

Morphological Core/Shell Structure and Dispersion Stability of Water-Dispersible Copolyester Graft Polymerized with Acrylic Acid and Ethyl Acrylate

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SYNOPSIS

Anionic water-dispersible copolyester was prepared by the polycondensation of dimethyl isophthalate (DMI)/5-sodium sulfo dimethyl isophthalate (DMS) with ethylene glycol (EG)/diethylene glycol (DEG) to synthesize water-dispersible copolyester-*g*-AA/EAs by chemical method. In the case of graft polymerization of AA/EA onto DMI/DMS/EG/DEG copolyesters, graft yield increases with increase in the AA molar feed ratio. Copolyester-*g*-AA/EAs dissolve completely in 1N aqueous NaOH solution whereas DMI/DMS/EG/DEG copolyester does not. This is a result of the core/shell structure that was ascertained by the graft yield and the zeta potential of copolyester-*g*-AA/EAs. It appears that grafted AA/EA exists at the surface of copolyester-*g*-AA/EA particles, and the backbone polymer, i.e., DMI/DMS/EG/DEG copolyester, exists in the inner phase of the copolyester-*g*-AA/EA particles. The complete solubility of copolyester-*g*-AA/EAs in 1N NaOH aqueous solution seems to come mainly from the electrostatic repulsion between —COOs that are present at the surface of copolyester-*g*-AA/EA particles due to AA grafting and —OHs that are present at the dispersion medium due to NaOH decomposition and which cause the hydrolytic breakage and consequently the coagulation of copolyesters in alkaline medium.

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INTRODUCTION

Good adhesion of anionic water-dispersible polyesters to polyester fabrics make them prospective as warp sizing agents. But since alkali is commonly used for desizing, alkaline hydrolysis of water-dispersible polyesters may cause many problems downstream, especially in dyeing. Thus we attempted to overcome this defect of alkaline hydrolysis by grafting copolyesters with carboxylic acrylic monomers such as acrylic acid. Moreover, tensile properties such as strength, elongation, and toughness of polymer resin are expected to increase with the grafting by the mechanism of multiple deformation due to the branch structure of grafted poly-

mers.¹ Improvement of tensile properties of film by the graft polymerization is well known, as is in the case of acrylonitrile butadiene styrene (ABS) rubber.

REAGENTS

Dimethyl isophthalate [(DMI) first grade reagent, Aldrich Co., USA], 5-sodium sulfodimethyl isophthalate [(DMS) first grade reagent, Aldrich Co., USA] ethylene glycol [(EG) Honam Petrochemicals Co., Korea], and diethylene glycol [(DEG) Honam Petrochemicals Co., Korea] were used without further purification. Acrylic acid [(AA) first grade reagent, Junsei Chem. Co., Japan] was vacuum-distilled and kept in the refrigerator. Ethyl acrylate [(EA) first grade reagent, Junsei Chem. Co., Japan] was washed with 5% aqueous NaOH solution three times and then washed with a saturated aqueous

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CaCl₂ solution two times under reduced pressure.² Benzoyl peroxide [(BPO) Hayashi Pure Chem. Ind., Japan] was dissolved in acetone and precipitated in distilled water. Distilled water (HPLC grade, EM Science Co., Germany) was used in measuring zeta potential, and distilled and deionized water was used in polymerization and solubility tests. Other reagents such as NaOH, CaCl₂, methanol, ethanol, antimony trioxide, zinc acetate, and trimethyl phosphate were first grade reagents and were used without further purification.

