Preparation of an Acrylics-Grafted Polyester and Its Aqueous Dispersion

TOSHIYUKI SHIMIZU, SHINYA HIGASHIURA, MASAKATSU OHGUCHI

Polymer Research Laboratory, Research Center, Toyobo Co., Ltd., 2-1-1 Katata, Ohtsu, Shiga, 520-0292 Japan

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ABSTRACT: An investigation was undertaken to develop a new class of water-borne polyesters having excellent dispersibility without using emulsifiers. Grafting reactions of hydrophilic acrylics to polyesters and the relationships between reaction conditions and the dispersion diameters are discussed. Aqueous dispersions of particles having small diameters were obtained by use of an unsaturated polyester. Particle diameters were related to the grafting efficiency that could be enhanced by copolymerization of reactive monomers with the unsaturated bonds of polyesters. The relationships between particle diameters and the kind of acrylic monomers were described by the copolymerization reactivity ratio of the unsaturated polyester and acrylic monomers. Also, the influences of the solvency of the reaction medium and the influence of concentration of unsaturated bonds of the polyesters in the reaction medium were discussed to explain the low reactivity between the unsaturated bonds and acrylic monomers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1817–1825, 1999

Key words: unsaturated polyester; copolymerization reactivity ratio; aqueous dispersion; grafting reaction

INTRODUCTION

The reduction of volatile organic compounds and $\rm CO_2$ 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.¹ High-solids coatings, powder coatings, and water-borne coatings have been developed to replace conventional solvent-borne coatings; however, these coatings involved several problems,² for example, high-solids 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.

As conventional water-borne coatings, acrylic emulsions, produced by emulsion polymerization, are widely used. However, for high demands, high-performance water-borne coatings like epoxy emulsions,^{3,4} polyester dispersions,^{5,6} and polyurethane dispersions⁷ are intensively developed.

The methods to disperse these resins in aqueous media are: (1) emulsifying mechanically using emulsifiers, and (2) self-emulsifying by introduction of hydrophilic groups into the molecules of resins. By the former method, the water resistance and adhesion of the coatings obtained from the dispersion are reduced because emulsifiers migrate to the surfaces and interfaces. To avoid the use of emulsifiers, polyesters are copolymerized with hydrophilic monomers. In the case of linear high molecular weight polyesters, often so-

Correspondence to: T. Shimizu.

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dium 5-sulfoisophthalic acid⁸ or polyethylene glycol⁹ or hydrophilic monomers are copolymerized. However, the copolymerization increases the melt viscosity, and decreases water resistance and adhesion.

We developed a new class of water-borne polyesters that are excellently dispersible without using additional emulsifiers. These water-borne polyesters, which are of the acrylics-grafted type, forms a stable aqueous dispersion. They consist of "core-shell" particles with a core of high molecular weight polyester. The structure of the acrylicgrafted polyester determines the particle diameter, efficiency of curing, rheological properties of dispersion, water resistance of the coating, and rewet properties (redispersing of particles from the coating film after drying at room temperature by washing of water or the dispersion). In this article, we report grafting of acrylic acid and acrylic esters to unsaturated polyesters, and discuss the relation between reaction conditions and the particle diameters.

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 and 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. Other polyesters were similarly prepared.

Preparation of Grafted Polyester and Its Aqueous Dispersion

A polyester (60.0 g), methyl ethyl ketone (MEK, 45.0 g), 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 acid (AA, 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 obtain a solution of the grafted-reaction product. To the solution of the grafted-reaction product, triethylamine (33.6 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.

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 an refractive index detector and tetrahydrofuran as a solvent. The column was calibrated using polystyrene standard samples of defined molecular weights. The results are shown in Table I.

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.

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.

Grafting Efficiency

The grafting efficiency was measured by a 220 MHz ¹H-NMR spectrometer (manufactured by Varian Inc.; solvent, CDCl₃/DMSO-d₆). As a measure of the fumaric acid units before and after copolymerization, the variation of the intensity of

	(Unit)	1	2	3	4	5
DMT	(g)	460.8	480.2	470.5	451.1	436.5
DMI	(g)	460.8	480.2	470.5	451.1	436.5
FA	(g)	29.0	5.8	17.4	40.6	58.0
EG	(g)	443.3	443.3	443.3	443.3	443.3
NPG	(g)	400.4	400.4	400.4	400.4	400.4
Amount of FA	(mol %)	5	1	3	7	10
M_n	(-)	6400	7200	7800	6800	7500
M_w^n	(-)	37,500	36,000	35,500	34,000	34,000
CŇ	$(molar/10^6 g)$	3.5	4.4	4.1	3.1	3.2

Table IComposition of Polyesters

the signal (6.8 ppm) was determined. The grafting efficiency was expressed by the following equation.

