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FLOW-INDUCED CRYSTALLIZATION OF POLY(VINYL ALCOHOL) FROM THE ETHYLENE GLYCOL-WATER SOLUTION*

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The crystallization of poly(vinyl alcohol) (PVA) from the aqueous solution containing ethylene glycol (EG) was carried out under a steady-state flow. The extent of crystallization was maximum at EG content, ca. 10 vol. % and was zero at 30 vol. % at 30°C. Moreover, the effects on the yield of the precipitate of the adsorption of PVA molecules to the solution surface and the dissolved state of PVA molecule in the solvent mixture were described.

1. INTRODUCTION

In the preceding papers^{1,2)}, the authors have reported on the flow-induced crystallization of syndiotacticity-rich and atactic PVA's from the aqueous solution. Naito³⁾ has recognized that PVA dissolved in water-ethylene glycol (EG) mixtures up to the EG content, ca. 70 vol. %, shows a characteristic variation in the intrinsic viscosity, giving a maximum at the EG content, ca. 10 vol. %. Here, the flow-induced crystallization of PVA (PVA_{VTFA}), derived from vinyl trifluoroacetate, from the aqueous EG solutions was studied from the viewpoint that the dissolved state of PVA molecules in water-EG mixture be correlated to the flow-induced crystallization.

It is generally known that the addition of alcohols of low molecular weight lower the surface tension of aqueous PVA solution. The authors⁴⁾ have recognized that octyl alcohol (OA), which was considered to interfere with the adsorption of PVA molecules to the solution surface, lowers the flow-induced crystallization of PVA_{VTFA} molecules from the aqueous solution. Therefore, the relationship between the surface tension and the flow-induced crystallization for the PVA_{VTFA} solution in aqueous EG was investigated.

2. EXPERIMENTAL

2.1 Samples

Vinyl trifluoroacetate (VTFA) was polymerized in bulk at 60°C employing benzoyl peroxide as an initiator. Poly(vinyl trifluoroacetate) was converted to PVA (PVA_{VTFA}), by dissolving it in 2,2'-diaminodiethylamine. The degree of polymerization, *DP*, and the contents of syndiotactic diad in %, were 2610 and 54.5, respectively. EG was a commercial product of the highest quality available.

2.2 Flow-Induced Crystallization

PVA was crystallized under a steady-state flow as follows: The sample was dissolved in pure water or in an aqueous solution containing a given amount of EG. The dissolution was carried out at ca. 130°C in a sealed tube. After filtration through a glass filter while the solution was hot (ca. 90–95°C), the solutions except that in pure EG were agitated with a stainless steel, rod-like stirrer (diameter: 10 mm) at 30°C with a rate of 2070 rotations per minute in a test tube (inner diameter: 15.6 mm).

2.3 Surface Tension of Solution

The surface tension of solution was measured by the Wilhelmy method at 30°C. The hot, filtered solution was allowed to stand for 5 minutes at 30°C in Erlenmeyer's flask with a stopper and then the surface tension was measured immediately after the solution was transferred into a cell. The tension was measured when a glass-plate came in contact with the solution by using the torsion

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balance for 500 mg.

2.4 Viscosity and Aging of Solution

The viscosity of the solutions was measured by use of a B-Type Viscometer of Tokyo Keiki Co., Ltd. at 30°C. The change of the solution viscosity with time of standing was measured.

2.5 Electron Microscopy

The observation by means of a scanning electron microscopy (Mini SEM of Akashi-Seisakusho) was carried out by shadowing under vacuum with Au-C vapour. Samples obtained by stirring were immersed in water in order to remove EG for 24 hours and then were freeze-dried.

3. RESULTS

3.1 Process of Crystallization

In the case of crystallization of PVA from the aqueous solution in contact with air and under steady-state flow, we^{5,6)} have reported that a fine fibrillar crystal was formed under the surface of the solution in the initial stage of stirring under various conditions such as different initial polymer concentrations, various molecular weight of polymer, temperatures, rate of stirring and annular gap between the inner and outer cylinders. This phenomenon was also observed for the solutions in aqueous EG, when they were stirred keeping in contact with air. However, in the case of the PVA_{VTF}A solutions in 30 vol.% aqueous EG (height of solution: 5 cm) and 25 vol.% EG (height of solution: 10 cm), fibrillar crystal did not appear even after stirring for 60 minutes.

The process of crystallization was observed as follows: Fibrillar crystals were produced just under the surface of the solution after a few seconds of stirring, then air bubbles appeared on the fibrillar crystal surface and finally a film-like precipitate wound around the stirrer.

For the solutions containing EG over 20 vol. %, the growth of fibrillar crystals without buildup of foam was followed by the sedimentation from the solution surface in an irregular manner.

