Studies of Aqueous Resins. I. Water-Dispersed Polyesters Containing Polar Groups

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Water-borne polyesters which can provide a flexible film having a high resistance to water have been designed. Such hydrophobic polyesters can be dispersed into water by introducing small amounts of hydrophilic groups. When a few mol% of sodium 5-sulfonatoisophthalic acid is used as a hydrophilic group and some water-soluble organic compounds, such as 2-butoxyethanol, are used as additives, stable aqueous dispersions of polyester resins are obtained, having a fine particle size under 1.0 μm.

Hitherto, many polyesters have widely been used in various fields such as fibres, films, adhesives, painting binders, and the like. Such polyesters can be used as water-resisting films when they are solved in organic solvents and form films by evaporation. Recently, however, in view of saving natural resources and preventing environmental pollution, the conversion of organic solvents into inorganic solvents is highly recommended.

It is known that branched polyesters with low molecular weight can be solubilized into water when they have carboxyl groups at the end of polymer chain and are neutralized with alkali.[1] In order to obtain a water-resisting cured film, it is necessary to bake the film at high temperature after drying.

Next, when sodium 5-sulfonatoisophthalic acid (**IS**) is copolymerized with diethylene glycol (**DEG**) or polyethylene glycol (**PEG**), the resulting hydrophilic polyesters are soluble in hot water and the solutions are stable at room temperature.[2] On the other hand, when polyesters are combined with nonionic surface-active agents, the polyesters can be solubilized in water by increasing their affinity to water.[3] However, when a film formed from the polymers is dipped into room temperature water or hot water, it becomes muddy and is finally solubilized. This prevents its use as a water-resisting film. Technical problems concern how to satisfy both the solubilization of polyesters in water and high resistance of their film to water. These two properties of polyesters seem to be in conflict with each other. However, these problems have hitherto been solved for other polymers, except for the polyesters. For example, when low-hydrophilic materials in an acrylic system are polymerized, water-resisting films are obtained from a fine particle dispersion of the polymers.[4] In this study, when **IS** was copolymerized with other hydrophobic materials, both the concentration of **IS** and an additive effect of water-soluble organic cosolvents were examined.

Experimental

Preparation of Polyesters. As an example of the preparation, definite amounts of terephthalic acid (**TP**), isophthalic acid (**IP**), sodium 5-sulfonatoisophthalic acid (**IS**), ethylene glycol (**EG**), 2,2-dimethyl-1,3-propanediol (**DPD**), diethylene glycol (**DEG**), and catalysts such as zinc acetate or antimony trioxide were charged into a reactor and subjected to an esterification reaction at 140 to 220 °C for three hours. The mixture was then subjected to a polycondensation reaction under reduced pressure (0.1 mmHg, 1 mmHg≈133.322 Pa) at 220 to 270 °C for two hours. The polyesters, thus obtained, and their physical properties are shown in Table 1. In this table, the number-averaged molecular weights ($\overline{M}_n$) are given which were determined by the GPC method; the numbers of the carboxyl groups (*CN*) were determined by titrating the polymer solution in chloroform with 0.1 equiv potassium ethoxide. The water content of each polyester was determined from the change of weight when a sheet of the polyester (0.5 mm thick, 1 cm length, and 1 cm width) was allowed to stand at temperature of 40 °C and moisture of 80%.

Table 1. Characteristics of Copolyesters

Component	E-1	E-2	E-3	E-4
TP[a]	50	50	50	50
IP	50	48	42	42
IS	0	2	8	8
EG	50	50	50	0
DPD	50	50	50	0
DEG	0	0	0	100
Properties				
$\overline{M}_n(\times10^{-4})$	1.10	1.20	1.21	1.10
CN(equiv/10^6 g)	12	13	20	20

a) Abbreviations are given in the text.

