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IV. Characteristics of water-dispersed polyesters containing polar groups

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Summary

Polyesters were modified by introducing small amounts of sodium sulfonate groups as hydrophilic groups in their backbones. Stable aqueous dispersions of the polyesters could be obtained by using 2-butoxyethanol (BEA) as a cosolvent. To clarify the role of the cosolvent, they were separated into two layers, polymer and supernatant layers, by ultracentrifugation. Cosolvent contents were found to be different in the former and latter layers; i.e., the contents of BEA in the former layer are low in the case of crystalline polyesters and high in the case of noncrystalline ones. Characteristics of the dispersions such as viscosity are strongly affected by the content of the cosolvent.

Introduction

At the present time polyesters are widely used as fibres, films, adhesives, painting binders, and the likes. Moreover, such polyesters are of interest in the utilization as water-resistant films. Usually, in the case of crystalline polyesters, the films are formed by melting. On the other hand, in the case of noncrystalline polyesters the films are formed by dissolving in organic solvents followed by evaporation. Recently, however, in view of saving natural resources and preventing environmental pollution, organic solvents are recommended to be converted into inorganic solvents. So far, authors have studied how crystalline or noncrystalline hydrophobic polyesters could be dispersed into water as colloidal particles. As previously described (1), hydrophobic polyesters which contain a small amount of sodium sulfonate groups could be solubilized in water in the presence of cosolvent and form a stable water-borne dispersion. They can be used to make water-resistant films by evaporation. Such water-borne dispersions, which contained water-soluble cosolvents, have so far been known. For example, for a water-borne acrylic resin a colloidal dispersion under 0.1 μm was obtained in the presence of some cosolvents by neutralizing a carboxylic substituent with a base (2). Also, hydrophilic polyesters can be dispersed into aqueous 1-propanol. The physical properties of the dispersions are dependent upon the amount of hydrophilic components but not upon the amount of hydrophobic components (3,4). However, the behavior of aqueous cosolvents has not yet been clarified in colloidal dispersions. In this study, dispersions of hydrophobic polyester, water, and 2-butoxy-ethanol (BEA) cosolvent were examined. To clarify the role of the cosolvent, the dispersions were separated into a polymer layer and a supernatant layer by an ultracentrifugal separator. Then the amount of the cosolvent in each layer was determined. This is the first time. The distribution of the cosolvent contained in such dispersions has been quantitatively determined. From the results obtained several models are presented for oil-in-water dispersions. Characteristics of the dispersions are discussed in terms of crystallinity of the polyesters, temperature, viscosity, and amount of the cosolvent.

Experimental

Preparation of Polyesters

Polyesters were prepared by a method similar to that described in our earlier paper (1). As an example of preparation, definite amounts of terephthalic acid (TP), isophthalic acid (IP), sodium 5-sulfonatoisophthalic acid (IS), adipic acid (AA), 1,2-ethanediol (ED), 2,2-dimethyl-1,3-propanediol (DPD), 1,4-butanediol (BD), and catalysts such as potassium titanium (IV) oxalate were charged into a reactor and subjected to esterification at 140 to 240 °C for three hours. The charge was then subjected to polycondensation under reduced pressure (0.1 mmHg, 1 mmHg= 133.322 Pa) at 240 to 270 °C for two hours. Examples of the compositions and properties of the polyesters thus obtained are given in Table 1. The number-average molecular weights (M_n) were obtained by GPC with polystyrene standards. The number of the carboxyl groups (N_C) was determined by titrating a polymer solution in chloroform with 0.1 equiv. potassium ethoxide. Melting points (T_m) were measured with a DSC7 differential scanning calorimeter (Perkin-Elmer Co. Ltd.) with 20 °C per minute temperature rise. Softening points (T_s) were obtained by the ring and ball method. Elem. anal. Calcd for A-1 from the components in Table 1: C, 64.46; H, 5.13; O, 29.90; S, 0.30; Na 0.21. Found: C, 63.68; H, 5.23; S, 0.29; Na, 0.21. Calcd for C-1 from the components in Table 1: C, 61.86; H, 6.02; O, 31.59; S, 0.31; Na, 0.22. Found: C, 60.18; H, 6.10; S, 0.28; Na, 0.24.

Solubilization of Polyesters in Water

The polymer (300 g) given in Table 1 was dissolved in 150 or 100 g of BEA at 135 °C for 2 h. To this solution 550 or 600 g of water was gradually added and it was stirred for 2 h at 70 °C. The mixture was then cooled to room temperature. The dispersions thus obtained are shown in Table 2. BEA was commercially available from Nacalai Tesque, Inc. Deionized water was used throughout this study. The dispersed particle size was measured with a COULTER (model N4) at 25 °C and solid concentration of the sample dispersion was 0.1% in water.

