ELSEVIER

Polymer 40 (1999) 497–505

polymer

In situ fibrillation of poly(vinyl alcohol) during saponification of poly(vinyl ester) (I). Chemorheological and morphological investigations of *in situ* fibrillation

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Received 13 November 1997; revised 18 December 1997; accepted 16 January 1998

Abstract

The syndiotacticity-rich (syndiotactic diad content of 57–65%) high molecular weight (number-average degree of polymerization of 4500–20 000) poly(vinyl alcohol) (PVA) microfibrillar fiber was directly produced via the saponification reaction of poly(vinyl pivalate) (PVPi) by controlling structural factors such as molecular weight and stereoregularity of PVA chains, and appetence between PVA and solvent without existing spinning procedures. By examining and observing the changes of flow birefringence, shear viscosity of reaction solution, degree of saponification, and shape of reaction product during the saponification reaction, the following novel formation mechanism of high strength microfibrillar PVA fiber is proposed. As PVPi converts into syndiotactic PVA by means of saponification using saponifying agents containing water, an oriented gel structure appears first by the interaction between water and hydroxyl groups of syndiotactic PVA formed during the saponification reaction, and then the microfibrillar structure is formed by the collapse of water–PVA interbridges and the resultant chain packing between syndiotactic PVA molecules. The larger the syndiotacticities of both PVPi and PVA, the higher the molecular orientation and the smaller the hydroxyl groups in P(VPi-VA) copolymer needed for *in situ* fibrillation. The well oriented microfibrillar PVA fiber prepared by such a manner had irregular cross-sections, needle-point-like ends, accumulated ultrafine microfibril structure.

Keywords: Syndiotacticity; Saponification; Microfibrillar PVA fiber

1. Introduction

As a material for the production of high performance fiber, high molecular weight (HMW) syndiotactic poly(vinyl alcohol) (PVA) has received considerable attention. The commercial and scientific interests in this polymer arise from its high limit strength of 236 g/d and high crystal modulus of 2251 g/d. These properties seem to be ascribable to molecular structural characteristics including extended-chain conformation and high molecular orientation due to its HMW, high stereoregularity and high linearity. The major drawbacks of this material for the preparation of high strength and high modulus fibrous substances, however, are the necessity of complicated processes of manufacture such as dissolving polymer, determining initial optimum spinning concentration, spinning, drawing, heat treatment, etc. and the difficulty in fully molecular orientation owing to the presence of strong intra- and intermolecular hydrogen bondings[1]. Hence, the derivation of a new fiber forming method (fibrillation) for syndiotacticity-rich HMW PVA, not a conventional spinning process, is necessary.

Since a silk solution was first spun from orifices, almost all the synthetic fibers have been produced by spinning, followed by longitudinal orientation. In the mid 1980s, it was found that poly(*p*-phenylene terephthalamide), a rigid rod polymer forming a lyotropic liquid crystal in a certain concentration range, could form a microfibrillar structure during its synthesis [2,3]. Yoon [2,3] suggested that the microfibril formation mechanism has some similarity to the self-ordering and chain-packing mechanism occurring during the growth of native cotton or ramie fibers.

Many attempts to directly prepare microfibrillar fiber from a solution of flexible chain polymers like PVA, polyacrylonitrile, and polyethylene during their synthesis have

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0032-3861/98/$ – see front matter
PII: S0032-3861(98)00066-4

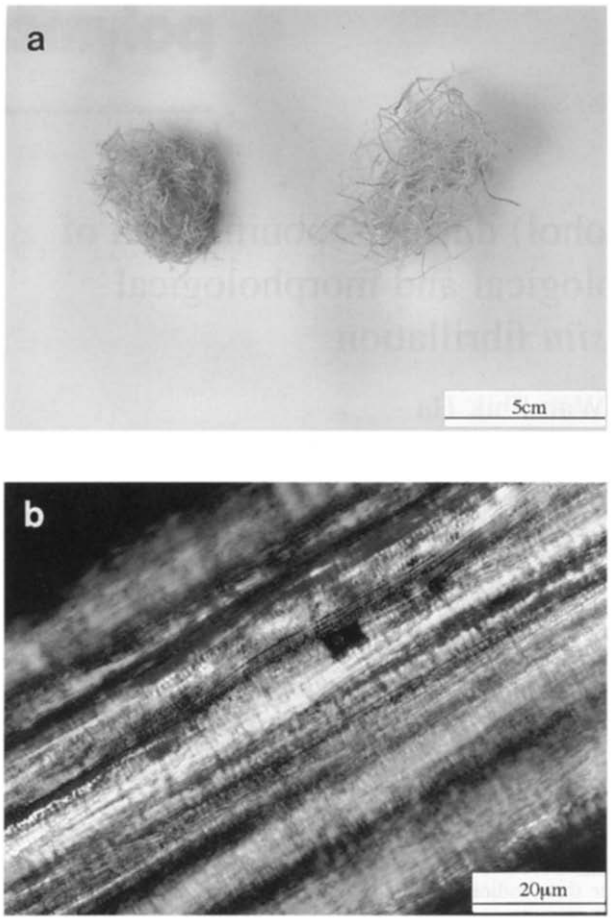


Fig. 1. Photograph (a) and polarizing micrograph (b) of microfibrillar PVA fiber prepared by the saponification of PVPi.

been made without success. Both ordinary and high strength, high modulus PVA fibers were obtained by the typical solution spinning using spinnerets [4,5,6,7,8,9] since the first preparation of PVA fibers by Herrmann and Haehnel [10] in 1931. In addition, up to now, the fibrillation of synthetic rigid rod and flexible chain polymers has depended entirely on the immiscible polymer blend procedure of extrusion/orientation/extraction [11,12,13, 14,15] without molecular growth or molecular structure alteration.