EXPERIMENTAL

Synthesis of DMI/DMS/EG/DEG Copolyesters

Comonomers (DMI, DMS, EG, and DEG) and catalyst (zinc acetate) were added to a two-necked reaction flask equipped with a distillation column and a thermometer. Ester-interchange reaction was carried out for 2–3 h at 230–240°C under atmospheric pressure until the volume of distillate (methanol) reached the value calculated theoretically. The oligomers thus obtained and constant amounts of catalyst (antimony trioxide) and heat stabilizer (trimethyl phosphate) were fed to another reaction flask (four-necked) equipped with a mechanical stirrer, a thermometer, and a condenser. The polycondensation reaction was carried out for 1 h under vacuum at 270°C to remove glycol and synthesize water-dispersible DMI/DMS/EG/DEG copolyesters. DMI/DMS/EG/DEG copolyester was synthesized at DMS/DMI molar feed ratios of 10/90 with the EG/DEG molar feed ratio of 3 : 1. In all this reaction, dimethyl ester (DMI + DMS)/diol(EG + DEG) molar feed ratio was fixed at 1/1.8. [Theoretically thinking, dimethyl ester (DMI + DMS)/diol(EG + DEG) molar feed ratio is 1/2 because during polycondensation reaction, twice the molar amount of diol (EG + DEG) components is consumed. But in most cases of copolyester syntheses, the usual component ratio of dimethyl ester/diol ranges from 1/1.6 ~ 1/2. In this experiment, we fixed the ratio as 1 : 1.8). Copolyester is denoted as P1031 according to the feed ratio of comonomers DMI/DMS/EG/DEG. After synthesis, this polymer was solidified by pouring it on an aluminium plate at room temperature. This solidified polymer was dissolved as follows. About 50 g of polymerized sample and about 200 g of deionized distilled water were exactly measured and fed into a three-necked flask equipped with a thermometer, a condenser, and a mechanical stirrer, then dissolved by stirring at 600 rpm for 4 h at 80°C.

Synthesis of Copolyester-*g*-(AA/EA)

Water, P1031, acryl monomers, and an initiator (BPO) were fed at a fixed feed ratio into a four-necked flask equipped with a thermometer, a condenser, a mechanical stirrer, and a nitrogen inlet. Graft polymerization was carried out for 2 h at 80–85°C with high speed agitation. The feed ratios of AA/EA were 1/0, 3/1, 2/1, 1/1, 1/2, 1/3, 0/1 (mole ratio) and the feed ratios of P1031/acryl monomers were 2/1, 4/3, 1/1, 4/5, 2/3 (wt ratio). The feed ratio of water (P1031 + acryl monomers) and BPO/acryl monomers were fixed at 4/1 and 1/100, respectively (wt ratios). For example, when the molar feed ratio of AA/EA was 1/1 and the weight feed ratio of P1031/acryl monomer was 1/1, 400 g of water, 50 g of P1031, 20.93 g of AA, 29.07 g of EA, and 0.5 g of BPO were fed.

P1031 dispersion in water of appropriate concentration was fed into a four-necked flask so that the solid content including acryl monomers would be 25 wt %, then heated with agitation. Subsequently, catalyst (BPO, dissolved in acryl monomers) and acryl monomers were fed at 50–60°C and graft polymerization was carried out for 2 h at 80–85°C with mechanical stirring.

The synthesized copolyester-*g*-AA/EAs are denoted as *Gwxyz*, where *G* represents graft polymer, *wx* represents wt feed ratio of P1031 (acryl monomers), and *yz* represents the molar feed ratio of AA/EA. For example, G1131 denotes a copolyester-*g*-AA/EA synthesized at the feed ratio of P1031 (acryl monomers) 1/1 (wt ratio) and AA/EA 3/1 (mole ratio).

Copolyester-*g*-AA/EA films were cast by pouring the dispersions synthesized above on a transfer paper and drying for 2 h at 80°C under atmospheric pressure; the film was then vacuum-dried for 24 h at 80°C. Homopolymers were extracted from a vacuum-dried film (1.5 g) with methanol for three days in a Soxhlet, and the graft yield was calculated according to following:

$$\text{graft yield (\%)} = \frac{W' - (W \times f)}{(W \times f)} \times 100$$

where *W'* is the dry weight of sample after Soxhlet extraction, *W* is the dry weight of sample before Soxhlet extraction, and *f* is the fraction of P1031 in the gross polymer,

