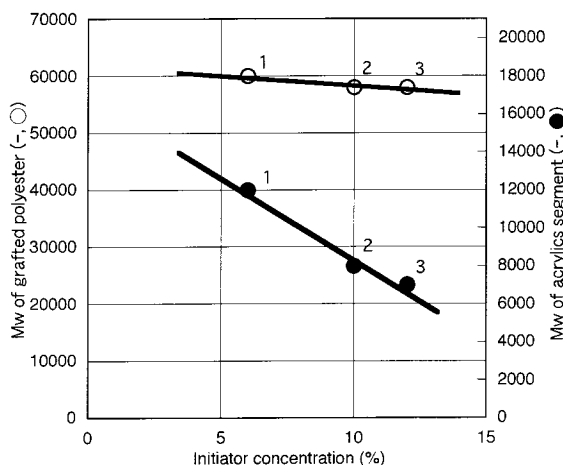
### Separation of Grafted Side Chains

The grafted reaction product (5.0 g) was hydrolyzed in a mixture of NaOH (4.0 g), deionized water (25.0 g) and methanol (125.0 g) under reflux for 4 h. The hydrolyzed product was extracted under acidic condition by using THF to purify the polymer that had formed the side chains.

## RESULTS AND DISCUSSION

### Molecular Structures of the Grafted Polyesters

To obtain predetermined particles from the acrylic-grafted polyesters, it is necessary to control the



**Figure 1** Relationships between the initiator concentrations and the molecular weights of the grafted polyesters and the acrylic segments. The numbers show the number the grafted polymers listed in Table II.

molecular structures of the grafted polyesters. First, we discuss the control of the molecular structures. The molecular weights of the polyester segments in the grafted polyesters can be controlled by the polymerization condition of the polyesters, for example, a reaction temperature and pressure. On the other hand, a method of controlling the molecular weights of acrylic segments in the grafted polyesters is not discussed enough. In this section, we discuss the control of the molecular weight ( $M_w$ ) of the acrylic segments. In previous articles we reported that the hydrophilic segments of the grafted polyester formed the shell layer of the particle. It is considered that the control of the  $M_w$ s of the acrylic segments enable control of the  $M_w$ s of the polymers on the surface of the particles.

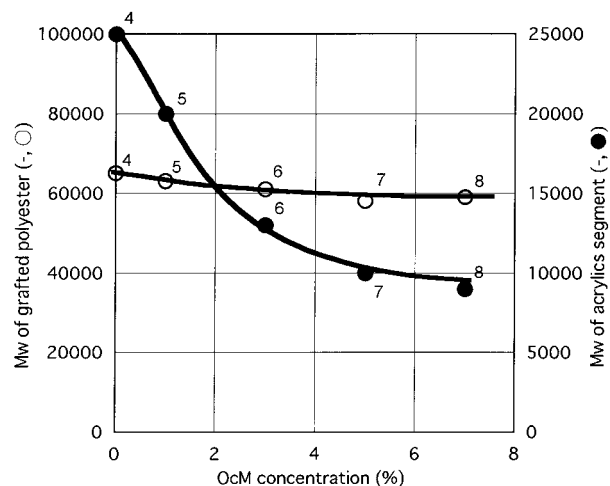
In radical polymerization, it is well known that the  $M_w$ s of the polymers can be controlled by an initiator concentration, a chain transfer agent concentration, monomer concentration, and reaction temperature. We discuss the effect of the concentration of an initiator, a chain transfer agent, and monomers on the  $M_w$ s of the acrylic segments of the grafted polyesters.

Figure 1 shows the weight-average molecular weights ( $M_w$ s) of the grafted polyesters and the acrylic segments of the grafted polyesters in the case of various initiator concentrations. The acrylic segments were separated by hydrolysis of the grafted polyesters. As for the  $M_w$ s of the grafted polyesters, no change was observed in each initiator concentration. However, an in-

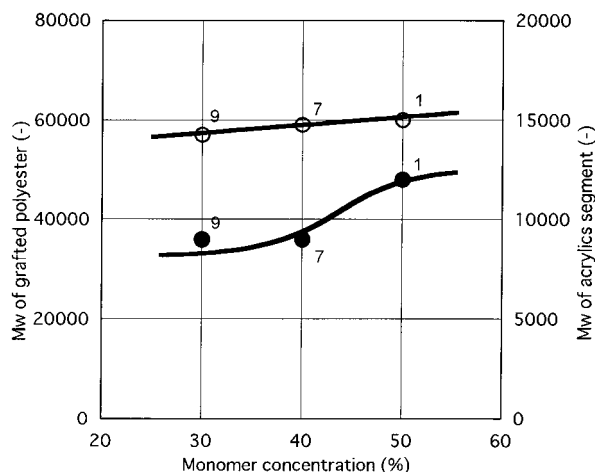
crease of the initiator concentration decreased the  $M_w$ s of the acrylic segments. The change of the  $M_w$ s of acrylic segments did not affect the  $M_w$ s of grafted polyesters because the grafted polyesters consisted of 75% polyester. As for the  $M_w$ s of the acrylic segments, this result is reasonable in terms of radical polymerization.

