

Preparation of an Acrylic-Grafted Polyester and Its Aqueous Dispersion: Grafting Utilizing Alternating Copolymerization

TOSHIYUKI SHIMIZU, SHINYA HIGASHIURA, MASAKATSU OHGUCHI

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

Received 11 January 1999; accepted 4 April 1999

ABSTRACT: An investigation was undertaken to develop a new method to obtain fine dispersion of grafted polyester without gelation. As a new method, grafting utilizing alternating copolymerization of hydrophilic polymers to unsaturated polyester was discussed. By use of grafting utilizing alternating copolymerization, the reaction tendency of grafted polymer radical for an unsaturated bond of the polyester was changed. The grafting utilizing alternating copolymerization was compared with the conventional grafting, and the calculated grafting efficiency is about twice. Moreover, it was possible to increase the incorporation of less reactive monomers into the grafted side chain by the grafting utilizing alternating copolymerization. From the above results, the grafting utilizing alternating copolymerization is considered a useful method to prepare grafted polymers. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1395–1403, 1999

Key words: unsaturated polyester; grafted polymer; aqueous dispersion; alternating copolymerization

INTRODUCTION

The reduction of volatile organic compounds and CO₂ 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 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.

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 sodium 5-sulfoisophthalic acid,⁸ polyethylene glycol,⁹ or hydrophilic monomers are copolymerized. However, the copolymerization increases the melt viscosity, and decreases water resistance and adhesion.

Correspondence to: T. Shimizu.

Journal of Applied Polymer Science, Vol. 74, 1395–1403 (1999)
© 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/061395-09

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, form stable aqueous dispersions. They consist of core-shell particles with a core of high molecular weight polyester.

In our previous article,¹⁰ we reported the grafting reactions of acrylic acid and other monomers to polyesters and the relationship between reaction conditions and the dispersion diameters. Aqueous dispersions of particles having small diameters were obtained by use of unsaturated polyester. Fine dispersion could be obtained without the gelation during the grafting reaction, when the mixture of ethyl acrylate and acrylic acid was grafted to the unsaturated polyester. However, in the case of grafting of monomers that have higher reactivities to the unsaturated bond in the polyester, for example, styrene, vinyl acetate, etc., gelation was observed, so the stable dispersion was not obtained. Particle diameters were related to the grafting efficiency that could be enhanced by copolymerization of reactive monomers with the unsaturated bonds of polyesters. Moderate reactive monomers should be used to avoid the gelation during the grafting.

In a previous article,¹¹ the amounts of acrylic that were actually grafted to polyesters were determined. We found that the actual grafting efficiency of acrylic was about 25%, even if a fine dispersion (less than 100 nm in diameter) was obtained. To increase the grafting efficiency, an investigation of the grafting of highly reactive monomers is needed.

In this article, we report the grafting reaction of styrene (St) as a highly reactive monomer to unsaturated polyester, and the alternating copolymerization method is considered to avoid gelation. Effects of the grafting monomer composition on the particle diameters of dispersions are discussed. An actual amount of polymer that was grafted to the polyesters is determined and it is compared with that obtained from the conventional grafting reaction.

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 performed 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 prepared similarly.

Preparation of Grafted Polyester by Use of the Conventional Grafting 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 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 added dropwise over 1.5 h. The reaction mixture was further reacted for 3 h to obtain a solution of the grafted reaction product. Triethylamine (33.6 g) was added to the solution of the grafted reaction product to neutralize it. Deionized water (160.0 g) was added to the neutralized mixture and stirred for 30 min. Then the remaining solvents and the excess triethylamine was removed by distillation to obtain an aqueous dispersion.