$$f = \frac{W_p}{W_p + W_a \times (1 - W_a'/100)}$$

where W_p and W_a are the amounts of P1031 and acryl monomers fed, respectively, and W_a' is the percent loss of acryl monomers. W_a' can be calculated from the total amount of P1031 and acryl monomers fed W_1 and the total amount of gross polymers obtained, W_2 , as follows:

$$W_a' = \frac{W_1 - W_2}{W_a}$$

Synthesis of AA/EA Copolymers

After feeding acryl monomers, catalyst (BPO), and water/ethanol into a four-necked flask equipped with a thermometer, a condenser, a mechanical stirrer, and a nitrogen inlet, polymerization reaction was carried out for 2 h at 80–85°C with high speed agitation. The feed ratio of AA/EA was varied as 1/0, 3/1, 2/1, 1/1, 1/2, 1/3, and 0/1 (mole ratio). The feed ratios of acryl monomers/(water/ethanol), water/ethanol, and BPO/acryl monomers were fixed at 1/9, 1/1, and 1/100 (wt ratios). For example, when AA/EA was 1 : 1, 225 g of water, 225 g of ethanol, 20.93 g of AA, 29.07 g of EA, and 0.5 g of BPO were used. BPO was dissolved in acryl monomers like the above experiment and added at 50–60°C.

Polymerized acryl copolymers are denoted as A_{xy} , where A represents acryl copolymer and xy represents the molar feed ratio of AA/EA. For example, A31 denotes an acryl copolymer synthesized at the molar feed ratio AA/EA of 3/1.

Solubility of Polymer Films

Films were cast by pouring the dispersion upon a transfer paper and drying for 2 h at 80°C under atmospheric pressure; then the film was vacuum-dried for 24 h at 80°C. Approximately 1 g of the vacuum-dried film was accurately weighed and immersed in water at a fixed condition. The water-swollen film was squeezed between filter papers to remove excess water and dried and weighed to calculate the solubility of the film according to the following:

$$\text{solubility (\%)} = \frac{\text{dissolved weight of sample after immersion}}{\text{dry weight of sample before immersion}} \times 100.$$

Zeta Potential

Zetasizer 4 (Malvern Co., UK) was used to check the zeta potential of the dispersions (0.1% concentration) by light scattering.

RESULTS AND DISCUSSION

Graft Yield

Figure 1 shows the graft yield of copolyester- g -AA/EAs of different molar feed ratios of AA/EA (the weight feed ratio of P1031/acryl monomers was fixed at 1 : 1). We can see that the graft yield of copolyester- g -AA/EAs increases with the increase in AA molar feed ratios. The graft yield of G1110 is 62.1%, and the graft yields of G1131 and G1112 are 40–30%. The reason for this reduced graft yield can be explained as follows. The reaction medium for the copolyester- g -AA/EA synthesis was water, and the comonomers (AA and EA) used are different in their relative degree of philicity with water; i.e., AA is hydrophilic, and EA is hydrophobic. Hydrophilic AA is expected to access the water-dispersible DMI/DMS/EG/DEG copolyester (P1031) easily, but hydrophobic EA is expected to access the water-dispersible DMI/DMS/EG/DEG copolyester only when dissolved and transported in AA. Therefore, AA is more likely to react with DMI/DMS/EG/DEG copolyester, and this may result in graft yields such as those shown in Fig. 2. The structure of the stem polymer, especially crystallinity and swellability, is known to have a significant effect on the graft yield. With the increase in crystallinity, graft yield decreases, whereas swelling induced by some

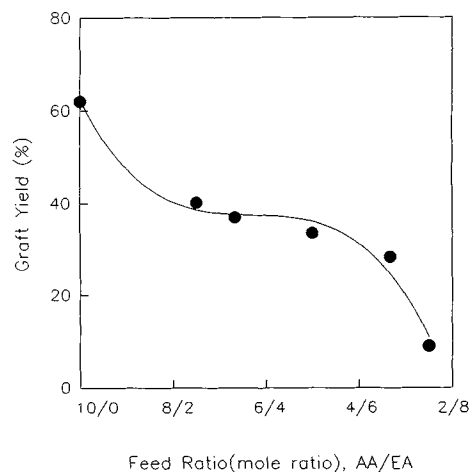


Figure 1 Graft yield of copolyester- g -AA/EAs (G11yz series). Soxhlet extraction: 3 days with methanol.

