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FLOW-INDUCED CRYSTALLIZATION OF SYNDIOTACTICITY-RICH POLY(VINYL ALCOHOL) FROM DIMETHYL SULFOXIDE-WATER SOLUTION*

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The flow-induced crystallization of syndiotacticity-rich poly(vinyl alcohol) from the dimethyl sulfoxide (DMSO)/water solutions was studied. With the DMSO content of ca. 5 vol%, the rate of crystallization was highest and fibrillar crystals formed near the surface of the solution at the initial stage of stirring. An expansion of polymer coil due to an increased solvation is considered to enhance the rate of crystallization. A stretching of the polymeric chains at the surface due to adsorption is also considered to accelerate the formation of nucleus.

1. INTRODUCTION

In the preceding paper¹⁾, we reported on the flow-induced crystallization of syndiotacticity-rich poly(vinyl alcohol) (PVA) from ethylene glycol (EG)-water solution. The rate of crystallization was maximum at the EG content of ca. 10 vol% and was zero at 30 vol% and more at 30°C. A maximum intrinsic viscosity of PVA (PVA_{VAc}), prepared from vinyl acetate, was observed at the EG content of ca. 10 vol%²⁾. An expansion of PVA molecular coils was considered to accelerate the growth of fibrillar crystals from the stirred solution. Naito²⁾ found that a PVA_{VAc} solution in dimethyl sulfoxide (DMSO)-water mixtures showed a maximum intrinsic viscosity at the DMSO content of ca. 30 vol%. We also obtained a similar result for PVA (PVA_{VTFA}), prepared from vinyl trifluoroacetate, in DMSO-water mixture³⁾. The degree of expansion of the PVA_{VTFA} coil in the solution was also correlated to the rate of flow-induced crystallization.

In this paper, we will report on a flow-induced crystallization of PVA_{VTFA} from the aqueous DMSO solutions in relation to the surface tension and viscosity of the solution.

2. EXPERIMENTAL

2.1 Samples and solvent

The bulk polymerization of vinyl trifluoroacetate (VTFA) was carried out at 60°C by use of benzoyl peroxide as an initiator. Poly(vinyl trifluoroacetate) was converted to PVA_{VTFA} by dissolving in 2,2'-diaminodiethylamine. Three samples were prepared. The degrees of polymerization (DP) were 3400, 1850 and 990, respectively and the contents of syndiotactic diad were 52.0, 56.2 and 53.9%, respectively. Since the PVA_{VTFA} with the higher molecular weight crystallized easily from the aqueous solution under the flow, the PVA_{VTFA} of $DP=3400$ was chosen for the flow-induced crystallization. On the other hand, the high molecular weight PVA_{VTFA} gives a film on the surface of the aqueous solution at an extremely short standing time, making the measurement of the surface tension difficult. The PVA_{VTFA} of DP around 1600 was more suitable for the measurement of the surface tension of the solution⁴⁾. Before the measurement of the solution viscosity by Ostwald viscometer, the solution is consciously pressed up through a fine capillary, so the PVA_{VTFA} with higher molecular weights crystallized easily in the capillary under the flow of solution. Therefore, the PVA_{VTFA} of $DP=990$ was chosen for the measurement. The DMSO was the spectroscopy grade of MERCK Co. Ltd..

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2.2 Flow-induced crystallization

The sample was dissolved in distilled water or in mixed solvents of water and DMSO at 120–140°C in a sealed tube. The polymer solution was filtered through a glass filter, keeping the solution hot (90–95°C). The initial polymer concentration of 1.0g/dl was chosen. Table 1 shows the stability of the 1g/dl PVA_{VTFA} solutions in test tubes for standing under a quiescent state. In the range of DMSO content of 45 vol%~60 vol%, the solutions gelled in a very short standing time. Therefore, the following experiments were done for the solution with the DMSO content below 40 vol%.