Grafting efficiency (%) = $(l - I_2/I_1)^*100$

where I_1 and I_2 are the relative strength of the signal of fumaric acid before and after copolymerization.

A relative strength of the signal was calculated from a comparison with an internal signal strength of the copolymerized terephtalic acid unit (8.1 ppm) as a standard.

RESULTS AND DISCUSSION

Dispersibility of PAA-Grafted Polyester

The grafting of acrylic acid (AA) to an unsaturated polyester containing various amounts of FA-units copolymerized is discussed. Figure 1 shows the relationship between the amount of FA copolymerized and the dispersion diameters of the grafted polyesters with a mass ratio of polyester to polymerized AA of 75 : 25. With a polyester containing 1 mol % of FA, the grafted product could not be dispersed in water. With polyesters containing more than 3 mol % of FA, dispersions with small diameters could be obtained. Polyesters that lacked hydrophilic groups could not be dispersed themselves in aqueous media. From these results, it seems that with the polyester containing unsaturated bonds, the grafting of PAA radicals occurred. The introduced hydrophilic groups made the grafted polyester dispersible in an aqueous medium. With a polyester containing 5 mol % of FA, the number of the Carboxyl Groups (CN) of the reaction product was ca. 3100.

It agreed with the conversion determined by gas chromatography. Therefore, CNs were used as a substitute for the conversion of monomers. Increase of the amount of FA copolymerized decreased the diameter of the particles. This means that an increase in the amount of the unsaturated bonds in the polyester enhanced the grafting efficiency for PAA radicals. However, when the polyester contained 10 mol % of FA, the viscosity of the reaction solution increased during the grafting reaction. Because the final reaction product could not be dissolved in tetrahydrofuran, it is

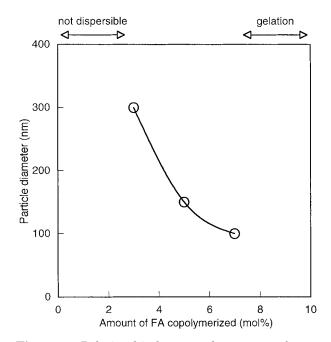


Figure 1 Relationship between the amount of copolymerized fumaric acid (FA) and the particle diameter of the grafted polyester. (Mass ratio of the polyester to PAA is 75/25.).

Monomers	Q_2	e_2	r	Particle Diameter (nm)	CN (molar/10 ⁶ g)
AA	0.83	0.88	11.18	120	3120
MMA	0.78	0.40	6.57	150	1990
BA	0.38	0.85	5.04	120	2060
EA	0.41	0.55	4.20	80	2070
HEMA	1.78	-0.39	2.53	120	1950
\mathbf{St}	1.00	-0.80	0.35	gelation	_
VAc	0.26	-0.88	0.0066	gelation	_
NVP	0.088	-1.62	0.0007	gelation	_

Table II Dispersions Obtained by Copolymerization with Various Acrylic Monomers

The mass ratio of polyester/AA/acrylic monomers is 75/16/9. The grafting conditions were same as with AA. DEF: $Q_2 = 0.25$, $e_2 = 2.26$.

assumed that the copolymerization of the excess FA caused the gelation. Therefore, in the case of the grafting of PAA radicals, it was impossible to decrease the particle diameters of the grafted polyesters.

Effect of Monomer Composition on Particle Diameter and Grafting Efficiency

The grafting efficiency of other acrylic monomers with different reactivities to FA was studied, i.e., ethyl acrylate (EA), butyl acrylate (BA), methyl methacrylate (MMA), 2-hydroxyethyl methacrylate (HEMA), styrene (St), vinyl acetate (VAc), and *N*-vinyl pyrrolidone (NVP). The mass ratio of polyester/AA/acrylic monomer was 75/16/9. The reaction conditions were the same as with AA. The results are shown in Table II. This also includes the reactivity ratios of acrylic monomers for fumaric acid units, for the same reactivity as diethyl fumarate (DEF) was assumed. The copolymerization reactivity ratio was calculated by the following equation:

$$r = Q_2/Q_1^* \exp[-e_2^*(e_2 - e_1)]$$

 Q_1 , e_1 (DEF), Q_2 , e_2 (acrylic monomer)

Q and e value were taken from the *Polymer* Handbook, 3rd ed., John Wiley and Sons (1989), and the like.