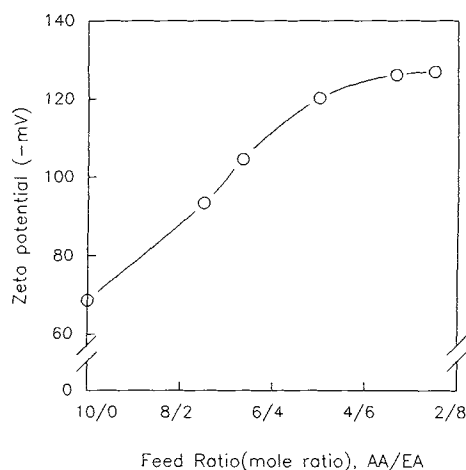


Figure 2 Zeta potential change of copolyester-*g*-AA/EAs (G11yz series) in water.

solvents allows easier penetration of monomers to increase graft yield.³⁻⁶ Because water-dispersible DMI/DMS/EG/DEG copolyesters are amorphous, high graft yield can be achieved.

Zeta Potential of Copolyester-*g*-AA/EAs

According to the DLVO (Deryaguin, Landau, Verwey, Overbeek) theory,^{7,8} total interaction (V_T) between particles in dispersion appears to be the sum of the attraction and repulsion energies (V_A and V_R , respectively).⁹

$$V_T = V_A + V_R = V_A + (V_E + V_S) \quad (1)$$

where, V_A is the van der Waals force; V_E is the electrostatic repulsion, and V_S is the steric repulsion.

Neglecting retardation correction, the attractive energy between two equal particles of radius a at a distance of separation H_0 for $a \gg H_0$ is

$$V_A = -\frac{A^*a}{12H_0} \quad (2)$$

where, A^* is the effective Hamaker constant describing attraction between the particles and the dispersion medium.¹⁰⁻¹²

$$V_E = \frac{\epsilon a \psi_0^2}{2} \ln[1 + \exp(-\kappa H_0)] \quad (3)$$

where, ψ_0 is the electrostatic potential at the particle surface and $1/\kappa$ is the Debye length.

$$\kappa = \left[\frac{8\pi n z^2 e^2}{\epsilon k T} \right]^{1/2} \quad (4)$$

where, n is the number of ionized groups (equal to the concentration of electrolytes), z is the valency, e is the elementary charge, ϵ is the dielectric constant, k is the Boltzmann constant, and T is the absolute temperature.

According to the above equation, if the zeta potential ($\psi\zeta$) increases, then ψ_0 will increase and V_E will increase. So if other conditions are kept constant, dispersion will be more stable with the increase in the zeta potential (electrostatic stabilization).

Steric stabilization refers to the prevention of flocculation of uncharged particles by the presence of nonionic polymer molecules.¹³ Napper¹⁴⁻¹⁶ interpreted steric stabilization of dispersions qualitatively by using the second law of thermodynamics. According to Hesselink, Vrij, and Overbeek,¹⁷ who attempted to explain steric stabilization quantitatively, the factor that has the major influence on Gibbs free energy change (ΔG_R) is α (α is the intramolecular expansion parameter for polymer in free solution). If α is large, free energy change in mixing (ΔG_M) becomes a positive value, and ΔG_R also becomes positive, resulting in more stable dispersions.