Figure 2 shows the  $M_w$ s of the grafted polyesters and the acrylic segments obtained under various chain transfer agent concentrations. Octyl mercaptane was used as a chain transfer agent in this case. Figure 3 shows the  $M_w$ s of grafted polyesters and the acrylic segments obtained under various monomer concentrations. As well in these cases, no change was observed in the  $M_w$ s of the grafted polyesters. However, an increase in the chain transfer agent concentration or a decrease in the monomer concentration decreased the  $M_w$ s of the acrylic segments. In general,  $M_w$ s of vinyl polymers depend on the reaction times of an initiator radical with monomers while the initiator radical is activated. The reaction times are decreased by the reaction of the polymer radicals with deactivated species, such as a solvent, a chain transfer agent, and other radicals. The above results agrees well with general facts.

From these results, we found that  $M_w$ s of the grafted side chain, which consisted of the acrylic segments, could be changed by the general ways in radical polymerization, for example, an initiator concentration, a chain transfer agent, and a



**Figure 2** Relationship between the chain transfer agent (OcM) concentrations and the molecular weights of the grafted polyesters and the acrylic segments. The numbers show the number of the grafted polyesters listed in Table II.



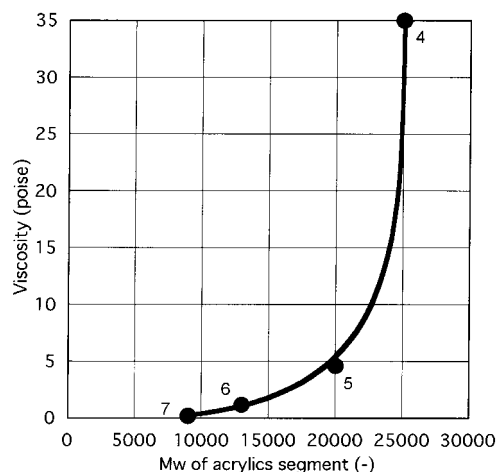
**Figure 3** Relationship between the monomer concentrations and the molecular weights of the grafted polyesters and the acrylic segments. The numbers show the number of the grafted polyesters listed in Table II.

monomer concentration. In the following sections, we discuss the dispersion characteristics of various grafted polymers prepared by use of the above techniques.

#### Viscosity of the Dispersions

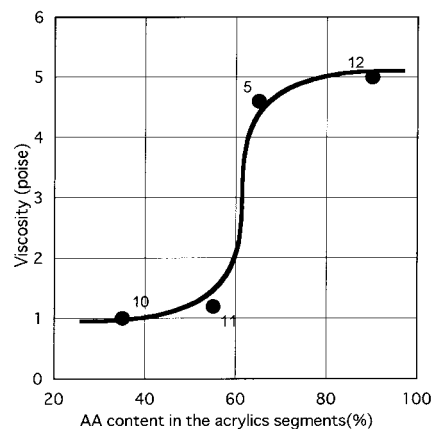
The viscosity arises from the interaction between the particles of dispersions. When there is a sufficient electrostatic repulsion force between the particles, the viscosity of dispersions is defined as the reciprocal of distance between the particles. Therefore, it is considered that the viscosity of the dispersions can be controlled by changing the  $M_w$ s or the composition of the acrylic segments, as in the case of the core-shell particles where the acrylic segments consist of the shell layer of the particles.

Figure 4 shows the relationship between the viscosity of dispersions and the  $M_w$ s of the acrylic segments. A decrease in the  $M_w$ s of the acrylic segments decreases the viscosity of the dispersions. The acrylic segments contained 65% of the acrylic acid (AA) unit in this case, and the repulsion force between the neutralized acrylic segments in the shell layer seemed to be very large. Therefore, it is considered that the shell layer became extended in the medium. When the  $M_w$ s of the acrylic segments decreased, it is thought that the thickness of the shell layer decreased and the viscosity of dispersion was also decreased. From these results, the thickness of the shell layer relates the viscosity of the dispersion.