Preparation of Grafted Polyester by Use of the Alternating Copolymerization and Its Aqueous Dispersion

A polyester (60.0 g), MEK, (72.0 g), IPA, 18.0 g, and maleic anhydride (MAnh) (12.0 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 to dissolve the polyester. After complete dissolution of the polyester, a mixture of St (8.0 g), azo-

Table I Composition of Polyesters

	FA					GMAE
	I	II	III	IV	V	I
DMT (g)	460.8	480.2	470.5	451.1	436.5	485.0
DMI (g)	460.8	480.2	470.5	451.1	436.5	485.0
FA (g)	29.0	5.8	17.4	40.6	58.0	—
EG (g)	443.3	443.3	443.3	443.3	443.3	415.4
NPG (g)	400.4	400.4	400.4	400.4	400.4	343.2
GMAE (g)	—	—	—	—	—	132.0
Content of unsaturated unit (mol %)	5	1	3	7	10	7
Mn ^a (—)	6400	7200	7800	6800	7500	6700
Mw ^a (—)	37,500	36000	35500	34000	34000	3000

^a PSt equivalent values.

bisisobutyronitrile (1.2 g), and octyl mercaptane (1.0 g) in MEK (24.0 g) and IPA (6.0 g) were added dropwise 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, ethanol (20.0 g) was added to react with MAnh in the grafted side chain for 0.5 h under reflux, and cooled to room temperature. Then, triethylamine (TEA) (13.6 g) was added to neutralize it. Deionized water (160.0 g) was added to the neutralized mixture and stirred for 30 min. The remaining solvents and the excess triethylamine was removed by distillation to obtain an aqueous dispersion.

Molecular Weight

The number average molecular weight (Mn) and weight average molecular weight (Mw) of polymers was determined by GPC apparatus (Shimadzu Seisakusho Inc., 6A series) using a column (Showa Denko Inc., KF80M 8 mm i.d. × 30 cm × 1, KF801 8 mm i.d. × 30 cm × 1, KF802 8 mm i.d. × 30 cm × 1). Measurement was carried out using a refractive index detector and tetrahydrofuran as a solvent. The column was calibrated using polystyrene (PSt) standard samples of defined molecular weights. The results are shown as PS equivalent values in Table I.

Glass Transition Temperature (T_g)

T_g s were determined by the use of differential scanning calorimetry (Seiko Instruments Inc.,

DSC 220). The samples were scanned at a heating rate of 20°C/min in a nitrogen environment.

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 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 performed under an average centrifugation at 82,000g 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 tetrahydrofuran (THF) to purify the polymer that had formed the side chains.

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 FA units before and after copolymerization, the variation of the intensity of the signal (6.8 ppm) was determined. The grafting efficiency was expressed by the following equation:

$$\text{Grafting efficiency (\%)} = (1 - I_2/I_1) \times 100$$

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

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

RESULTS AND DISCUSSION

Grafting of P(St-AA)

In our previous article,¹⁰ we reported that the grafting of P(St-AA) to unsaturated polyester often caused a gel. In this article, the relationship between the particle diameters and the grafting conditions is examined in detail. The results are shown in Table II. The stable dispersions could not be obtained under any grafting conditions. In our previous article, we found that the fine dispersions could be obtained under the intermediate conditions that are between the conditions that gelation occurred and the conditions that stable dispersions could not be obtained. However, in the case of grafting of St, there were no grafting conditions in which stable dispersions could be obtained. The results are summarized in

Table II Grafting of P(St-AA) to Polyesters Containing Various Amounts of FA

Grafting Condition	(%)	Results
FA 7 mol %		
Solid concentration	20	Gelation
FA 5 mol %		
Solid concentration	20	Not dispersible
Solid concentration	30	Gelation
FA 3 mol %		
Solid concentration	20	Not dispersible
Solid concentration	30	Gelation
Solid concentration	40	Gelation
FA 1 mol %		
Solid concentration	30	Not dispersible
Solid concentration	40	Not dispersible
Solid concentration	50	Not dispersible
Solid concentration	60	Gelation

Figure 1. For comparison, the results in the case of the grafting of ethyl acrylate (EA) and AA are included in Figure 1.