Recently, we [16,17,18] have found that a PVA fiber of well oriented microfibrillar structure, similar to a natural cellulose fiber (Fig. 1), is formed during saponifying a poly(vinyl pivalate) (PVPi) to PVA. This has proved to be true only for the saponification process of HMW PVPi which possesses high syndiotactic diad (S-diad) content. In fact, saponification of atactic poly(vinyl acetate) (PVAc) to PVA with similar molecular weight did not lead to any fibrillation. The fact that the fiber formation from the solution of a flexible chain polymer under low shear conditions (shear rates of below 100 s^{-1}) is very unusual, and hardly explained by conventional fiber formation concepts. It is not easy to analyze the reason for fibrillation because saponification accompanies change of chemical composition of the polymer.

In the present paper, we will describe a microfibrillar fiber formation by a physicochemical action between syndiotactic PVA and saponifying agent during the saponification of syndiotacticity-rich HMW PVPi. That is, the mechanism of fibril formation will be suggested on the basis of chemorheological and chemorheo-optical analyses of saponification reaction solution and structure observation of reaction product.

2. Experimental

2.1. Synthesis of PVPi

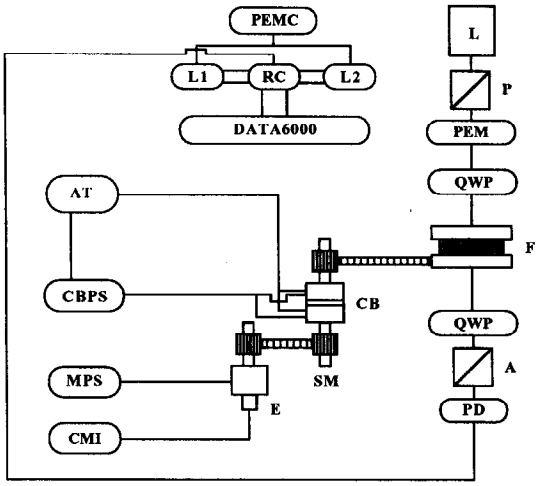
To synthesize the syndiotacticity-rich HMW (PVPi)s having various molecular weights and syndiotacticities, vinyl pivalate was photo-bulk polymerized on irradiation with ultraviolet ray at a low temperature with 2,2′-azobisisobutyronitrile and 2,2′-azobis(2,4-dimethylvaleronitrile) (ADMVN) as photoinitiators, respectively, and bulk- and solution-polymerized at a low temperature with ADMVN as an initiator [16,18]. The number-average degree of polymerization (P_n) of PVPi was determined by viscosity method [19].

2.2. Saponification and in situ fibrillation

The following is a typical example of PVA fibrillation experiments: In a flask equipped with a reflux condenser, a thermocouple, a dropping funnel, and a stirring device, 3 g of PVPi was dissolved in 300 ml of tetrahydrofuran (THF). The PVPi solution in the flask and 20% potassium hydroxide or 15% sodium hydroxide/methanol/water (90/10 v/v) solution in the dropping funnel were flushed with nitrogen. The ratio of saponification agent/PVPi solution was 0.05–0.25 (v/v). The alkali solution was added to the PVPi solution while being stirred at 50–60°C. After the saponification reaction had been completed, the solid fibrillar reaction mixture was tapped mechanically or treated on an ultrasonic generator containing methanol solution. The fibers thus produced were filtered and washed several times with methanol, and a quantitative yield of bright-yellow microfibrillar PVA fibers (PVA fibrils) was obtained.

2.3. Characterization of saponification reaction solution and reaction product

Changes in the shear viscosity of saponification reaction solution during the saponification of PVPi with different (P_n)s were observed by using a rheometer (Physica, MC 20) at a constant shear rate of 50 s^{-1}. Z-1 cell, double-gap coaxial type, was used as a flow cell. 0.2 g of PVPi was dissolved in 20 ml of THF, and 2 ml of potassium hydroxide/methanol/water was used as a saponification agent. The