Determination of Content of BEA in Dispersion

A dispersion was separated into two layers by ultracentrifugation (preparative ultracentrifuge, Hitachi Koki Co., Ltd, 4.5 x 10^4 rpm at 25 or 40 °C for 3 h). The supernatant solution was subjected to high-speed liquid chromatography

(LC-6A, Shimadzu Seisakusho, Co.) equipped with a Shim-pack CLC-ODS column (Showa Denko Co.) and then the amount of BEA was determined by using a predetermined calibration curve. Further, BEA in the polymer layer was calculated from the difference between the amount of BEA charged and that in the supernatant layer. High-speed liquid chromatography was carried out with THF as the eluent at a flow rate of 0.5 ml/min by using an RI detector. The viscosities of sample dispersions were measured with a rotation-viscometer (Tokyo Keiki Co. Ltd., Model EM) at 25 or 40 °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 dried for 4 h at 100 °C and 4 h at 150 °C under 0.1 mmHg vacuum.

Results and discussion

Properties of Polyesters

The compositions and properties of the polyesters prepared are shown in Table 1. The two typical polyesters, C-1 and A-1, have almost the same properties, such as M_n and N_C. They are, however, different in crystallinity. A-1 is noncrystalline and has a softening point of 125 °C, while C-1 is crystalline and has a melting point of 105 °C. Multiple use of the acids and glycols is closely related to the crystallinity of the polyesters.

Solubilization of Polyesters in Water

The polyesters, C-1 and A-1, were solubilized in water by the method described in the experimental part. The dispersions thus obtained are given in Table 2. As reported before, the presence of IS in the polymer skeleton is very important, even in a small amount, to produce dispersion (1). C-1 (300 g) could be dissolved well in 150 g of BEA above 135 °C. The addition of 550 g of water to the BEA solution provided an opaque dispersion, D-1, which had a mean particle size of 110 nm. On the other hand, A-1 was dissolved in 150 g of BEA more easily than C-1, and it could be dissolved well even in less BEA at 135 °C. The translucent dispersions, D-2 and D-3, were obtained by adding water to the polyester solutions in BEA, which had mean particle sizes of 75 and 90 nm,

Table 1. Characteristics of Copolyesters

Component[a]	C-1	A-1
TP	50	50
IP	8	48
IS	2	2
AA	40	0
ED	30	50
DPD	0	50
BD	70	0
Properties		
M_n (x10^{-4})	1.8	1.2
N_C (equiv/10^6g)	13	13
T_m (°C)	105	—
T_s (°C)	—	125

[a] Abbreviations are given in the text.

respectively. D-2 and D-3 are more transparent and viscous than D-1. Also, D-2 was smaller in the particle size and more viscous than D-3. As can be seen in Table 2, the amount of BEA affects strongly the nature of the dispersions, which is especially apparent in their viscosities. Further, the crystallinity of polyesters is related to the properties of the dispersions.

Stability of Dispersions

The basic properties of the dispersions, such as particle size and viscosity, were discussed previously in terms of the amount of IS (1). In this article, attention was especially drawn to their viscosities and the amount of cosolvent. The storage stabilities are shown in Table 3, which were examined after keeping the dispersions for 240 h at 40 °C. D-1 and D-2 were very stable in appearance and viscosity. While D-3 did not change its appearance, a big rise in its viscosity was observed with increasing temperature. The difference between D-2 and D-3 may be only in the amount of the cosolvent charged. Accordingly, the distribution of the cosolvent in the dispersion has to be known. In this regard, each dispersion was separated into two layers, i.e., supernatant and polymer layers, by ultracentrifugation.

Table 2. Characteristics of Water-Dispersed Coplyesters

Water-dispersed copolyester	D-1	D-2	D-3
Copolyester[a]	30(C-1)	30(A-1)	30(A-1)
BEA[a]	15	15	10
Water[a]	55	55	60
Characteristics			
Undispersed copolyester[a]	0	0	0
Appearance	opaque	translucent	translucent
Mean particle size (nm)	110	75	90
Viscosity[b] (cps)	100	1400	1100

[a] By weight. [b] Measured at 25 °C.

Table 3. Storage Stability of Water-Dispersed Copolyestersters

Water-dispersed copolyesters	D-1	D-2	D-3
Appearance[a]	no change	no change	no change
Viscosity[b]	60	200	16000

[a] After being kept at 40°C for 240 hrs. [b] Measured at 40 °C in cps.