Solubilization of Polyesters in Water. The polymer shown in Table 1 (30 wt%), a water-soluble organic compound (0 or 15 wt%) and water (70 or 55 wt%) were charged into a reactor, and then stirred for six hours at 70 °C. After cooling to room temperature, the mixture was filtered with a stainless-steel filter (200 mesh), thus becoming free from undispersed materials. The undispersed polyesters were determined by weight. The components and the properties of the polyesters, thus obtained (D-1—D-4), are shown in Table 2. The water-soluble organic compounds used were commercially available from Nakarai Chem. Co. Deionized water was used throughout this study. The dispersed particle size was measured with a COULTER (model N4) at 25 °C when the sample dispersion was adjusted with a solid

Table 2. Characteristics of Water-Dispersed Copolyesters

Water-Dispersed Copolyester[a]	D-1	D-2	D-3	D-4
Copolyester	E-1	E-2	E-3	E-4
Characteristics				
Undispersed copolyester/wt%	100	100	100	0
Appearance	No Change	No Change	No Change	Translucent
Mean particle size/nm	—	—	—	55
Viscosity/cps	—	—	—	2000

a) Copolyester/Water: 30/70 (by wt).

concentration of 0.1 wt% in water. The viscosity of sample dispersion was measured with a rotation-viscometer (Tokyo Keiki Co. Ltd., Model EM) at 25 °C for 10 rpm. The solid content of sample dispersion was determined from the weight change of the sample after 10 g of the dispersion was taken into a container, and kept for 4 h at 100 °C and 4 h at 150 °C under a vacuum of 0.1 mmHg.

Results and Discussion

Hydrophilic Property of Polyesters. The compositions and properties of the polyesters studied are given in Table 1. Those of E-1, E-2, and E-3 are the same, except for the content of **IS** instead of **IP**. On the other hand, the composition of E-4 is greatly different from the compositions of the others in the contents of hydrophilic **DEG**.

The four polyesters have almost the same characteristics, such as molecular weight ($\overline{M}_n$) and number of carboxyl groups (*CN*), and are noncrystalline. When the four polyesters were left standing under a constant temperature of 40 °C and humidity of 80%, E-1, E-2, and E-3 did not show any change in appearance, even after 48 h, while E-4 showed white colored turbidity and lost its transparency after 12 h. Then, after 48 h, its surface softened and partly solubilized out.

Third, changes in the moisture absorption of the four polyesters are shown in Fig. 1. Those of E-1, E-2, and E-3 ranged under a change of 0.5 wt% and almost reached equilibrium at 48 h; they showed a small increase in weight in the order E-1, E-2, and E-3. Therefore, the three polyesters can be recognized as being hydrophobic. On the other hand, E-4 showed a high water absorption and did not obtain equilibrium, even after 48 h. It is therefore a strong hydrophilic polyester. Its strong affinity to water seems to be caused by a high concentration of **IS** and **DEG**.

Solubilization of Polyesters in Water. E-1, E-2, E-3, or E-4 was charged into a vessel with water and then agitated at 70 °C for about 6 h. The dispersion, thus obtained, is shown in Table 2. E-4 showed good water dispersibility and gave a faint bluish-white viscous dispersion, D-4. On the other hand, E-1, E-2, and E-3 showed no water dispersibility and no change in appearence and viscosity, even after agitation. Only E-4, which contains a hydrophilic component of **DEG** with **IS**, could be solubilized in water. However, E-1, E-2, and E-3, which do not have a component of **DEG**, could not be solubilized in water.

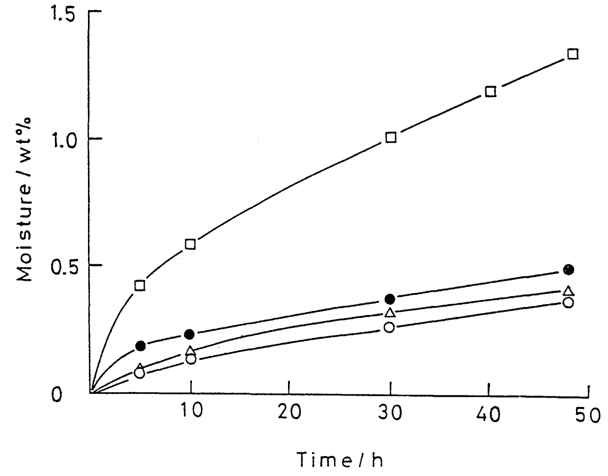

Fig. 1. Moisture absorption against to time for E-1 (○), E-2 (△), E-3 (●), and E-4 (□) respectively, when they are settled at 40 °C and relative humidity of 80%.