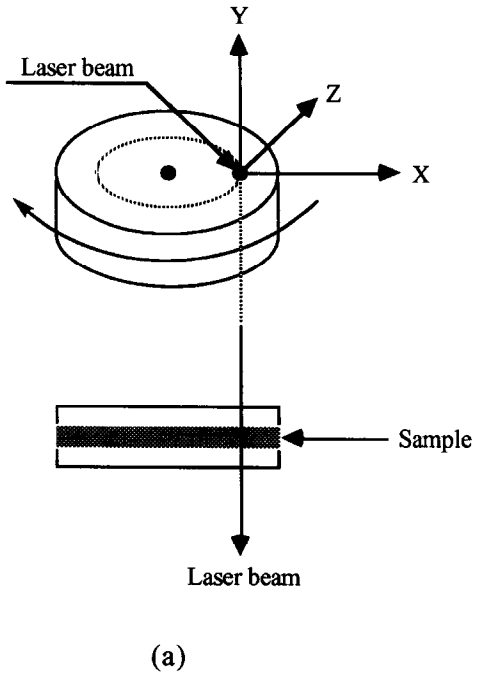
A: Analyzer
AT: Personal Computer
CB: Clutch/Brake
CBPS: CB Power Supply
CMI: Compumotor Indexer
DATA6000: Storage Oscilloscope
E: Encoder
F: Two Parallel Quartz Plates
L: Laser
L1: ω Lock-in Amplifier
L2: 2ω Lock-in Amplifier
MPS: Compumotor Power Supply
P: Polarizer
PD: Photo-Detector
PEM: Photo-Elastic Modulator
PEMC: PEM Controller
QWP: Quarter Wave Plate
RC: Ratio Circuit
SM: Stepping Motor

Fig. 2. Schematic diagram of phase-modulated flow birefringence experimental apparatus.

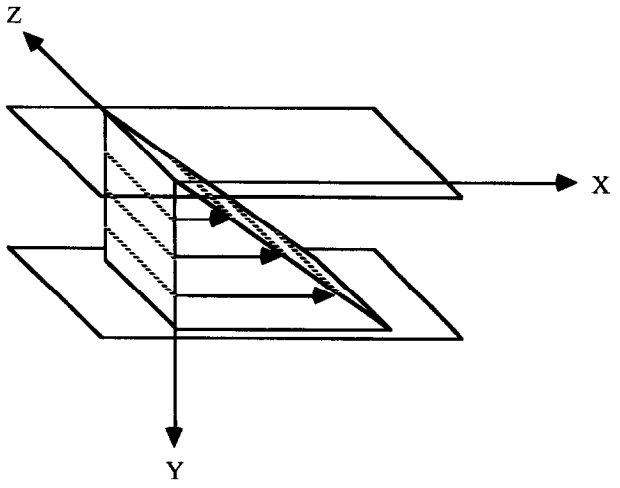
flow birefringence (Δn_f) of the saponification reaction solution during the saponification was measured using a phase-modulated flow birefringence (PMFB) technique [20, 21]. The PMFB technique can measure the time dependent birefringence and dichroism of polymer solutions, polymer melts, and colloidal dispersions with high sensitivity [22]. The PMFB apparatus is composed of He–Ne laser source, polarizer, photo-elastic modulator, a set of two quarter wave plates, analyzer, and photo-detector having relative optical orientation as schematically shown in Fig. 2. A rotational parallel plate geometry was adopted. Fig. 3 illustrates flow geometry during the birefringence measurements. 0.2 g of PVPi having P_n of 23 500 was dissolved in 20 ml of THF. Potassium hydroxide–methanol–water (2 ml) was used as a saponification agent. He–Ne laser was transmitted through the mixing solution of PVPi and saponification agent at a constant shear rate of 50 s^{-1}. The changes in Δn_f was obtained from the values detected on the apparatus. The Δn_f was calculated by Eq. (1) [21],

$$\Delta n_f = \delta' \lambda / 2\pi d \quad (1)$$

in which, δ', λ and d are phase retardance, wavelength of light, and thickness of solution, respectively. The degree of saponification (DS) of saponification reaction product was determined from weight loss after saponification and from



(a)



(b)

Fig. 3. Schematic diagram of (a) two parallel plates (the cell of phase-modulated flow birefringence experimental apparatus) and (b) flow geometry.

the ratio of *tert*-butyl proton peak area at 1.1 ppm to methylene proton peak area at 1.2–1.6 ppm on a proton-nuclear magnetic resonance (^{1}H n.m.r.) spectrum obtained by ^{1}H n.m.r. spectrometer (Varian, Sun Unity 300) [23]. The hydroxyl group content ([OH]%) of the gel obtained at a point of time exhibiting maximum shear viscosity (η_{max}) was also calculated from the ^{1}H n.m.r. spectrum and by determining the weight loss of polymer after the saponification. The surface structure of reaction products obtained during the saponification of PVPi was photographed using a video microscope (Scalar, VMS 3000) with a magnification of 10^3.

2.4. Characterization of fully saponified PVA fibril

The P_n of PVA fibril could be determined from the viscosity of the PVAc produced by acetylating the saponified PVA [24]. The S-diad content of the PVA fibril was calculated from the ratio of hydroxyl proton triple peak area at 4.1–4.7 ppm on the ^{1}H n.m.r. spectrum. Polarizing micrograph of the PVA fibril was obtained using a polarizing microscope with a Senarmont compensator (Nikon, Optiphot-Pol 104). The degree of crystal orientation was calculated by azimuthal scanning of the (020) diffraction (the crystal is monoclinic and the chain axis is parallel to the *b* axis) at a scanning speed of 2°/min. X-ray diffraction pattern of the PVA fibril was recorded on Kodak Direct Exposure film using pinhole collimation under vacuum. The load-elongation curve was obtained using an instron model 4201 with a sample length of 3 cm and a cross head speed of 10 mm/min. The tensile strength of the PVA fibril was indicated by an average of 20 values measured.