The flow-induced crystallization was carried out by rotating with a stainless steel rod (diameter: 10 mm) at 2070 revolutions per minute in a test tube (inner diameter: 15.4mm) at 30°C. The precipitates thus formed from the solution were picked up with a pair of tweezers and dried under a reduced pressure at 50°C for 24 hrs. The amount of the polymer in the residual solution was estimated by evaporating water at 80°C and dried under a reduced pressure at 50°C for 24 hrs. The yield of the precipitate was evaluated by the following equation:

$$\text{Yield of precipitate (\%)} = \frac{100W_1}{W_1 + W_2}$$

where W_1 is the weight of the precipitate and W_2 is that of the polymer in the residual solution.

2.3 Surface tension of solution

The filtered solution was allowed to stand for

5 minutes at 30°C in an Erlenmeyer flask with a stopper. Immediately after the solution was transferred into a cell (about one minute after pouring the solution in a cell), the surface tension was measured by the Wilhelmy method at 30°C, i.e., by contacting a glass-plate with the solution using a torsion balance for 500mg. This surface tension is represented by σ_i . Then it was measured at regular time intervals. The surface tension lowered with the standing time and reached to an equilibrium value after 10~15 minutes. The equilibrium surface tension is represented by σ_e .

2.4 Intrinsic viscosity of solution

The intrinsic viscosity $[\eta]$ of the polymer solution in water-DMSO mixtures was determined by using an Ostwald viscometer at 30°C. The range of polymer concentration was 0.05~0.50 g/dl.

3. RESULTS

3.1 Process of crystallization

A fine fibrillar crystal formed near the surface of the solution after a few seconds of stirring for the solutions containing DMSO less than 30 vol% just as in the cases of aqueous and EG-water solutions^{1,5,6}). In the case of the solutions containing 35 vol% and 40 vol% DMSO, crystals did not form even after stirring for 3 hrs, but a large number of fine gel particles were produced. The gel particles associated with each other to form the large aggregates gradually further stirring.

From the solutions containing DMSO less than

Table 1. Standing stability of the syndiotacticity-rich PVA solutions in DMSO/water mixture under a quiescent state. ($DP=3400$, polymer concentration=1g/dl, 30°C)

DMSO (Vol%)	Standing time (min)					
	10	20	30	60	120	240
0	T	T	T	T	T	T
10	T	T	T	T	T	T
20	T	T	T	T	T	Cs
40	T	T	Cs	Cs	C	C
50	Cs	C	C	G.Sn	G.Sn	G.Sn
60	T	Cs	Cs	C.G	C.G.Sn	C.G.Sn
80	T	T	T	T	T	T
100	T	T	T	T	T	T

T: Transparent (Stable), Cs: Slightly cloudy, C: Cloudy,
G: Gelation, Sn: Syneresis

15 vol%, fibrillar crystals formed just under the surface of the solution in the initial stages of stirring, then bubbles appeared and finally the stirrer was covered with a filmy precipitate comprising fibrillar crystals. The bubbles decreased in amount with increasing DMSO content and did not form in the solutions containing DMSO over 20 vol%.

3.2 Yield of the precipitate

Fig. 1 shows the relations between the yield of the precipitate and the time of stirring. The yield of the precipitate increased slowly up to about 10%, then increased rapidly and finally leveled off, depending upon the DMSO content.

Fig. 2 shows the relations between the yield of

Fig. 1 Yield of precipitate against stirring time. DMSO content (vol%); $\circ$: 0, $\bullet$: 15, $\triangle$: 30, $DP = 3400$

Fig. 2 Yield of precipitate against DMSO content. Stirring time (hr); $\circ$: 1, $\bullet$: 3, $\triangle$: 6, $DP = 3400$

the precipitate and the DMSO content in the mixed solvent. The yield of the precipitate increased with increasing DMSO content up to about 5 vol% and decreased thereafter. In case of the DMSO content over 35 vol%, a filmy precipitate did not form, but the aggregates of gel particles formed by stirring over 4 hrs. The high yields of the precipitate for 6 hrs that deviate from the curve of Fig. 2 are not due to the fibrillar or filmy precipitates but due to the aggregation of gel particles.

3.3 Surface tension of the solution

Fig. 3 shows the plots of the surface tensions against the DMSO content, where σ_i and σ_e are the initial and equilibrium surface tensions of the PVA_{VTFA} solution, respectively, and σ_s is the surface tension of the mixed solvent itself. The σ_e and σ_i are lower than σ_s at any solvent compositions in contrast to those for the solution in EG-water mixture where σ_e and σ_i approached σ_s closely as the EG content increased over 20 vol%¹⁾.