Figure 2 shows the change in the zeta potential of copolyester-*g*-AA/EAs in water. The zeta potentials of graft polymers of high AA molar feed ratio is much lower than those of low AA molar feed ratio. The zeta potentials of G1112 and G1113 of high EA contents are about -128 mV, but the zeta potentials of G1110 and G1131 of high AA contents decrease to -70 mV abruptly. As mentioned above, G1110 and G1131 of high AA molar feed ratios have high graft yields (Fig. 1), and their core/shell particle structures are expected to have thicker shells than G1112 and G1113 of low AA molar feed ratio. The grafted AA/EA parts of G1110 and G1131 would sufficiently cover P1031 particles, and the ratio of the contribution of $-\text{SO}_3\text{Na}$ to the zeta potential will decrease compared with that of G1112 and G1113. In the case of low molar feed ratios of AA, G1112, and G1113, graft yields of copolyester-*g*-AA/EAs are so low that grafted AA/EA cannot sufficiently cover P1031 particles, and contribution of $-\text{SO}_3\text{Na}$ to the zeta potential appears to be high. As a result, G1112 and G1113 seem to have higher zeta potentials.

Figure 3 shows the zeta potential change in copolyester-*g*-AA/EAs in 0.01N aqueous NaOH solution. With the change in dispersion medium from water to 0.01N aqueous NaOH solution, the zeta potential becomes much lower. According to eq. (4), Debye length ($1/\kappa$) decreases with an increase in

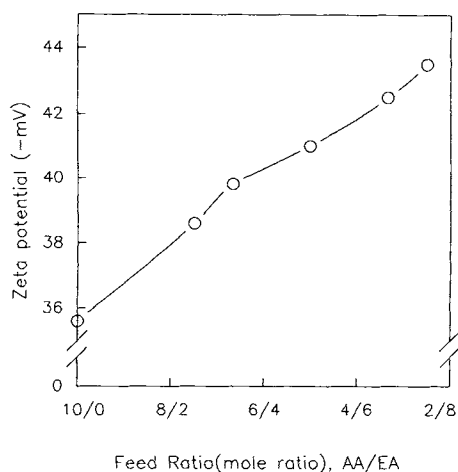


Figure 3 Zeta potential change of copolyester-*g*-AA/EAs (G11yz series) in 0.01*N* NaOH solution.

electrolyte concentration (n) and the ionic valency (z). That is, the electrical double layer becomes more compact. So with the change in dispersion medium from water to 0.01*N* aqueous NaOH solution, Debye length is expected to decrease, resulting in a decrease in the zeta potential.¹⁸ Colloids are known to coagulate with the decrease of zeta potential.¹⁹

Solution Property of Copolyester-*g*-AA/EA

Figures 4–7 show the solubility of copolyester-*g*-AA/EA and AA/EA copolymer films. Solubility of copolyester-*g*-AA/EA films under various conditions in water are shown in Figure 4. When treated at 50°C for 2 h, the solubilities of copolyester-*g*-AA/EA films increase with the increase in the molar

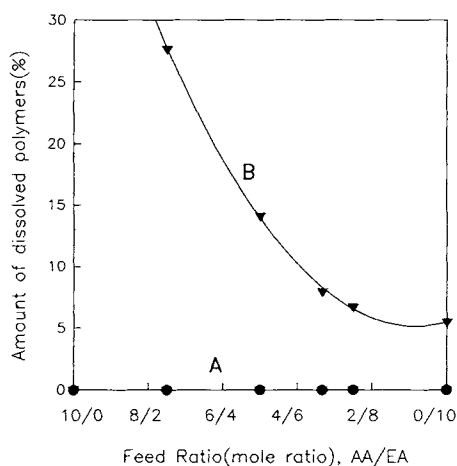


Figure 4 Amount of dissolved copolyester-*g*-AA/EAs (G11yz series) in water at various conditions (liquor ratio = 50/1). (A) 20°C, 1.5 days; (B) 50°C, 2 h.