3. Results and discussion

3.1. Optimum conditions for fibrillation

Factors affecting the fibrillation of PVA were molecular weight of PVPi and PVA, syndiotacticity of PVA, DS of PVA, type and amount of solvent for PVPi, type and amount of alkali solution, saponification temperature and time, presence or absence of oxygen, shear speed and type of stirring device. The optimum conditions of these factors are listed in Table 1. Good solvents for PVPi are presented in Table 1. The degree of branching for pivaloyl group of synthesized PVPi was less than 1. The P_n of the PVA fibril was 4500–20 000. In the P_n of below about 4500, strong PVA fibril could not be prepared. The S-diad content of the PVA fibril was 57–65%. In the case of PVA prepared by the saponification of PVAc, the S-diad content was only 47–53%, and at such a range of S-diad content, effective fibrillation could not occur.

The PVA fibril thus prepared has very unique features in microstructure. That is, this fiber has irregular cross-sections, needle-point-like ends, and accumulated ultra-fine microfibril structure which is totally different from conventional man-made fibers prepared by spinning (Fig. 1). Such a fiber structure has been observed only in naturally occurring cellulose fibers, but never been observed spun PVA fibers. The fibers formed by our fibrillation method had a dimension of 0.1–50 μm in diameter and 0.5–300 mm in length. By dint of the optimum combination of complex fibrillation factors, it was possible to control the thickness and length of the PVA fibril to a certain degree. These PVA fibrils could be split again to finer ones. The diameter and length of the PVA fibril were dependent upon several factors: The higher the syndiotacticity, the shear speed, and the saponification temperature, the finer and longer the fibrils.

Table 1
Parameters for fibrillation of PVA

Solvent of PVPi	THF, acetone or methylethylketone
Saponification agent	20% potassium hydroxide or 15% sodium hydroxide/methanol/water solution
P_n of PVPi	11 300–33 000
P_n of PVA	4500–20 000
S-diad content (%) of PVA	57–64
D.S. (%) of PVA	85.0–99.9
Saponification temperature(°C)	50–60

3.2. Chemorheological analysis of in situ fibrillation

Shear viscosity changes during the saponification of (PVPi)s having different (P_n)s and similar S-diad contents of about 63% were checked by using a rheometer (Fig. 4). During the initial reaction stage, the shear viscosity decreased due to the mixing of PVPi/THF and alkali solutions. The duration of initial reaction stage increased with an increase in the P_n of PVPi, and this was considered that the time to mix higher molecular weight PVPi and alkali solutions lengthened owing to higher solution viscosity. As the saponification proceeded, the pivaloyl groups of PVPi were converted into hydroxyl groups, and the shear viscosity increased, exihibiting a η_{max}, at which the Weissenberg effect was observed. The time to reach η_{max} was constant and independent of P_n of PVPi and PVA. Finally the shear viscosity decreased gradually to a low value due to the gelation and then the fibrillation of PVA occurred. S-diad content and DS of the resulting PVA fibrils were about 63

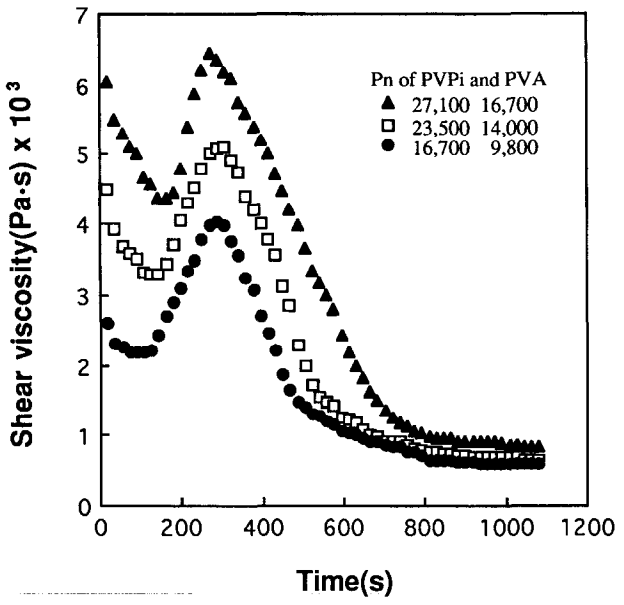


Fig. 4. Shear viscosity with saponification time of PVPi having different (P_n)s and similar S-diad contents of about 63%.

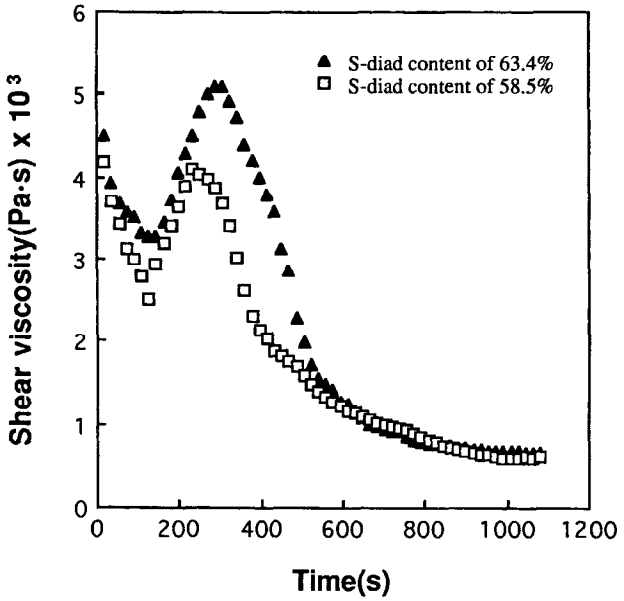


Fig. 5. Shear viscosity with saponification time of PVPi having different S-diad contents and similar (P_n)s of about 23,500.