The reason that the gelation occurred was considered. During a grafting, an initiator forms radicals first. Next, the initiator radicals react with monomers, and the growing radicals repeat the reaction. The grafted polymer is considered to be made by the reaction of the growing radicals with an unsaturated bond in the polyester. Finally, the growing radicals are deactivated by the reaction with other radicals, by the chain transfer reaction, or by the recombination of the growing radicals. When the growing radical reacts twice with the unsaturated polyester molecules, the crosslinking reaction of the polyester molecules takes place, and therefore gelation is observed. On the other hand, when the growing radical does not react with any unsaturated bonds, the grafting reaction of the growing radicals to the polyester molecules does not take place, and therefore the stable aqueous dispersion cannot be obtained. In the case of grafting of P(EA-AA) described in the previous article, a moderate reactivity of EA with the unsaturated bond of polyester increases the grafting efficiency without gelation. Also, in the case of grafting of monomers that have lower reactivities, such as methyl methacrylate (MMA), etc., change of the reaction condition that collision probability of monomers and unsaturated polyester increases is needed to obtain fine aqueous dispersions. However, in the case of grafting of St, fine dispersions could not be obtained even by optimization of the unsaturated bond concentra-

tions in the reaction media. These results suggest that an alternating approach is needed to obtain fine dispersions.

Grafting Utilizing Alternating Copolymerization

The approach to avoid gelation during grafting is discussed. During the grafting of St and AA to an unsaturated polyester, two kinds of polymer radicals exist. One is the polymer radical that the chain ending is an St radical, and another is the polymer radical that the chain ending is an AA radical. With a polyester containing a fumarate unit as an unsaturated bond, St radicals are much more reactive than AA radicals and EA radicals to the fumarate unit. In radical copolymerization, copolymerization reactivity of free radical on the end of polymer chain is determined as a copolymerized reactivity ratio (CRR) by the Q - e value of copolymerized monomers. Table III

Table III Calculated Results of CRRs

M_1	M_2	r_1	r_2
Fumaric acid ^a	Acrylic acid	0.0133	11.183
Fumaric acid ^a	Ethyl acrylate	0.0128	4.201
Acrylic acid	Ethyl acrylate	0.5923	1.514
Fumaric acid ^a	Styrene	0.0002	0.3459
Styrene	Maleic anhydride	0.0320	5.5E-8
Fumaric acid ^a	Maleic anhydride	7.3620	0.0176

Acrylic acid, $Q = 0.83$, $e = 0.88$; ethyl acrylate, $Q = 0.41$, $e = 0.55$; styrene, $Q = 1.00$, $e = -0.80$; maleic anhydride, $Q = 0.86$, $e = 3.69$.

^aThe value is assumed to be the same as that of diethyl fumarate ($Q = 0.25$, $e = 2.26$).

