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Adsorption of stereoregular poly(vinyl alcohols) at air-water interface

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With 6 figures and 5 tables

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Introduction

Frisch et al. (1) and Fukawa et al. (2) have found that the surface tension of the aqueous solution of commercial (atactic) poly(vinyl alcohol) (PVA) decreased with time after preparing a fresh surface to reach an equilibrium value which was smaller than that of pure water and they attributed this to the decrease in the diffusion rate of PVA molecules to the surface in comparison with that in the interior of water. Uberreiter et al. (3) have found that the time dependency of the surface tension for the water-dimethyl sulfoxide solution of PVA of 5 g/dm³ depends on the stereoregularity of PVA. The rate of the decrease in the surface tension is in order of syndiotactic PVA > isotactic PVA > atactic PVA. They attributed this to the extent of the arrangement of segments at the surface. This article shows the detailed investigation of the time dependency of the surface tension of the aqueous solutions of syndiotactic, isotactic and atactic PVAs, and the spinnability of the surface film prepared from the aqueous solution of syndiotactic PVA.

Experimental

Samples

A commercial PVA of the degree of polymerization (DP) of 1700 and the syndiotactic diad percent (s-(diad) %) of 45 was used as an atactic PVA. Isotactic PVA was prepared by the debenzylolation by dry hydrogen bromide of poly(vinyl benzyl ether) obtained through the cationic polymerization at -78 °C (4). The DP and s-(diad) % were 785 and 16 (isotactic diad percent=84). The syndiotactic PVA used for the measurement of surface tension was prepared by the ammonolysis of poly(vinyl trifluoroacetate) obtained through the radical polymerization at 60 °C (5). The DP and s-(diad) % were 2610 and 55. The syndiotactic PVAs used for the study of the spinnability were prepared by the ammonolysis of poly(vinyl trifluoroacetates) obtained through the radical polymerization at 60 °C and the photo-sensitized polymerization at −78 °C (6). The DPs were determined from intrinsic viscosities in water for atactic and isotactic PVAs using the formula \[ [\eta] = 7.50 \times 10^{-3} \text{DP}^{0.64} \text{ (dl/g, 30 °C)} \] and those in benzene for acetylated syndiotactic PVAs using the formula \[ [\eta] = 8.91 \times 10^{-3} \text{DP}^{0.62} \text{ (dl/g, 30 °C)} \] (8). The s-(diad) % was estimated from the ratio of the optical density at 916 cm⁻¹ to that at 849 cm⁻¹ using the equation given by Murahashi et al. (9) \( s-(\text{diad}) \% = 72.4 \times (D_{916}/D_{849})^{0.43} \) where \( D_{916} \) and \( D_{849} \) are the absorbances at 916 cm⁻¹ and 849 cm⁻¹.

Surface tension

The atactic PVA was dissolved in water at about 100 °C. The isotactic PVA was dissolved in water at about 30 °C. The syndiotactic PVA was dissolved in water at 120 °C in sealed glass tubes. The surface tensions of the solutions were measured by the Wilhelmy method at 30.1 ± 0.2 °C. A glass plate which was hung by a poly(vinyl chloride) filament was immersed in the solution. The total force due to the surface tension and the weight of the glass plate was measured by a torsion balance. The apparatus used was similar to that reported by Fukawa et al. (2).

Spinning

A filament was prepared by picking up slowly the surface film of the syndiotactic PVA solution. The degrees of orientation, \( f \), of molecules were estimated from the width of the half value, \( H \), of the intensity curve of the X-ray diffracted from the (101) plane using the equation \( f = \{(180- H)/180\} \times 100 \).
tension which is the surface tension after a certain time when the change with time became very small. The times are 5 to 40 min. for the solutions of the syndiotactic PVA and about 3hrs for those of the isotactic and atactic PVAs. The equilibrium surface tension decreased with the increase in the concentration for isotactic and atactic PVAs, whereas for syndiotactic PVA that decreased with the increase in the concentration up to the concentration 3 g/dm$^3$ and then increased.

$\log 2.303 \log \frac{\gamma_0 - \gamma_\infty}{\gamma - \gamma_\infty} = n \log t + \log K \quad [1]$

where $\gamma_0$ and $\gamma$ are the surface tension of the solution at the time 0 and $t$, $\gamma_\infty$, the equilibrium surface tension and $t$, the time. The data were analyzed with the equation. The $n$ and $K$ values

Fig. 1. Surface tension versus time (Syndiotactic PVA)

Fig. 2. Surface tension versus time (Isotactic PVA)

Fig. 3. Surface tension versus time (Atactic PVA)

Fig. 4. Equilibrium surface tension versus concentration.

Ueberreiter et al. (10) have considered the time dependency as the similar process as crystallization and analysed using the Avrami equation [1]