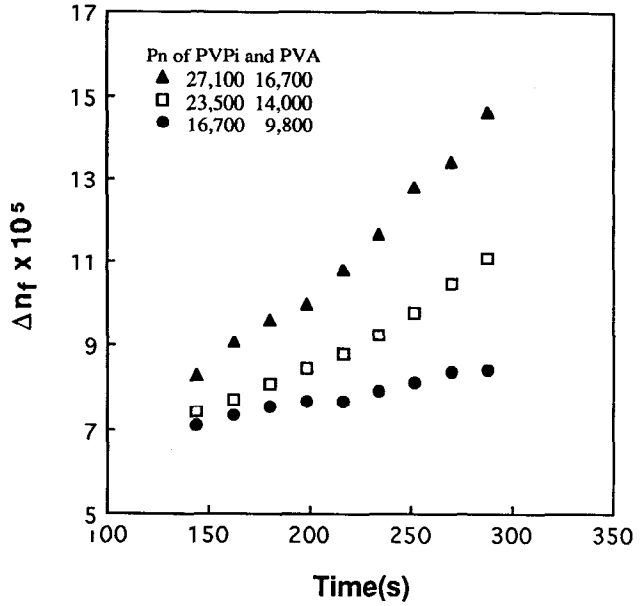


Fig. 7. Flow birefringence (Δn_f) with saponification time of PVPi having different (P_n)s and similar S-diad contents of about 63%.

and 99%, respectively. Fig. 5 shows shear viscosity changes during the saponification of (PVPi)s having different S-diad contents and similar (P_n)s of about 23 500. The (P_n)s of (PVA)s prepared by saponification of these (PVPi)s were about 14 000. For more precise investigation of tacticity effect on the *in situ* fibrillation of PVA, two (PVPi)s having molecular parameters described above were prepared in this study. In comparison with the results in Fig. 4, two things are worth noting in Fig. 5. Firstly, the time to reach η_{max} shortened with a decrease in the syndiotacticity. Secondly, a stronger gel exhibiting higher viscosity was formed in higher syndiotactic PVPi. That is, it may be concluded

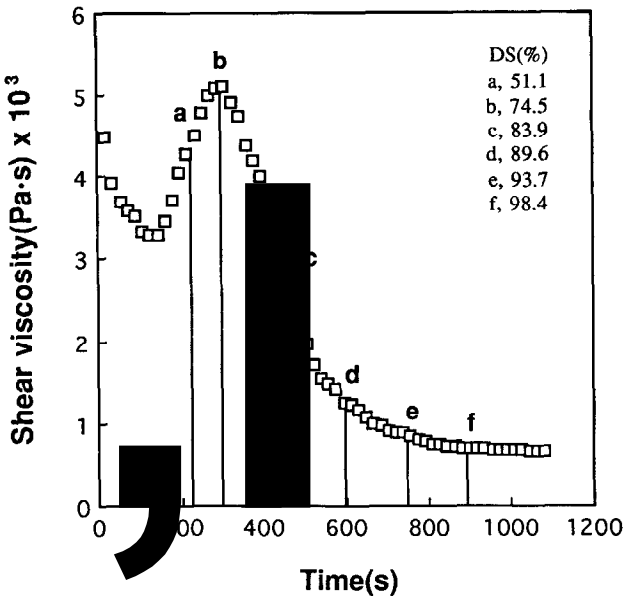


Fig. 6. Changes in shear viscosity and DS during the saponification of PVPi having P_n of 23,500.

that the larger the syndiotacticity of PVPi, the longer the gelation time and the higher the solution viscosity under the same *in situ* fibrillation conditions.

The changes in shear viscosity and DS during the saponification of PVPi are shown in Fig. 6. The value of DS measured for the gel formed after 300 sec of saponification time was 74.5%. While the saponification proceeded to the points, *c* (83.9%), *d* (89.6%), and *e* (93.7%), the gel was converted into the fibril. The shear viscosity decreased after the Weissenberg effect, as the gel fibrillated and the PVA fibrils separated from the reaction solution. From the fact that the shear viscosity in this system changed little near point *f* (98.4%), it was apparent that the fibrillation was almost finished. The molecular chains of syndiotactic PVA are easily packed together due to the formation of orderly intermolecular hydrogen bonding. It seems that the chain packing of PVA molecules occurs by the collapse of the solvent bridges in a short time in comparison with that for the rigid rod poly(*p*-phenylene terephthalamide) [2]. Fig. 7 shows Δn_f changes of reaction solution during the saponification of (PVPi)s having different (P_n)s and similar S-diad contents of about 63%. The increase of Δn_f continued until the Weissenberg effect appeared by the formation of gel, as the pivaloyl groups of PVPi converted into hydroxyl groups. The Δn_f increased with an increase in the P_n of PVPi. The changes in Δn_f of reaction solution during the saponification of (PVPi)s having different S-diad contents and similar (P_n)s of about 23 500 are shown in Fig. 8. Steep increase in Δn_f of higher syndiotactic PVPi was found. On the other hand, in the case of PVPi having S-diad content of 58.5%, increasing rate of Δn_f was much smaller than that of higher syndiotactic PVPi. This implies that a higher syndiotactic chain develops molecular orientation more easily.