With acrylic monomers of reactivity ratios > 2, particle diameter were small, for example, in the case of EA only about 80 nm (Fig. 2). If the reactivity ratio was smaller, the diameter of the particles decreased. However, gelation was observed during grafting, in the case of St, VAc, and NVP, which have the reactivity ratios < 1 (Table II). These reaction products could not be dispersed. In the case of HEMA, which has a higher copolymerization reactivity than EA, it was observed that either gelation occurred or the particle diameter was further decreased. However, gelation was not observed, and the particle diameter was larger than that of the particles obtained by copolymerization with EA. This result is strange.

The grafting efficiency of the grafting reaction product was discussed. The results are shown in Figure 3. When gelation occurred during grafting, the grafting product could not be dissolved in solvents, so no NMR analysis was possible.

With smaller copolymerization reactivity ratios, the grafting efficiency increased. Copolymerization with monomers that have small copolymerization reactivity ratios provides high grafting efficiency for polyesters containing AA units, so the high grafting efficiency causes smaller particles. When the amount of an introduced hydrophilic group increases, the particle diameter of the polyester is decreased. To make the polyester more hydrophilic, it is necessary to graft the hydrophilic polymer (AA unit-containing polymer) to the polyester efficiently. In the case of copolymerization of HEMA, which has a sufficiently small copolymerization reactivity ratio similar to that of AA, the grafting efficiency was low. This result is explained by the different solubilities of the polyesters and the growing HEMA chain radicals in the reaction medium. These chain radicals are not compatible with the polyester in the reaction medium. Therefore, it seems that HEMA chain radicals were not grafted. In the case of grafting homopolymerization of AA, the grafting efficiency was low. However, the particle diameter, ob-

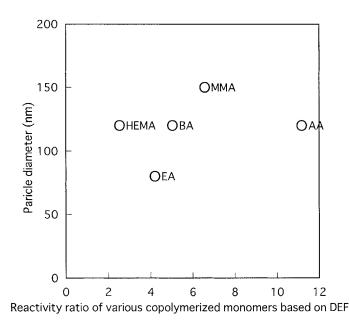


Figure 2 Relationship between the reactivity ratio of various copolymerized monomers based on DEF and particle diameter.

tained in the case of grafting of PAA homopolymer radicals, was smaller than that obtained in the case of copolymerization of MMA. It caused the amount of AA incorporated into the grafted polymer to increase, despite less grafted acrylics.

It has to be concluded from above results that a higher grafting efficiency is needed to obtain dispersions with sufficiently small particle diameters. This may be achieved by (1) copolymerization with acrylic monomers having a small reactivity ratio; and (2) the use of polyesters having the largest amount of unsaturated bonds unless gelation occurs. To enhance the grafting efficiency it is also necessary that the acrylic chain radicals

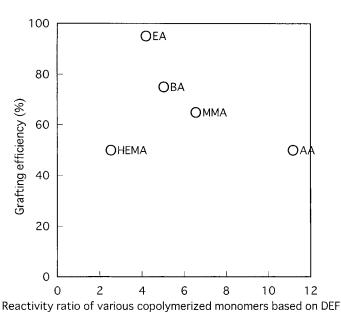


Figure 3 Relationship between the reactivity ratio of various copolymerized monomers based on DEF and grafting efficiencies.

Amount of FA (mol %)	MEK/I	PA	THF		
	Particle Diameter (nm)	CN (molar/10 ⁶ g)	Particle Diameter (nm)	CN (molar/10 ⁶ g)	
1	not dispersible	1880	>300	2050	
3	300	1890	120	1980	
5	100	1950	80	2110	
7	80	1930	gelation	_	
10	gelation	_	gelation	—	

Table III Particle Diameters of P(EA-AA)-Grafted Polyesters Obtained in Different Reaction Media

The reaction condition were the same as in the above experiments. Solid concentration 40%.

are compatible with the polyester in the reaction medium.

Effect on Reaction Medium

The influence of the solvency of the reaction medium and of the concentration of unsaturated bonds in the reaction medium were studied to explain the low reactivity between fumaric acid units and acrylic monomers. It seems that better solvents for the polyester improves the reaction with the acrylic monomers. On the other hand, an increase of the polyester concentration enhances the grafting efficiency. Results are shown in the following.