Combined Use of Water-Soluble Cosolvents. As stated in the previous section, E-3 was not dispersed into water. However, when it was agitated at 70 °C for about 6 h with water in the presence of some amounts of cosolvent, it could be dispersed into water. The results are shown in Table 3. 2-Buthoxyethanol (**BEA**), 3-propoxy-1,2-propanediol (**PPA**), 2-propanol (**IPA**), and N,N-dimethylformamide (**DMF**) were used as such cosolvents. In such cases, opaque viscous dispersions (D-5—D-8) were obtained with small mean particle sizes. The suitable cosolvents seem to be regulated by their solubility parameters (SP). Toluene (**TLN**), however, showed no dispersion effect. Therefore, suitable cosolvents are also related to their solubilities in water (Table 3). Thus, a combination of hydrophobic polyesters, water-soluble cosolvents, and water makes it possible to produce dispersions which can form highly water-resisting films. The mean particle sizes of the obtained dispersions are also given in Table 3. The values are those obtained 24 h after the formation of the dispersions, and are similar to those measured at 720 h (given in parentheses). This shows that the dispersions are very stable for many hours.

Concentration Effect of SO_3Na Group, Particle Size, and Viscosity. Three hydrophobic polyesters

Table 3. Characteristics of Water-Dispersed Copolyesters Using Copolyester E-3, Cosolvent, and Water[a]

Water-dispersed copolyesters	D-5	D-6	D-7	D-8	D-9
Cosolvent	**BEA**[b]	**PPA**	**IPA**	**DMF**	**TLN**
Cosolvent properties					
Solubility parameter	9.2	8.8	11.5	11.5	8.9
Solubility (wt% in water)	100	100	100	100	0
Characteristics of dispersions					
Undispersed copolyester/wt%	0	0	0	0	100
Appearance	Translucent	Translucent	Opaque	Opaque	No change
Mean particle size/nm[c]	5.1(5.1)	8.6(8.6)	23(23)	18(18)	—
Viscosity/cps	700	750	300	400	—

a) Copolyester E-3/Cosolvent/Water: 30/15/55 (by wt). b) Abbreviations are given in the text. c) The values were measured at 24 h after preparing the dispersion. Those in parentheses were measured at 720 h.

Table 4. Influence of **IS** Concentration on Dispersion of Copolyesters[a]

Water-Dispersed Copolyesters	D-10	D-11	D-5
Copolyesters	E-1	E-2	E-3
Cosolvents	**BEA**[b]	**BEA**	**BEA**
Caracteristics			
Undispersed copolyester/wt%	100	0	0
Appearance	No change	Opaque	Translucent
Mean particle size/nm	—	74	5
Viscosity/cps	—	1200	700

a) Copolyester/Cosolvent/Water: 30/15/55 (by weight). b) Abbreviations are given in the text.

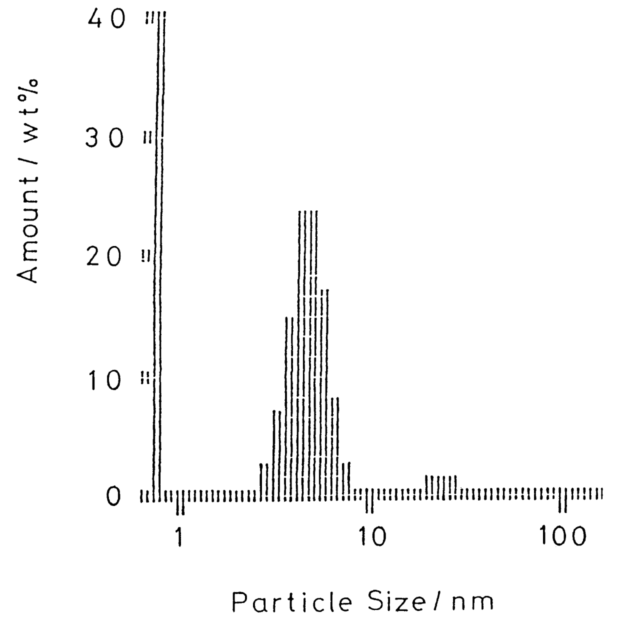

Fig. 2. Relative distribution of the particle size of D-5.