Fig. 9 shows [OH]% of the gel exhibiting η_{max} with

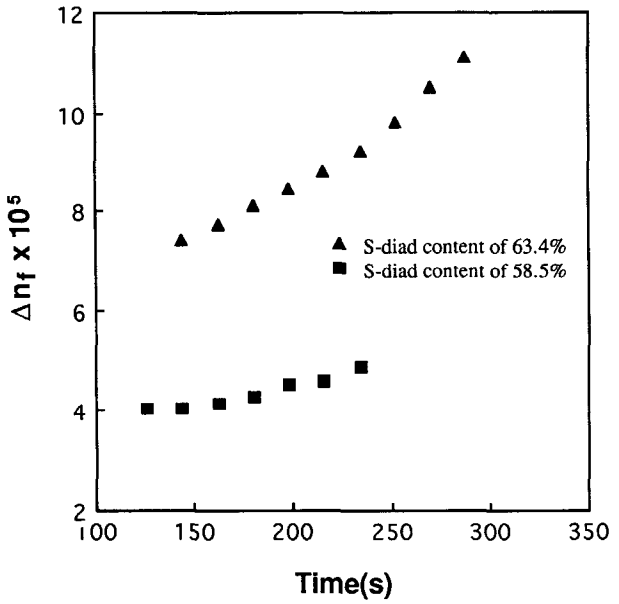


Fig. 8. Flow birefringence (Δn_f) with saponification time of PVPi having different S-diad contents and similar (P_n)s of about 23,500.

respect to molecular weight and syndiotacticity. In case of PVPi having P_n of 16 700 and S-diad content of about 63%, η_{max} was obtained at [OH] of 80.1%. While, in the case of P_n of 27 100 and S-diad content of about 63%, η_{max} appeared at [OH] of 71.5%. [OH]% of (PVPi)s having lower S-diad content of about 58% was larger than that having higher S-diad content of about 63%. From these results, we can recognize that the larger the P_n of PVPi and syndiotacticity, the smaller the hydroxyl groups in syndiotactic P(VPi-VA) copolymer needed to form the gel during *in situ* fibrillation.

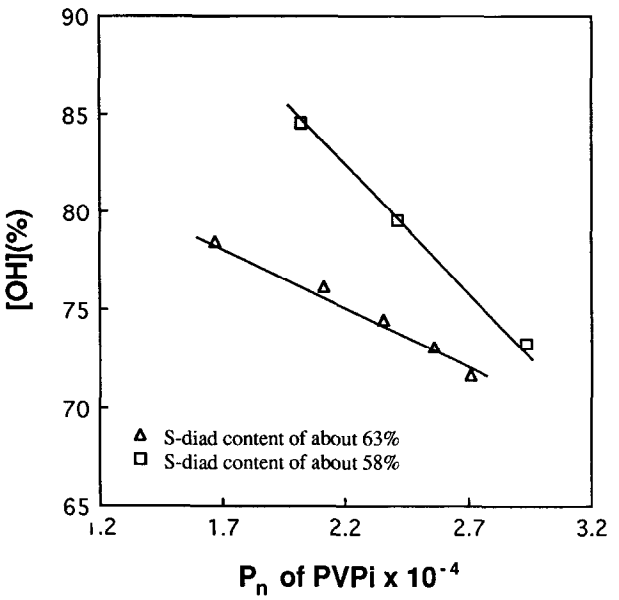


Fig. 9. [OH]% of P(VPi-VA) copolymer gel exhibiting η_{max} during the saponification of (PVPi)s having different (P_n)s and S-diad content.

3.3. Morphological investigation of in situ fibrillation

The changes in the surface structure of products formed during the saponification of PVPi are shown in Fig. 10. The photograph of PVPi, -$[CH_2$-$CH(OCOC(CH_3)_3)]_n$-, having P_n of 23 500 and DS of 0% is Fig. 10*a*. This was synthesized by the photoinitiated-bulk polymerization of VPi. Fig. 10*b* shows the precipitate of P(VPi-VA) copolymer, -$[CH_2$-$CH(OCOC(CH_3)_3)$-CH_2-$CH(OH)]_n$-, having DS of 51.1%. The sample was obtained from the saponification reaction solution before the gel formation. The gel of P(VPi-VA) copolymer having DS of 74.5% is shown in Fig. 10*c*. The gel was taken at η_{max}. The gel of P(VPi-VA) copolymer having DS of 83.9% is shown in Fig. 10*d*. At this time the collapse of solvent bridges occurred. Fig. 10*e* shows the fibrillar precipitate of P(VPi-VA) copolymer having DS of 89.6%. The photograph of microfibrillar fiber having DS of 93.7%, S-diad content of 63.4%, and P_n of 15 200 is given in Fig. 10*f*. From the photographs presented above, it becomes clear that as DS increased, the fibrillar structure was developed. In particular, the gel obtained at η_{max} had an oriented molecular structure (Fig. 10*c*) and at DS of over 85%, a nearly perfect microfibrillar structure was formed (Fig. 10*e* and 10*f*).