3.2 Yield of Precipitate

Fig. 1 shows the relations between the yield of the precipitate and EG content at the heights of the solution of 10 cm and 5 cm. The remarkable effect of the addition of EG to the solution was recognized and the maximum yield appeared at about 10 vol. % of EG. Moreover, the yield for the

Fig. 1. Effect of EG content on the yield of the precipitate of PVA ($DP = 2610$, 10 g/dm^3 , 30°C , 2070 rpm , stirring time; 60 min. , height of solution; $\circ$: 5 cm , $\bullet$: 10 cm).

solution height of 5 cm was higher than that for solution of 10 cm .

3.3 The Surface Tension of Solution

Fig. 2 shows the surface tension at zero standing time, σ_i and the surface tension at equilibrium, σ_e , for the solution of PVA_{VTF}A, and the surface tension σ_s of the solvent against EG content. With increasing EG content from 0 to 20 vol. %, the

Fig. 2. Effect of the addition of EG to the aqueous solution on the surface tension for the solution of PVA_{VTF}A ($DP = 2610$, 30°C , 7.9 g/dm^3 , σ_s : surface tension of solvent, σ_i and σ_e : surface tensions of solution at zero-standing time and at equilibrium).

lowering of σ_i and σ_e from σ_s in the aqueous solution disappears. When the EG content is increased over 20 vol. %, σ_e approaches σ_s sufficiently.

3.4 The Viscosity of Solution

Fig. 3 shows the relations between the zero-shear viscosity of solution at zero-standing time and the EG content at a polymer concentration of 10 g/dm³. The zero-shear viscosity at the zero-standing time increases with increasing EG content, namely, $3.1 \times 10^{-3} \text{ N}\cdot\text{s}\cdot\text{m}^{-2}$ to $6.9 \times 10^{-3} \text{ N}\cdot\text{s}\cdot\text{m}^{-2}$ for the EG content, 0 vol. % to 30 vol. %. The solution containing EG over 80 vol. % gels immediately after standing at 30°C.

Fig. 3. Relationships between the zero-shear viscosity at zero-standing time and the EG content for the water-EG mixed solvents (●, 30°C) and the solutions of PVA_{VTFA} (○, $DP=2610$, 10 g/dm³, 30°C).

3.5 Morphology

Fig. 4 and Fig. 5 show the scanning electron micrographs of replicas of the crystals obtained by stirring solutions containing EG in 15 and 20 vol. %, respectively. The fibrillar crystals are aligned in the direction of the shearing force and have smooth surfaces.

4. DISCUSSION

As shown in Fig. 1, the yield of precipitate was maximum at ca. 10 vol. % EG content and was zero at 30 vol. %. The viscosity of the solution

Fig. 4. Scanning electron micrograph of crystals obtained by stirring of a PVA_{VTFA} solution of EG content of 15 vol. % ($DP=2610$, 10 g/dm³, 30°C, 2070 rpm, 60 min.).

Fig. 5. Scanning electron micrograph of crystals obtained by stirring of a PVA_{VTFA} solution of EG content of 20 vol. % ($DP=2610$, 10 g/dm³, 30°C, 2070 rpm, 60 min.).

which contained EG from 0 to 30 vol. % increased from 3.1×10^{-3} to $6.9 \times 10^{-3} \text{ N}\cdot\text{s}\cdot\text{m}^{-2}$ with the increase in EG content as shown in Fig. 3. These values of viscosity are lower than the one, $13.8 \times 10^{-3} \text{ N}\cdot\text{s}\cdot\text{m}^{-2}$, at which the solution turns from laminar to turbulent flow¹⁾; the solution containing EG are considered to give turbulent flow under the present experimental conditions. These results imply that in order to explain the growth of fibrillar crystals one must take into account suitable factors other than the flow pattern.

As shown in Fig. 2, the difference between σ_s and σ_e decreased with the increase in EG content.

This fact is considered to mean that the adsorption of PVA molecules to the surface of the solution is prevented by the addition of EG. However, the yield of precipitate does not increase monotonously with the decrease of the content of EG.

According to Naito, the intrinsic viscosity has a peak at a certain content of EG for aqueous PVA solution containing EG³⁾. The initial increase in the intrinsic viscosity, $[\eta]$, with the addition of EG is considered to be attributable to the prevention of water association by EG and hence the increased interaction between PVA and H₂O molecules. The coil-like molecules of PVA expand in the solution with the addition of EG. However, when the content of EG goes beyond the one giving the maximum of $[\eta]$, the interaction between PVA and H₂O molecules becomes weak because of the presence of excess EG in solution and so the expansion of PVA molecules becomes gradually smaller again. This is considered to be coincident with the existence of a maximum yield of precipitate at EG content ca. 10 vol. %, the expansion of

PVA molecule is considered to accelerate the growth of fibrillar crystals.

In the case of the flow-induced crystallization for PVA from the water-EG solution in contact with air, however, a fibrillar crystal is always produced just under the surface of the solution after a few seconds of stirring. Therefore, it is considered that the adsorption of PVA molecules to the surface of the solution plays an important role for the nucleation of the fibrillar crystal¹⁾.

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