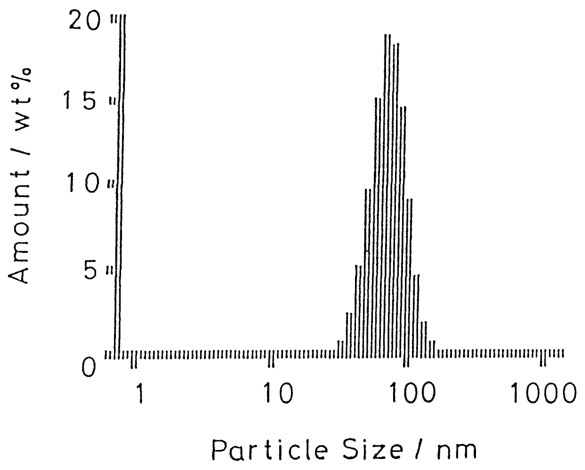

Fig. 3. Relative distribution of the particle size of D-11.

(E-1, E-2, and E-3) were subjected to solubilization in water with the use of various cosolvents; the results are shown in Table 4. E-1 showed no solubilized effect in water, even upon the addition of **BEA**. E-2, however, gave a homogeneous dispersion (D-11) with fine particle size. This shows that the presence of **IS** in the polymer skeleton is very important, even in small amount, to produce dispersion. The dispersion, thus obtained (D-11), was opaque and milk-white, and its mean particle size was larger than that of D-5. The distribution of the particle sizes is shown in Figs. 2 and 3. Although both D-5 and D-11 gave a small distribution range, D-5 was smaller in size and more clear in transparency. It also behaved as a homogeneous solution. This is considered to be caused by a slightly different hydrophilic property between polyesters which have different contents of the SO_3Na

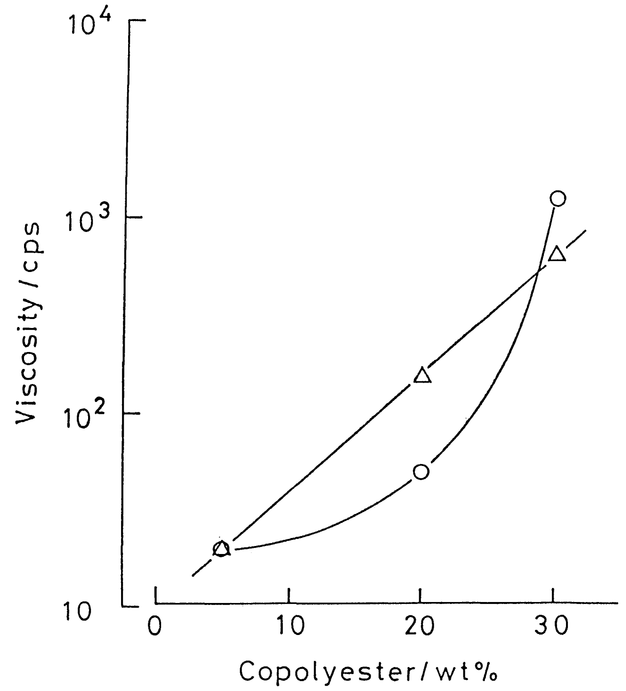

Fig. 4. Viscosity of the copolyesters, E-2 (O) and E-3 (Δ), dispersed in water against to the amount of E-2 and E-3 with BEA (15 wt%).

group.

Next, as shown in Fig. 4, a dispersion made of E-2 rapidly increased its viscosity with an increase in its copolyester concentration. That made of E-3, however, gradually increased its viscosity. The former behavior is a typical of that observed for the dispersion system.[5] The latter one, however, is similar to that observed for aqueous solutions.

The structures and formation mechanisms of these dispersions are quite interesting. As shown in Table 1, E-2 and E-3 have a hydrophobic polymer skeleton. Further, the content of the SO_3Na group is extremely low. Such hydrophobic polymer skeletons can thus associate with each other. On the other hand, hydrophilic groups like SO_3Na can be oriented so as to come into contact with aqueous solutions which comprise a mixture of water and organic cosolvents. The whole polymer chain can then make a particle. Thus, E-3 has a greater affinity with aqueous solutions than E-2 with increased contents of the SO_3Na group; it also shows lower association among polymer chains. This is a cause further of the smaller mean particle size and higher transparency in D-5 than in D-11.

References

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