3.4. Role of water in the fibrillation

To produce high strength and high modulus material, it is necessary to orient the molecular chains. However, it is difficult to prepare highly oriented PVA due to the presence of tight intermolecular hydrogen bonding between adjacent hydroxyl groups in both crystalline and non-crystalline regions. To improve the molecular chain orientation of PVA, Choi *et al.* [25] utilized iodine as a substance which reduces the intermolecular hydrogen bonding of PVA [1]. Colvin [26] and Tadokoro *et al.* [27] reported that water, which has a high affinity to PVA, seemed to intrude easily into the crystal of PVA and modify the molecular packing arrangement. In the present work, a definite amount of water as a substance which interferes with the strong intermolecular hydrogen bonding of syndiotactic PVA was added to the saponifying agent. From this point of view, the water content was very significant. The reason for this is that above or below optimum water concentration, the high strength PVA fibril could not be prepared effectively or poor oriented fibrillar-shape lump was formed. X-ray diffraction photographs in Fig. 11 clearly explain water effect on the *in situ* fibrillation of PVA. In case of water-presence saponification system, highly oriented PVA fibril having degree of crystal orientation of over 0.88 could be prepared (Fig. 11*a*). On the contrary, it can be seen that non-oriented product was obtained when water was not employed in the saponification process (Fig. 11*b*). During the saponification of PVAc, a common precursor of PVA, as the amount of water increases, blocky hydroxyl groups are formed and the saponification reaction rate is lower under alkaline

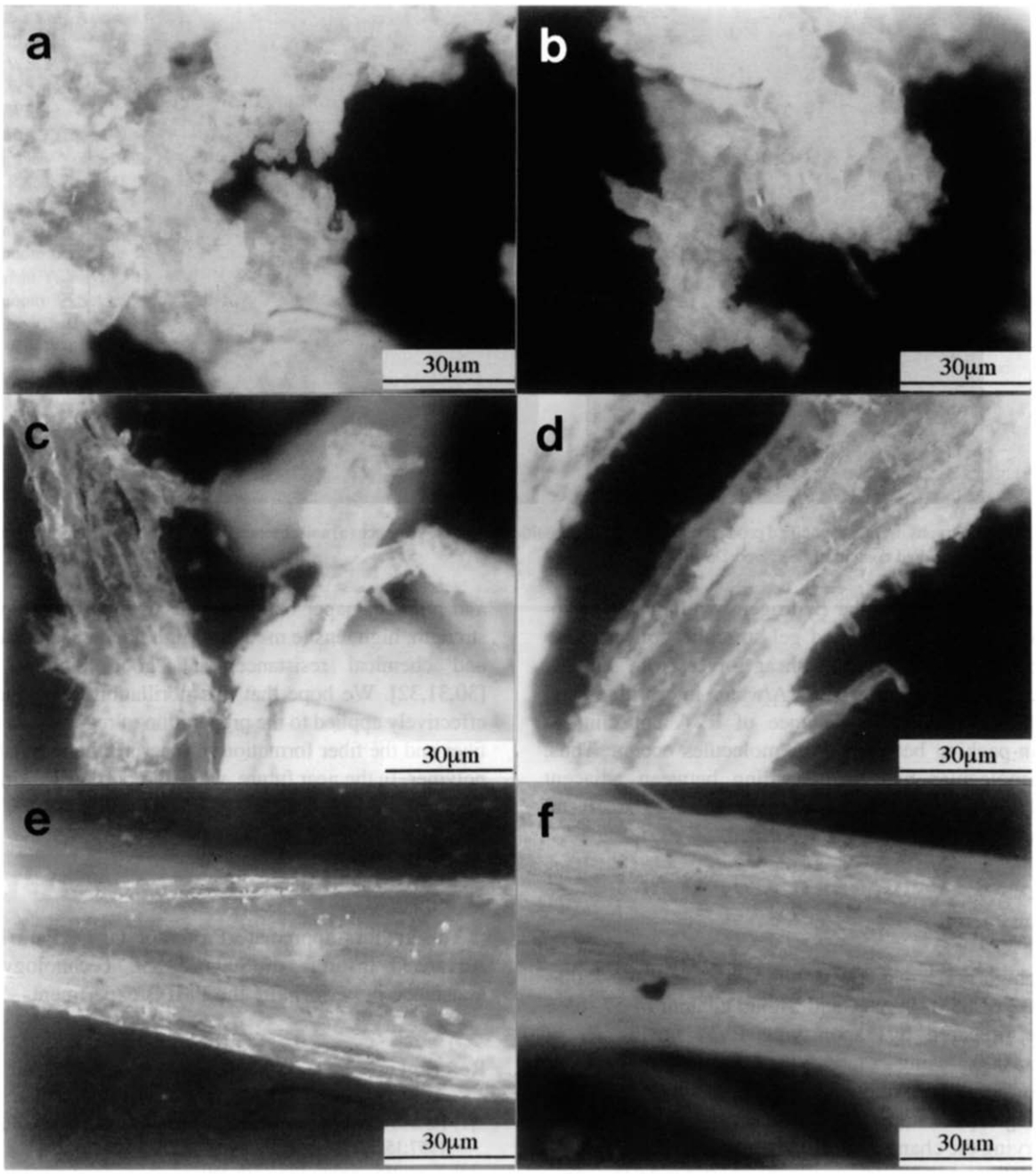


Fig. 10. Changes in the surface structure of reaction products obtained during the saponification of PVPi having P_n of 23,500: DS: a, 0%; b, 51.1%, c, 74.5%; d, 83.9%; e, 89.6%; f, 93.7%.

conditions. However, random hydroxyl groups are formed under acidic conditions even if water alone is used as the saponification medium [28]. We attempted the saponification using a water-free medium, but the effective fibrillation was not achieved. So, the optimum ratio of methanol/water was determined experimentally. In addition, we had characterized a sequence distribution of the hydroxyl groups of P(VPi-VA) copolymer formed during the saponification in the presence of optimum water and found that the copolymer formed had a much more blocky structure in comparison with that formed during the saponification in the absence of water [29], resulting in *in situ* fibrillation.