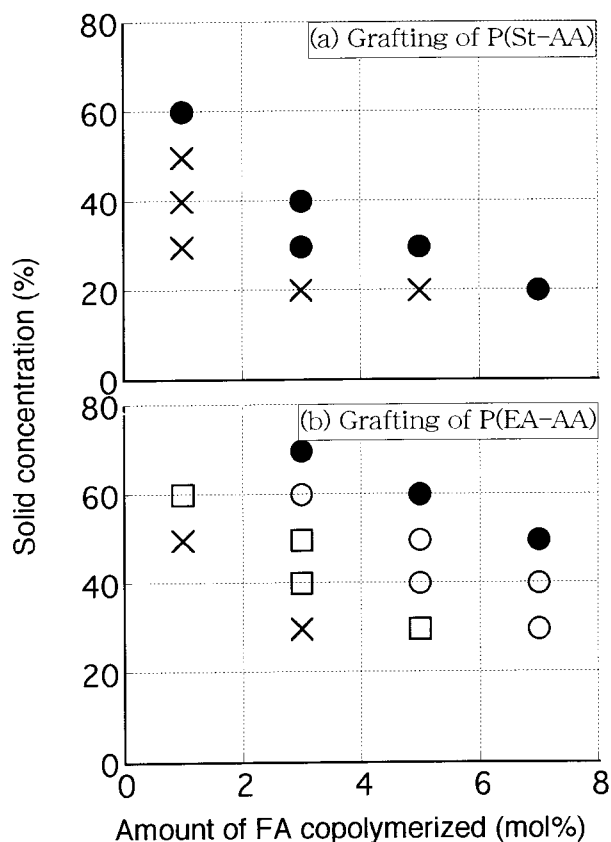


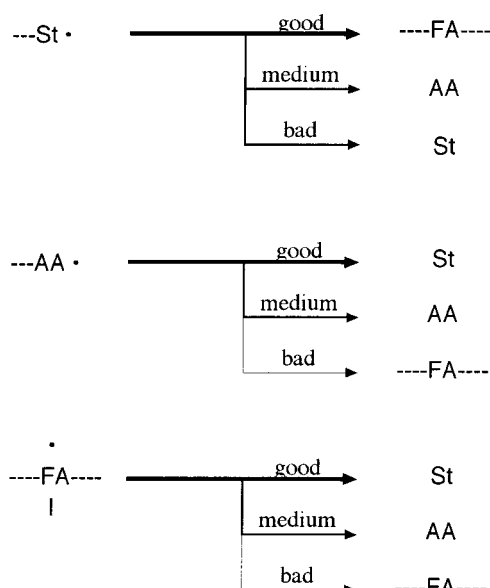
Figure 1 The particle diameters obtained with various amounts of FA copolymerized and various solid concentrations in grafting of P(St-AA) and P(EA-AA) to the polyester. The particle diameter: (○), <100 nm; (□), 100 ≈ 300 nm; (X), not dispersed; (●), the gelation occurred during the grafting reaction.

shows the CRRs that calculated from the Q - e values.¹² In the Table, r_1 means the reactivity tendency of (monomer₁)/(monomer₂). If r_1 is large, a monomer₁ radical on the polymer chain ending tends to react with monomer₁, not monomer₂. On the other hand, if r_2 is large, a monomer₂ radical tends to react with monomer₂. To decrease the reactive tendency of the growing polymer radical to the fumarate unit in the polyester, it is effective to add the monomer that has the higher reactivity with St radicals than the fumarate unit, in the reaction medium. In this study, MANh is used as the more reactive monomer with St radical than fumarate, and preparation of P(St-MANh)-grafted polyester is discussed. In this system, it is known that alternating copolymer of P(St-MANh) forms.¹³ The reactivity of MANh is almost the same as that of FA, therefore the grafting tendency of the growing polymer radical, that the chain ending is St, is determined by the molar ratio of MANh/FA in the reaction medium. If the amount of MANh is insufficient, the grafting tendency of the growing polymer radicals will be increased. Scheme 1 shows the above estimation.

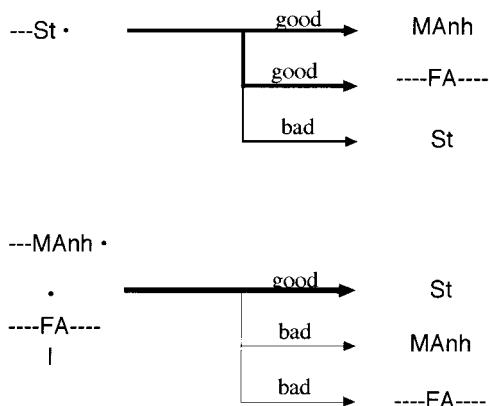
Figure 2 shows the relationship between the mass ratios of St/MANh and the particle diameters of dispersions obtained. In certain ratios, fine dispersions were obtained. In the grafting that the content of MANh was small, gelation was observed. On the other hand, in the grafting that the content of MANh was large, the grafting of P(St-MANh) did not occur because a stable dispersion could not be obtained. The reactivity of the growing radicals was changed by the mass ratios of St/MANh.

Figure 3 shows the relationship between the unsaturated bond concentrations in the medium and the particle diameters, under the

(a) Grafting of P(St-AA)



(b) Grafting of P(St-MAnh)



Scheme 1 Relative copolymerization reactivities of polymer radicals for other monomers.

grafting that the mass ratio of St/MAnh was 40/60. In this case as well, fine dispersions were obtained in certain unsaturated bond concentrations.

From above results, by use of MAnh instead of AA, fine dispersions were obtained without gelation during the grafting. St radical tends to react not with fumarate unit but with MAnh; therefore, the reaction tendency that has a St radical on the chain ending to the fumarate unit is depressed.