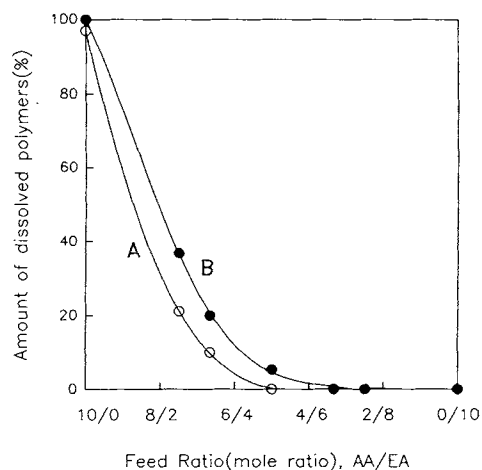


Figure 5 Amount of dissolved AA/EA copolymers in water at various conditions (liquor ratio = 50/1). (A) 20°C, 2 h; (B) 20°C, 1.5 days.

feed ratio of AA. But all copolyester-*g*-AA/EA films do not dissolve when treated at 20°C for 1.5 days. On the contrary, Figure 5 shows that some amount of AA/EA copolymer films of high AA contents dissolves in water when treated at 20°C for 1.5 days or at 50°C for 2 h. We may conclude that the solubilities of polymers were changed significantly by graft polymerization.

Figures 6 and 7 show the solubility of copolyester-*g*-AA/EA and AA/EA copolymer films in 1*N* NaOH aqueous solution. All AA/EA copolymer and copolyester-*g*-AA/EA films of AA/EA molar ratios of 1/0 ~ 1/3 dissolve completely when treated at 20°C for 1.5 days. Here, we can ascribe the solubility of AA/EA copolymers in 1*N* NaOH aqueous solution

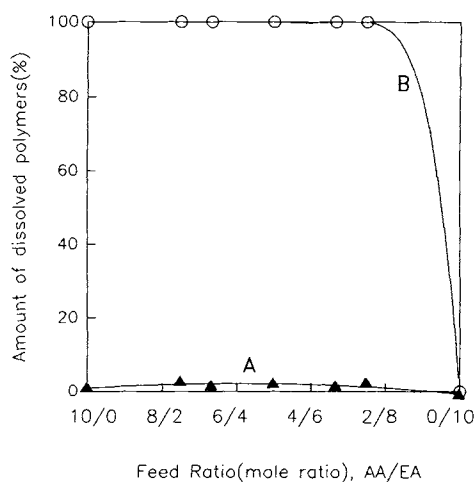


Figure 6 Amount of dissolved copolyester-*g*-AA/EAs (G11yz series) in 1*N* NaOH solution at various conditions (liquor ratio = 50/1). (A) 20°C, 2 h; (B) 20°C, 1.5 days.

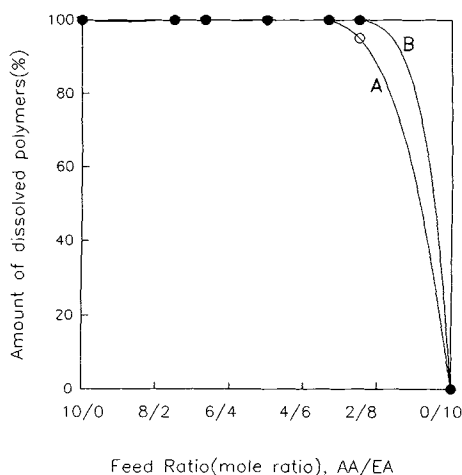
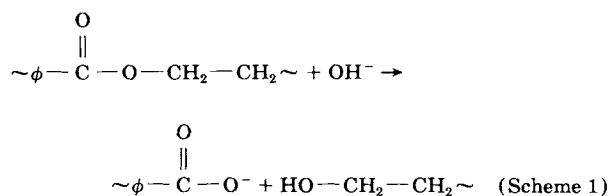


Figure 7 Amount of dissolved AA/EA copolymers in 1N NaOH solution at various conditions (liquor ratio = 50/1). (A) 20°C, 2 h; (B) 20°C, 1.5 days, or 50°C, 2 h.

to the AA residue, but the complete solubility of copolyester-*g*-AA/EA films in 1N NaOH aqueous solution is in some sense difficult to understand because, generally, polyesters are very weak towards the attack of alkaline medium and they tend to hydrolyze at the backbone ester linkages (Scheme 1) and precipitate in water.



where, ϕ is *m*-substituted benzene ring.