3.5. Mechanism for fibrillation

Now, we suggest the following mechanism for the PVA fibrillation. The pivaloyl groups initially convert into the blocks of hydroxyl groups and a definite fraction of hydroxyl groups formed are concerned with binding with water. The oriented gel structure appears as a result of the

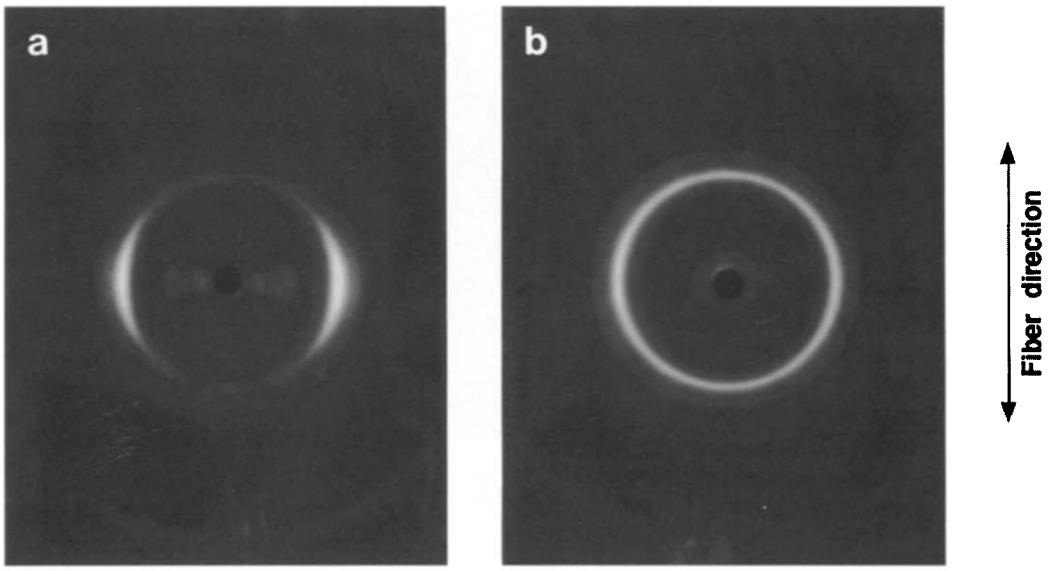


Fig. 11. X-ray photographs of fully saponified product obtained by the saponification in the presence (a) and absence (b) of water (Two saponified products had similar P_n of 14,000, S-diad content of 63%, and DS of 99%.

weakening of intermolecular hydrogen bonding of syndiotactic PVA. Then, the oriented gel structure converts into the microfibrillar structure by shear forces from stirring, which causes the collapse of PVA/water interbridges and makes the intermolecular distance of PVA constant, so that chain-packing between PVA molecules occurs. Thus, the intermolecular hydrogen bonding between adjacent hydroxyl groups in PVA is strengthened and the crystal structure of syndiotactic PVA is formed.

4. Conclusions

Novel high performance PVA fibril having P_n of 4500–20 000, DS of 85.0–99.9%, and S-diad content of 57–65% could be prepared by saponifying PVPi having P_n of 11 300–33 000, using saponifying agent composed of THF/potassium hydroxide/water/methanol while being stirred at a high speed and a fixed temperature. By examining and observing the changes of Δn_f, shear viscosity of reaction solution, DS, and shape of reaction product during the saponification, the formation mechanism of the PVA fibril was proposed: As PVPi converts into syndiotactic PVA by means of saponification using alkali saponifying agent containing water, an oriented gel structure appears first by the interaction between water and hydroxyl groups of PVA formed during the saponification reaction, and then the microfibrillar structure is formed by the collapse of water/PVA interbridges and the resultant chain packing between PVA molecules. These phenomena were more predominant in higher syndiotacticity.

It is expected that this high strength PVA fibril having tensile strength of over 15 g/denier [17] can be used as a high performance replacement material for natural carcinogenic asbestos fiber, reinforcing fiber, ultra-low denier fiber, and pulp for paper based product owing to its high tensile strength, high tensile modulus, high fineness, excellent alkali and chemical resistance, and good binding property [30,31,32]. We hope that this fibrillation technique will be effectively applied to the preparation of regenerated cellulose fiber and the fiber formation of other synthetic flexible chain polymer. In the near future, we will report on the kinetics and spectroscopic analysis results of this fibrillation.

Acknowledgements

The authors appreciate Professor O. O. Park in Korea Advanced Institute of Science and Technology for his assistance in performing the PMFB experiments.

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