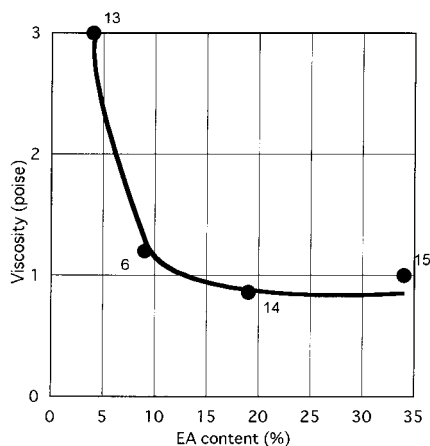


**Figure 4** Relationship between the molecular weights of the acrylic segments and the viscosity of the dispersion. The numbers show the number of the grafted polyesters listed in Table II.

Figure 5 shows the relationships between the viscosity of the dispersions and the AA content in the acrylic segments. We confirmed that the triethylamine-neutralized acrylic acid-ethyl acrylate copolymer is insoluble in water when the acrylic segment contains less than 60% of the AA unit. It was considered that a decrease of the viscosity was caused by shrinkage of the shell layer because of the change of solubility of the acrylic segments in water. Moreover, the same results were obtained when the EA content increased under the constant AA content in the grafted polyesters (Fig. 6). From these results, the viscosity of the dispersion could be



**Figure 5** Relationship between the AA content in the grafted polyesters and the viscosity of the dispersions. The numbers show the number of the grafted polyesters listed in Table II.

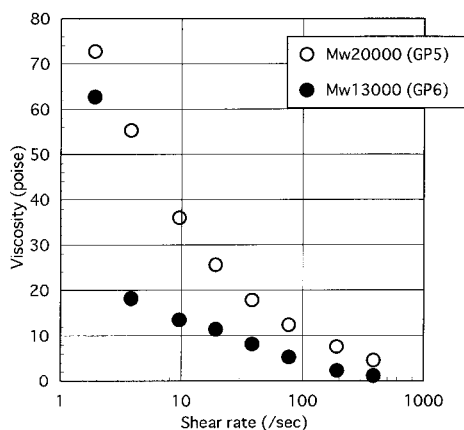


**Figure 6** Relationship between the EA content in the grafted polyesters and the viscosity of the dispersions. The numbers show the number of the grafted polyesters listed in Table II.

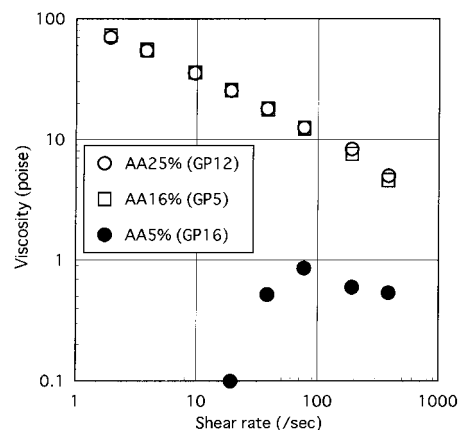
changed by the molecular structure of the grafted polyesters. The composition or the  $M_w$  of the acrylic segments affected the thickness of shell layer of the particles.

### Rheology of the Dispersions

We discuss the effect of the molecular structures of the grafted polyesters on the rheology of the dispersions. Figure 7 shows the relationships between the shear stress and the shear rate of the dispersions with various  $M_w$ s of the acrylic segments. All dispersions were thixotropic, for example, non-Newtonian, and an increase in the shear rate decreased the shear stress. This result shows



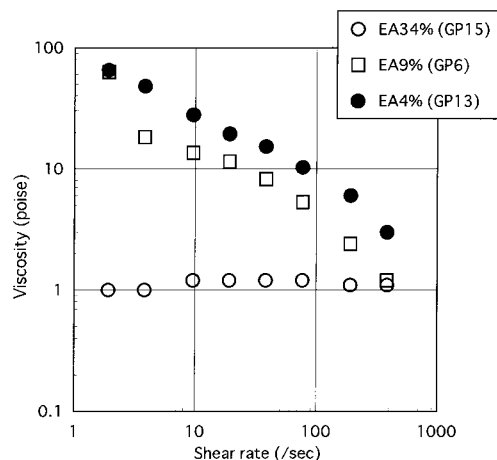
**Figure 7** Relationship between the shear rate and the shear stress in various molecular weights of the acrylic segments.