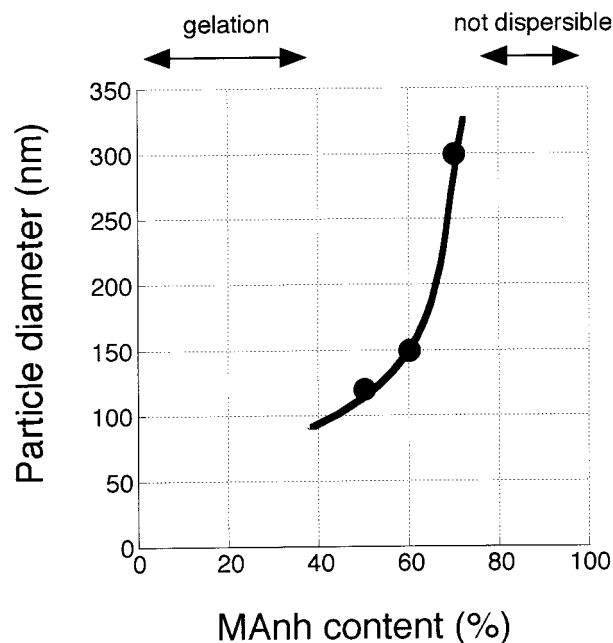


Figure 2 Relationship between MANh content and the particle diameter. P(St-MAnh) was grafted to polyesters containing 5 mol % of FA. The mass ratio of polyester/(St-MAnh) was 75/25.

Moreover, MAnh radical does not react with fumarate unit. It is also effective to avoid the gelation during the grafting.

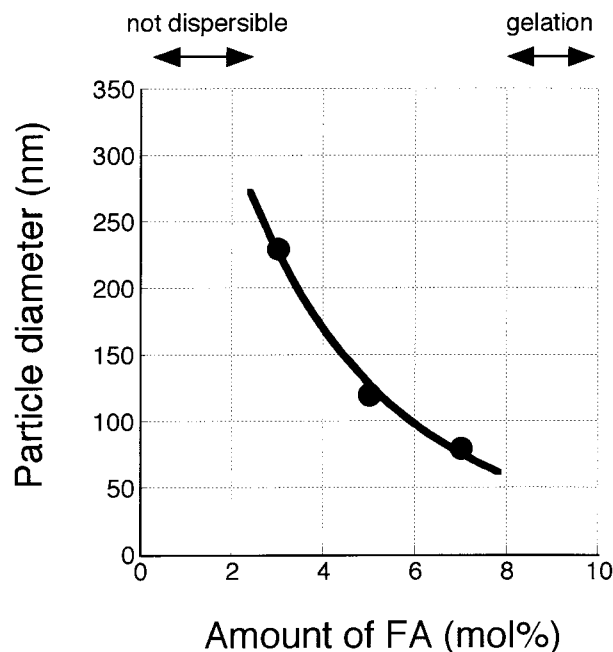


Figure 3 Relationship between the amount of FA copolymerized in the polyester and the particle diameters. The mass ratio of polyester/St/MAnh was 75/10/15.

Table IV Calculated Results of CRRs

M_1	M_2	r_1	r_2
Fumaric acid ^a	Styrene	0.0002	0.3459
Fumaric acid ^a	Maleic anhydride	7.3620	0.0176
Styrene	Maleic anhydride	0.0320	5.5E-8
Glycerol allyl ether ^b	Styrene	0.0018	344.577
Glycerol allyl ether ^b	Maleic anhydride	2.8E-6	8.9E-7
Styrene	Maleic anhydride	0.0320	5.5E-8

Acrylic acid, $Q = 0.83$, $e = 0.88$; ethyl acrylate, $Q = 0.41$, $e = 0.55$; styrene, $Q = 1.00$, $e = -0.80$; maleic anhydride, $Q = 0.86$, $e = 3.69$.

^a The value is assumed to be the same as that of diethyl fumarate ($Q = 0.25$, $e = 2.26$).

^b The value is assumed to be the same as that of allyl alcohol ($Q = 0.005$, $e = -1.48$).