3.4 Viscosity of the solution

Fig. 4 shows the relation between the intrinsic viscosity and the DMSO content. A peak at the DMSO content of about 10 vol% is observed.

4. DISCUSSION

The maximum yield of the precipitate was obtained at the DMSO content 5~10 vol%, as is shown in Fig. 2, where the surface tension (Fig.

Fig. 3 Surface tensions of solution and solvent against DMSO content (30°C, PVA: $DP = 1850$, polymer concentration = 0.15g/dl). $\bullet$: solution (σ_i), $\triangle$: solution (σ_e), $\circ$: solvent (σ_s)

Fig. 4 Intrinsic viscosity against DMSO content (30°C, PVA: $DP = 990$).

3) and the intrinsic viscosity (Fig. 4) also drastically changed.

A linear flexible polymer chain adsorbed on the surface of solution have been considered to be arranged in a conformation with loops of segments in solution and trains of the other segments on the surface^{7,8}). Recently the conformation of a polymer chain at the surface has been studied from the time dependence of the surface tension of a polymer solution^{9~11}). The buildup of the polymer solution surface with time is considered as a kind of crystallization phenomenon^{9~11}). Denoting the surface tension at time t by σ_t , a quantity corresponding to the degree of crystallization is given by $(\sigma_t - \sigma_e)/(\sigma_i - \sigma_e)$ and Avrami equation is written by

$$\ln[(\sigma_i - \sigma_e)/(\sigma_t - \sigma_e)] = kt^n$$

where k and n are constants. n refers to the form of nucleus. The value n is nearly equal to unity for the solutions of polystyrene in benzene⁹), syndiotacticity-rich PVA in water¹⁰) and syndiotacticity-rich PVA in water (95 vol%)-DMSO (5 vol%)¹¹). In this study, $n \approx 1$ was also obtained (see Fig. 5), indicating that polymer chains are aligned parallel to the surface. The polymer molecules adsorbed on the surface are considered to form nuclei for the flow-induced crystallization.

Fig. 5 Plots of $\log[2.303 \log \frac{\sigma_i - \sigma_e}{\sigma_t - \sigma_e}]$ versus $\log t$ according to Avrami equation ($DP=1850$, DMSO content 10 vol%, 0.075g/dl, 30°C).

However, at the present time, we can not confirm the nuclei formed by adsorbing the polymer molecules on the solution surface, so the confirmation is considered to be also a subject of a future study.

On the other hand, the intrinsic viscosity has a peak at the DMSO content of about 10 vol%, suggesting that the polymer coil is largely expanded. Therefore, the expanded polymer coils turn to be easily uncoiled, i.e., stretched and consequently crystallize easily under the flow.

With increasing DMSO content above 5~10 vol%, the interaction of PVA with water seems to decrease due to the excess DMSO to give a decrease in the intrinsic viscosity. Namely, the contraction of polymer coils might prevent the intermolecular crystallization by the flow, even if the polymers are adsorbed to the surface of solution. The gel formation in the solution with the DMSO content of 40 vol% suggests a very weak intra- and intermolecular hydrogen bondings of the polymer. Less or no intra- and intermolecular hydrogen bondings seem to take place at such high DMSO contents as 80 and 100 vol%, giving a transparent solution although the intrinsic viscosities are high. Therefore, nuclei for the flow-induced crystallization decrease in amount and the yield of the precipitate decreases with increasing DMSO content.

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ジメチルスルホキシド-水系溶液からのシンジオタク
チシティに富んだポリビニルアルコールの流動結晶化

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シンジオタクチシティに富むポリビニルアルコールのジメチルスルホキシド(DMSO)-水系溶液からの流動結晶化をDMSO含量0~40%の範囲で研究した。DMSO含量5 vol%の混合液の溶液からの結晶化速度は最大で

あった。また、繊維状結晶化物が攪拌初期に溶液表面の下に生じた。溶媒和の増加に伴う溶液中の分子コイルの膨張が結晶化速度を増加させ、吸着にもとづく表面での分子コイルの伸長が核形成を促進すると考えた。