The dispersion of DMI/DMS/EG/DEG copolyester (P1031) actually precipitated in 1N NaOH aqueous solution. Or we can here ascribe the precipitation of DMI/DMS/EG/DEG copolyester (P1031) in alkaline medium to the coagulation effect of polyelectrolytes in salts.¹⁸ The reason for the enhanced dispersion stability of the copolyester-*g*-AA/EAs in 1N NaOH aqueous solution appears to be as follows. As the graft yield of copolyester-*g*-AA/EAs ranges from 8.9–62.1% (Fig. 2), we may assume that grafted AA/EA parts of copolyester-*g*-AA/EAs will be sufficient to cover the surface of the original P1031 globules. In the graft polymerization of AA/EA onto P1031, some amount of AA/EA monomers may be expected to enter the internal phase of the copolyester-*g*-AA/EA particles due to the amorphous nature of P1031, but most are expected to be graft polymerized at the surface of copolyester-*g*-

AA/EA particles. And the original backbone polymer, i.e., DMI/DMS/EG/DEG copolyester (P1031), is, contrarily, expected to exist in the internal phase of copolyester-*g*-AA/EA particles. According to Figure 2, the zeta potential of copolyester-*g*-AA/EAs in water decreases with the increase in the molar feed ratio of AA. And this result seems to come from the morphological fact that —COOH groups are situated at the surface of copolyester-*g*-AA/EA particles and DMI/DMS/EG/DEG copolyester (P1031) situated in the internal phase of copolyester-*g*-AA/EA particles. Alkaline hydrolysis occurs at the main chain of copolyester-*g*-AA/EAs, i.e., DMI/DMS/EG/DEG copolyester (P1031). And as noted above, this part exists in the internal phase of polymer particles such that the location of hydrolysis or coagulation is blocked completely by the core/shell structure of copolyester-*g*-AA/EA particles in 1N NaOH aqueous solution. So the mechanism of hydrolysis blocking appears to be as follows. The carboxylic groups among the outer part (shell) of copolyester-*g*-AA/EA particles is electrolyzed to —COO[−] in 1N NaOH aqueous solution and appear to repel the OH[−]s, such that they can not enter the internal phase (core) of copolyester-*g*-AA/EA particles and bring about alkaline hydrolysis of the polyester backbone. And Na⁺ (in NaOH), which causes coagulation of P1031, will also be prevented to enter the core region of copolyester-*g*-AA/EA particles by the presence of COOH at the shell region of copolyester-*g*-AA/EA particles. Consequently, copolyester-*g*-AA/EA particles seem to have core/shell structure where the backbone polymer, i.e., DMI/DMS/EG/DEG copolyester exists in the internal phase, and grafted AA/EA exists at the outer surfaces of copolyester-*g*-AA/EA particles.

CONCLUSIONS

1. In the case of graft polymerization of AA/EA onto DMI/DMS/EG/DEG copolyesters, graft yield increases with increase in the AA molar feed ratio.
2. Copolyester-*g*-AA/EAs dissolve completely in 1N aqueous NaOH solution, whereas DMI/DMS/EG/DEG copolyesters do not. This is a result of the core/shell structure that was ascertained by the graft yield and the zeta potential of copolyester-*g*-AA/EAs. It appears that grafted AA/EA exists at the surface of copolyester-*g*-AA/EA particles, and the backbone polymer, i.e., DMI/DMS/EG/DEG

copolyester, exists in the inner phase of the copolyester-*g*-AA/EA particles. The complete solubility of copolyester-*g*-AA/EAs in 1*N* NaOH aqueous solution seems to come mainly from the electrostatic repulsion between OH⁻ responsible for hydrolytic breakage and —COO⁻ at the surface of copolyester-*g*-AA/EAs particles and from the lessening of Na⁺ coagulation effect.

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