If better solvents (THF) for the polyester were used, the particle diameter of the grafted polymers decreased (Table III). The solvency was measured by the solution viscosity. The grafting was more efficient with better solvents; however, gelation tendency increased. In order to avoid gelation, the amount of FA must be decreased.

Effect of Reaction Condition

When the amount of FA copolymerized was fixed and the solid concentration (SC) of the reaction was changed, the influence on the particle diameters obtained was studied. Reaction conditions are listed in Table IV. Results are shown in Table V. When the amount of FA units was small, the particle diameter could be made smaller in the grafting reaction with higher SC. However, when grafting was carried out at very high SC, the gelation occurred. It was important to optimize the amount of FA units and solid concentration, to keep the particle diameter small.

In Figure 4, the influence of the unsaturation of the polyester and of its concentration on the particle diameter is shown. X is defined as the amount of unsaturated bond, and y is defined as the solid concentration. As for the reaction conditions that can provide the dispersions having the small particle diameters, approximation was carried out by use of the equation $y = a + x^b$. In the case of the grafting of P(EA-AA) in MEK/IPA, the

	(Unit)	1	2	3	4	5
Polyester	(g)	60.0	60.0	60.0	60.0	60.0
MEK	(g)	45.0	120.0	72.0	30.0	25.0
IPA	(g)	15.0	20.0	18.0	10.0	5.0
AA	(g)	12.0	12.0	12.0	12.0	12.0
EA	(g)	8.0	8.0	8.0	8.0	8.0
AIBN	(g)	1.2	1.2	1.2	1.2	1.2
OcM	(g)	1.0	1.0	1.0	1.0	1.0
MEK	(g)	15.0	40.0	24.0	10.0	8.0
IPA	(g)	5.0	6.5	6.0	3.3	2.3
SC	(%)	50	30	40	60	70

Table IV Composition of Reaction Mixture for Grafting

	FA = 3 n	nol %	FA = 5 mol %		
SC (%)	Particle Diameter (nm)	CN (molar/10 ⁶ g)	Particle Diameter (nm)	CN (molar/10 ⁶ g)	
30	>300	1870	150	1850	
50	150	2050	80	2070	
60	120	2080	gelation	—	

 Table V
 The Particle Diameters of P(EA-AA)-Grafted Polyesters Obtained under the Reaction

 Conditions with Various Solid Concentrations (SC)

The reaction condition were the same as in the above experiments.

value of a was 125 and the value of b was -0.65. When the particle diameter needs to be smaller, it is effective to change a reaction condition so that the value of a becomes larger. On the other hand, when the gelation occurs in the grafting reaction, it is effective to change a reaction condition so that value a becomes smaller. In other words, to optimize a reaction condition to obtain the fine dispersion means to optimize the value. The values a and b are thought to be decided by the kind of the acrylic monomer composition or the kind of the reaction medium.

Grafting Reaction of P(MMA-AA)-Radicals

It is discussed how the reaction conditions can be optimized in the case of MMA, when no small

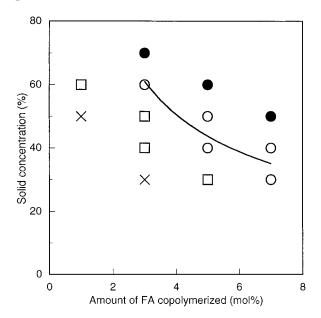


Figure 4 The particle diameters obtained with various amounts of FA copolymerized and various solid concentrations. (Grafted side chain, P(EA-AA). The particle diameter: $(\bigcirc) < 100 \text{ nm}$. $(\Box) 100-300 \text{ nm}$. (\times) not dispersible. (•) gelation occurred during grafting.

particles were obtained. The curve of MMA with the small particle diameter, was compared with the curve of EA (Fig. 5). The dotted line shows the result when EA was used, and the solid line shows the result with MMA. The figure showed that a curve of the MMA-containing polymers moved to the right of the curve for EA. From the approximation, the value of a was 190 and the value of b was -0.69. Compared with EA, the value of *a* was larger and change of the value of *b* was little. This result shows that the kind of monomers changed the value of a and did not change the value of *b*. The value of *a* is seemed to be the reactivity of each monomer to an unsaturated bond unit in polyester because the value of a was changed by the kind of monomers. Also, the value of b is seemed to express the tendency for FA to react with monomers in each reaction solvent, so this result is reasonable, because the reaction solvent is not changed.