Distributions of BEA in Dispersions

Table 4 shows the contents of BEA in the two layers obtained by ultracentrifugation. D-1 contained a high amount of BEA in the supernatant but a very low amount in the polymer layer at both 25 and 40 °C. However, D-2 had a different amount of BEA from those of D-1 particularly in the latter layer. One third of the total amount of BEA charged was found in the polymer layer for D-2. What controls the distribution of BEA? The ratios of the components initially charged in D-1 and D-2 were the same. Therefore, the difference in the BEA distribution is due to the nature of the copolyesters used. Copolyester in D-1 is crystalline while that in D-2 is noncrystalline. Thus, the aggregates between the polymer chains in D-1 seem to be dense and to be hardly invaded by other molecules such as the cosolvent. The interaction between the polymer molecules in D-2, however, is weaker than in D-1, as expected from their crystallinity. Consequently, the cosolvent can enter into the aggregates of the polymer chains in D-2. In the case of D-3, the lower amount of BEA charged affected significantly to the amount in the polymer layer at lower temperature, but it reached that of D-2 at higher temperature. Such temperature effect was not found for D-2. Also, it was found that BEA could move slowly from one layer to the other to satisfy an equilibrium depending on the temperature and the amount of the cosolvent charged. Therefore, the amount of BEA is particularly important in the nature of these dispersions. It must be noted that the viscosity of D-3 reversibly changes with temperature. This reversible effect by temperature is also found in the amount of BEA in D-3, as given in Table 4. From these results, it is concluded that the cause of the temperature effect of the viscosities is due to the amount of BEA in the dispersion.

Table 4. Distributions of BEA in the Dispersions

Dispersion	Temp. (°C)	Amount of BEA[a] (g)		
		charged	supernatant layer	polymer layer
D-1	25	15.0	14.1	0.9
D-1	40	15.0	12.9	2.1
D-2	25	15.0	10.4	4.6
D-2	40	15.0	10.5	4.5
D-3	25	10.0	7.6	2.4
D-3	40	10.0	5.5	4.5

[a] Amount of BEA per 100 g of the dispersion.

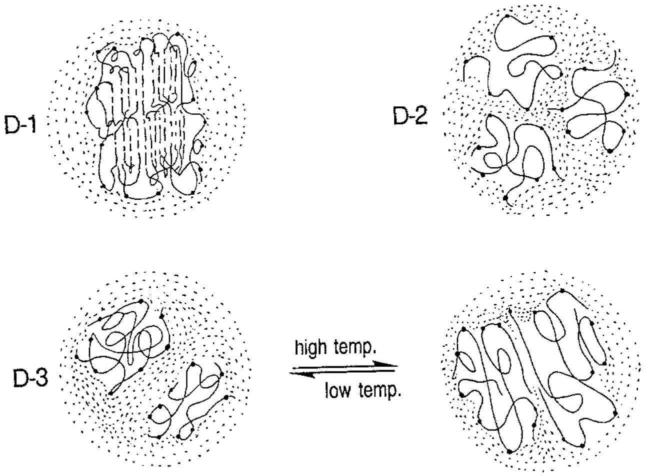

Figure 1. Schematic models for D-1, D-2, and D-3. Black large and small points denote polar groups in the copolyester and water or BEA molecules, respectively. See the text.

To understand the curious behavior of these oil-in-water dispersions, a possible structural model of the colloidal particle in the dispersions is considered as follows. Each polymer particle is surrounded by medium A, which consists of water and a little cosolvent. The interior of the particle can also contain medium B, which consists of little water and much cosolvent, so that the polar pendant groups in the polymer chain would be arranged at the exterior of the particle. Therefore, the interior of the particle will be relatively hydrophobic. Thus, water molecules cannot enter easily into the particles. Four possible models of the colloidal particles for three dispersions can be visualized as shown in Fig. 1. Temperature effects that appeared in D-3 are shown by moving from the left to the right. BEA molecules can move slowly into the polymer particle from the surrounding medium A with increasing temperature. Then they cause a swelling of the particle. The content of BEA in the polymer particles of D-3 approaches to that of D-2 but that at the outside of the polymer particles is much lower than D-2. In this circumstance, the polymer particle in D-3 becomes larger than in D-2. Thus a reasonable size of D-2 or D-3 will be dependent upon the distribution of BEA in media A and B. The mutual interaction between the particles in D-3 will become stronger with increasing temperature. This is consistent with the viscosity change observed. The most curious fact is that the viscosity of D-3 strongly increases with increasing temperature. As far as we know, this strange viscosity behavior has not been reported so far. This phenomenon is related to the distribution of BEA in media A and B, which drastically affects the viscosity of the dispersion and is dependent upon the temperature.

Conclusions

First, cosolvent molecules in the dispersions are found in both the supernatant and polymer layers. Second, as shown in the case of D-3, which is a dispersion with less BEA, cosolvent molecules move slowly from the supernatant layer to the polymer layer with increasing temperature. This is accompanied by a big rise of dispersion viscosity, which is evidence for strong mutual interaction between the polymer particles. Therefore, the nature of the dispersion is strongly dependent upon the amount of cosolvent. Finally, in the case of D-1, little cosolvent exists in the polymer layer, as expected from its crystallinity.

References

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