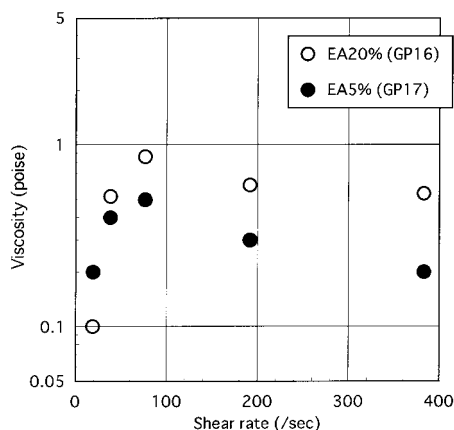
**Figure 8** Relationship between the shear rate and the shear stress in various AA contents in the grafted polyesters.

that the  $M_w$  of the acrylic segments in the grafted polyesters did not affect the rheological profile.

Figure 8 shows the relationships between the shear stress and the shear rate of the dispersions with various composition of the acrylic segments. GP12 and GP5 showed the thixotropic tendency. However, the rheological profile of GP16 was different from the others. The rheological profile seemed to be changed by the acrylic segments. Next, the relationships between the shear stress and the shear rate of the dispersion was shown in Figure 9, when the AA content was fixed and the mass ratio of the polyester to the EA content was changed. With increasing the EA content (polyester/AA/EA = 50/15/35 in mass ratio), the rheological profile of dispersion changed from thixotropic to Newtonian.



**Figure 9** Relationship between the shear rate and the shear stress in various EA contents in the grafted polyesters.



**Figure 10** Relationship between the shear rate and the shear stress in various EA contents in the grafted polyesters.

As shown in Figure 9, with an increase in the hydrophobic monomer content, the rheological profile of the dispersion was changed from thixotropic to Newtonian. However, this was not observed in Figure 8. To discuss the difference in the rheological profiles, the relationships between the shear stress and shear rate of the dispersions with less AA content were determined. The results are shown in Figure 10. In this case, the change of the rheological profile was not observed. From these results, the dispersion with the Newtonian flow can be obtained, when sufficient amounts of the acrylic segments, which contain the sufficient amounts of hydrophilic groups, are grafted to the polyester.

As described above, we discussed the relationships between the viscosity, the rheology, and the molecular structure of the grafted polyesters. The viscosity of the dispersions could be changed by the molecular structure of the grafted polyester. The solubility in water or the  $M_w$  of the acrylic segments in the grafted polyesters affected the viscosity. These characteristics are related to the thickness of the shell layer of the particles; therefore, the viscosity of the dispersion seemed to be controlled by the acrylic segments in the grafted polyesters. The rheological profile of the acrylic-grafted polyesters was almost thixotropic. However, the dispersion, which has the Newtonian flow, could be obtained when sufficient amounts of the acrylic segments, which contain sufficient amounts of the hydrophilic groups, were grafted to the polyester. From the above results, we found that the viscosity and the rheology could be controlled by

the composition or the  $M_w$  of the acrylic segments in the acrylic-grafted polyesters.

## CONCLUSION

We discussed the control of the molecular structures of the acrylic-grafted polyesters. We discussed the effect of the grafting conditions. The  $M_w$  of the acrylic segments in the grafted polyesters could be changed by the grafting conditions, for example, an initiator, a chain transfer agent, and a monomer concentration.

The hydrophilic segments of the grafted polyester formed the shell layer of the particle. It is considered that the control of the  $M_w$ s of the acrylic segments enable control of the  $M_w$ s of the polymers on the surface of the particles. We discussed the effect of the  $M_w$ s or the composition of the acrylic segments in the acrylic-grafted polyester on the viscosity and the rheology of the dispersions. The viscosity of the dispersions decreased as the  $M_w$  of the acrylic segments decreased. It was considered that an interaction between the particle of the dispersion decreased with a decrease in thickness of the shell layer. The viscosity of the dispersions also decreased as the solubility of the acrylic segments in water decreased. It was considered that an interaction between the particles of the dispersions decreased with the shrinkage of the shell layer. The rheological profiles of the dispersions obtained from the grafted polyesters were changed not by the  $M_w$  but the composition of the acrylic segments. The dispersions, having various rheological profiles, could be obtained by the control of the molecular structure of the grafted polyester.

In the following articles, the mechanical property of grafted polyesters having various side chains will be discussed.

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