From these results, in the case of less reactive monomers such as MMA, the change of the reaction condition that makes the value of a larger is needed to obtain fine dispersions.

Grafting Reaction in THF

The same experiment was done with THF, a solvent that often caused gelation during grafting (Fig. 6). The figure shows that the curve in case of THF moved to the left of the curve for the MEK/IPA solution. In the case of HEMA in MEK/IPA, it is considered that the compatibility of the polyester and the growing polymer radicals affects the grafting efficiency. In the case of THF, the compatibility in the reaction medium increased and the reaction efficiency was considered to be further enhanced.

From the approximation, the value of a was 106 and the value of b was -0.78. Compared with MEK/IPA, the value of a was smaller, and the absolute of the value of b was larger. This result

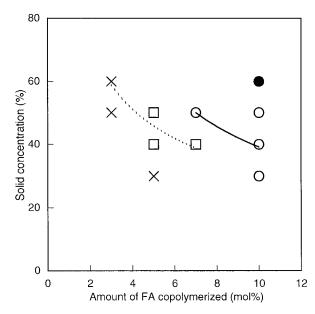


Figure 5 The particle diameters obtained with various amounts of FA copolymerized and various solid concentrations. (Grafted side chain: solid line = P(MMA-AA), dotted line = P(EA-AA). The particle diameter: (\bigcirc) < 100 nm. (\square) 100–300 nm. (\times) not dispersible. (\bullet) gelation occurred during grafting.

shows that the kind of reaction solvents changed not only the reaction efficiency of FA but also the reactivity of polymer radicals.

From the above results it is assumed that the polyester has a more extended conformation in THF, and therefore, the collision probability of the unsaturated polyester bonds and acrylic monomers should be enhanced.

From the above results it was found that several points were important for efficient grafting. There are the unsaturated bond concentration in the reaction medium, the reactivity of the unsaturated bond in the polyester and of the acrylic monomers to be grafted, and solvency of the solvents. When the concentration of the unsaturated polyester bond is low, radicals cannot react with it during their state. Therefore, grafting does not take place, and only a mixture of polyester and acrylic homopolymer is obtained. When the concentration of the unsaturated bond is high, radicals react with the several unsaturated bonds of several polyesters, or a recombination of chain radicals and gelation takes place.

CONCLUSION

A new class of water-borne polyesters was synthesized, having an excellent dispersibility without using emulsifiers. Grafting of hydrophilic acrylic monomers to unsaturated polyesters and the relationships between reaction conditions and the particle diameters were studied. Aqueous dispersions having small particle diameters were obtained by use of polyesters having the largest amount of unsaturated bonds unless gelation occurs. An increase in the grafting efficiency decreased the particle diameters, and the grafting efficiency could be enhanced by the copolymerization of the reactive monomers with the unsaturated bonds of polyesters. The relationship between the particle diameter and acrylic monomer was explained by the reactivity ratio of the unsaturated bonds and acrylic monomers. The influences of the solvency of the reaction medium and of the concentration of unsaturated bonds in the reaction medium were discussed to explain the low reactivity between the unsaturated bonds and acrylic monomers. Aqueous dispersions with a particle diameter of less than 100 nm could be obtained not only by the optimization of the reaction media and the solid concentrations in the grafting reaction, but also by use of the monomers having a high reactivity toward the unsaturated polyester bonds.

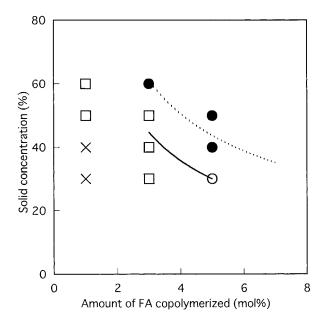


Figure 6 The particle diameters obtained with various amounts of FA copolymerized and various solid concentrations. (Reaction medium, solid line = THF, dotted line = MEK/IPA. Grafted side chain, P(MMA-AA). The particle diameter: $(\bigcirc) < 100$ nm. (\square) 100–300 nm. (\times) not dispersible. (•) gelation occurred during grafting.

In following articles, a new method to enhance the grafting efficiency and avoid gelation, the formation mechanism of the core-shell particles from the acrylics-grafted polyesters, the rheological control of the aqueous dispersion, and the mechanical property of grafted polyesters having various side chains will be discussed.

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