The Grafting to the Polyester Containing an Allyl Group

Next, the grafting reaction of P(St–MAnh) to the polyester containing an allyl group that has the reactivity opposed to that of fumarate, is discussed. In this case, St radicals rarely react with the allyl group, and MAnh radicals are easy to react with the allyl group. Therefore, it is considered that the opposite behavior in the case of fumarate is observed. Table IV shows the CRRs calculated from the Q – e values.

Figure 4 shows the relationship between the

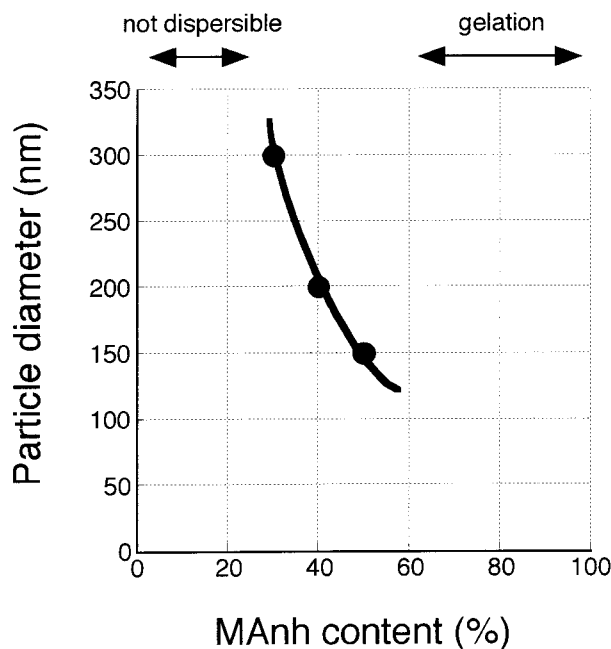


Figure 4 Relationship between MAnh content and the particle diameter. P(St–MAnh) was grafted to polyesters containing 7 mol % of GMAE. The mass ratio of polyester/(St + MAnh) was 75/25.

mass ratios of St/MAnh and the particle diameters. In this case as well, fine dispersions were obtained in certain ratios. In the grafting that the content of MAnh was large, gelation was observed. On the other hand, in the grafting that the content of MAnh was small, the grafting of P(St–MAnh) did not occur because a stable dispersion could not be obtained. The condition that the gelation occurred in the case of the polyester containing an allyl group is opposite to that in the case of the polyester containing a fumarate unit. It is due to the difference of the reactivity of the unsaturated bond in the polyester.

As described above, we found that the reactivity of the growing radicals could be changed by the mass ratios of St/MAnh. The optimization of the mass ratios of St/MAnh provides high grafting efficiencies without gelation.

Grafting Efficiency

In our previous article,¹¹ we reported that fine dispersions were obtained in the grafting of P(EA–AA) to the polyester and the amount of water-soluble component and the average molecular weight of the grafted side chain were determined. In this study, comparison of the grafting efficiencies of the grafting of P(EA–AA) and that of P(St–MAnh) to the polyester was done. Methods of determination were similar to those described in our previous article.¹¹ Molecular weights of the grafted side chains, that were separated by extraction of hydrolyzed grafting products, were determined as PS equivalent values by GPC. The conversions of the fumarate unit in the polyester were determined by use of ¹H-NMR.¹⁰ Table V shows the results of the comparison.

From the Table, it can be seen that the amount of water-soluble component in the case of P(St–MAnh) is smaller than that in the case of grafting

Table V Comparison of the Grafting Reaction Products of P(St-MANh)-Grafted Polyester and P(EA-AA)-Grafted Polyester

	P(St-MANh)-Grafted Product ^a	P(EA-AA)-Grafted Product ^b
Particle diameter (nm)	80	80
Amount of water-soluble components (%)	14	20
Average molecular weight of grafted side chain ^c (—)	10,500	9030
Grafting efficiency (%)	44	25
Conversion of fumarate in the polyester (%)	60	ca. 100

^a The mass ratio of polyester (containing 7 mol % of FA)/St/MANh was 75/10/15.

^b The mass ratio of polyester (containing 5 mol % of FA)/EA/AA was 75/10/15.

^c PSt equivalent values.

of P(EA-AA), and the calculated grafting efficiency is about twice. This result shows that the formed P(St-MANh) radicals effectively reacted with the unsaturated bond of polyester. The conversion of the fumarate unit was about 60%, and this value is smaller than that in the case of P(EA-AA). This result shows that it is not important for enhancement of the grafting efficiency to increase the conversion of the unsaturated bond of polyester.

Grafting Copolymerization of St, MANh, and the Other Monomer

St is a typical electron-donative monomer, and MANh is a typical electron-accepting monomer. Electron states of the unsaturated bonds in almost all monomers are intermediate between electron-donative and electron-accepting. In the case that the difference between the e value of each monomer is large, the monomers highly copolymerized to each other. Therefore, it is considered that incorporation of the monomers into the grafted side chain is increased by copolymerization with St and MANh. In this study, the grafting copolymerization of MMA or AA, which is less reactive with fumarate, is discussed.

Table VI shows the results of the particle diameters of grafted polyesters obtained under various grafting monomer compositions. The addition of less reactive monomers did not increase the particle diameters. Moreover, in the case that dibutyl fumarate was used instead of MANh and AA was used as a hydrophilic monomer, fine dispersion was obtained. From the above results, it was possible to increase the incorporation of less reactive monomers into the grafted side chain by grafting copolymerization with St and MANh.

CONCLUSION

To obtain fine dispersion of grafted polyester without gelation, grafting utilizing alternating copolymerization of hydrophilic polymers to unsaturated polyester was discussed. In the presence of MANh in the reaction medium, the reaction tendency of St radical for fumarate of the polyester was depressed. Therefore, it was considered that the reactivities of the grafted polymer radicals were changed by the addition of MANh. The grafting utilizing alternating copolymerization was compared with the conventional grafting, and the calculated grafting efficiency is about twice. Moreover, we found that it was possible to increase the incorporation of less reactive monomers into the grafted side chain by the grafting utilizing alternating copolymerization. From above results, it is considered that the grafting utilizing alternating copolymerization is a useful method to prepare grafted polymers.

In the articles to follow, the rheological control of the aqueous dispersion and the mechanical property of grafted polyesters having various side chains will be discussed.

Table VI Characteristics of the Dispersion

Composition	Diameter (nm)	Viscosity (Poise)
Polyester ^a /St/MMA/MANh (75/10/8/7)	150	0.5
Polyester ^b /St/AA/DBF (75/10/10/5)	120	0.8

^a Polyester contains 5 mol % of FA.

^b Polyester contains 3 mol % of FA.

REFERENCES

1. Misev, T. A. *J Jpn Soc Colour Mater* 1993, 66, 195.
2. Robinson, P. V. *J Coat Technol* 1981, 674, 23.
3. Woo, J. T. K.; Ting, V.; Evans, J. *J Coat Technol* 1982, 689, 41.
4. Buter, R.; Roelofs, A. H. J.; Wemmemhove, A. P. (Akzo N. V.) *Eur. Pat.* 90200518, 1990.
5. Yu, Y.; Funke, W. *Angew Makromol Chem* 1982, 103, 203.
6. Baumann, H.; Joos, B.; Funke, W. *Makromol Chem* 1986, 187, 2933.
7. Hautung, M.; Grabbe, M.; Mayenfels, P. (BASF Lacke + Farben AG) *WO* 9115528, 1991.
8. Kotera, N.; Takahashi, K. *Bull Chem Soc Jpn* 1990, 63, 2283.
9. O'Neill, G.; Rothwell, A. R. (Eastman Kodak Company) *U.S. Pat.* 4300580, 1981.
10. Shimizu, T.; Higashiura, S.; Ohguchi, M. *J Appl Polym Sci*, 1999, 72, 1817.
11. Shimizu, T.; Higashiura, S.; Ohguchi, M.; Murase, T.; Akitomo, Y. *Polym Adv Technol*, 1999, 10, 1.
12. Brandrup, J. Immergut, E. H. (Eds.) *Polymer Handbook* (3rd ed.); Wiley: New York, 1989; Section 2, p 267.
13. Trivedi, B. C.; Culbertson, B. N. *Meleic Anhydride*; Plenum Press: New York, 1982; p 307.