

Effects of Polymer Concentration and Zone Drawing on the Physical Properties of Poly(*N*-vinylcarbazole) Thick Film

WON SEOK LYOO,¹ JOON HO KIM,¹ WON SIK YOON,¹ DAE HEUM KIM,² JIN HYUN CHOI,³
BYUHG CHUL JI,³ CHUL JOO LEE⁴

¹ School of Textiles, Yeungnam University, Daedong, Kyongsan 712-749, South Korea

² Department of Chemical Engineering, Kwangjuon University, Wolgye-dong, Nowon-gu, Seoul 139-701, South Korea

³ Department of Dyeing and Finishing, Kyungpook National University, Taegu 702-701, South Korea

⁴ Electronic Materials and Devices Research Center, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, South Korea

Received 16 June 2000; accepted 21 August 2000

ABSTRACT: To check the possibility of zone-drawn poly(*N*-vinylcarbazole) (PVK) thick films as base materials of photorefractive polymers, the effects of the initial polymer concentration and zone drawing on the physical properties of PVK film were investigated. PVK films were prepared from 1,1,2,2-tetrachloroethane (TCE) solutions with different initial concentrations. To investigate the drawing behavior of the PVK films with different solution concentrations, the films were drawn under various zone-drawing conditions. Through a series of experiments, it turned out that the initial concentration of the PVK solution in TCE caused significant changes in the draw ratio of the PVK film, that is, the zone draw ratios of the film at an initial concentration of 9.8 g/dL exhibited their maximum values and gradually decreased at higher or lower concentrations. Thus, it was determined that the initial concentration of 9.8 g/dL is the optimum polymer concentration to produce the maximum draw ratio in this work. The lightness (whiteness) of the zone-drawn PVK film was much higher than that of the hot-drawn PVK film, resulting from diminishing microcrystallite formation, crystallization, and back-folding of molecular chains by zone drawing. Moreover, the mechanical properties of the PVK film were dominantly improved by introducing a zone-drawing technique, maintaining lightness of the zone-drawn film to a similar degree as that of the undrawn film. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1297–1304, 2001

Key words: PVK film; initial polymer concentration; zone drawing; lightness; mechanical properties

INTRODUCTION

Poly(*N*-vinylcarbazole) (PVK) film is one of the most promising materials for good photoconduc-

tors,^{1–3} charge-transfer complexes,³ electroluminescent devices,^{4–8} and photorefractive materials.^{9–13} To prepare the best film (especially thick film above 100 μm thickness for photorefractive application) having good performance for photorefractive base materials, many parameters related to the structure and properties of the film should be considered. The important factors affecting the photorefractivity of PVK film are the physical

Correspondence to: W. S. Lyoo (wslyoo@yu.ac.kr).
Contract grant sponsor: RRC Research Fund.

Journal of Applied Polymer Science, Vol. 81, 1297–1304 (2001)
© 2001 John Wiley & Sons, Inc.

properties such as the crystallinity, lightness (whiteness), surface smoothness, uniformity of thickness, and mechanical properties. Thus, to control these physical properties, in general, hot drawing of PVK thick film has been done.¹⁴ However, in producing various films having high and regular chain orientations, uniform dimensions, and good physical properties accompanied with fine and easy controlling of properties for particular uses, hot-drawing methods have problems such as higher probabilities of microcrystallite formation, the back-folding of molecular chains, a lightness decrease, and thermal degradation of the samples.¹⁵⁻²⁰

In general, the molecular weight,^{19,21-24} molecular weight distribution,²⁵ and concentration of the polymer solution^{26,27} have a marked influence on the drawability (orientation) of polymers. The drawability increases as the molecular weight increases.²⁸ Under the same molecular weight, this property depends principally on the initial concentration of the polymer solution from which the film was made.^{21,26} This is due to a reduced number of entanglements per molecule of the solution-cast or spun polymers in comparison with those obtained from the melt²⁹; that is, macromolecules are thought to form a transient network with entanglements acting as friction centers or non-localized junctions. Because high-entanglement density impedes a large deformation of solidified high molecular weight polymers, their drawability might be improved by reduction of the number of entanglements. However, in the case of a dilute solution, which has fewer entanglements, the maximum draw ratio cannot be obtained, owing to rare coil overlap and chain slippage occurring at the drawing step. Therefore, a proper level of entanglements is needed to increase the orientation of polymer chains which can be realized by the control of the solution concentration.

Zone drawing,^{16,19,20,24} a method inducing necking on one point of a film by heat, has many advantages as described above compared to hot drawing. It reveals that higher orientation is significantly related to the zone draw ratio.^{15,17,18,30-32}

In this study, effects of the initial polymer concentration and zone drawing on physical properties such as the orientation, crystallinity, lightness, and tensile properties of the PVK film were investigated. A convenient one-step zone-drawing method was introduced for finely controlling the physical properties of solution-cast PVK film, for improving the mechanical properties and resis-

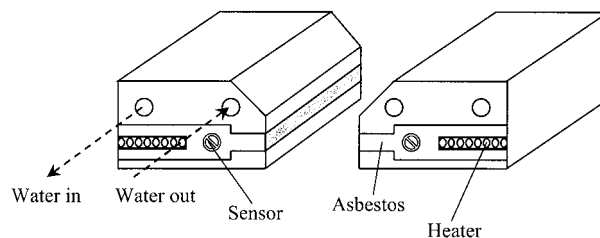


Figure 1 Schematic representation of band heater assembly.

tance in a high electric field, and for obtaining both higher orientation and higher lightness than those of general hot-drawing methods.

EXPERIMENTAL

Preparation of PVK Film

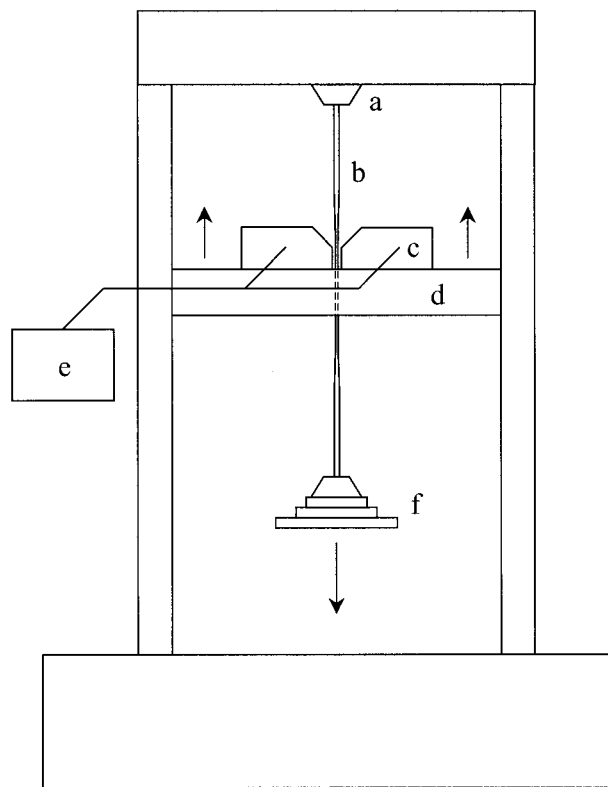
The relative viscosity of the PVK (Aldrich Chemical Co., Milwaukee, WI, weight-average molecular weight 1.1×10^6) solution was measured at 25°C using an Ubbelohde viscometer. From these results, the reduced viscosity for film casting was calculated. The concentrations of PVK solutions in 1,1,2,2-tetrachloroethane (TCE) used in the film casting were 6.5, 9.8, 13.0, and 16.0 g/dL, respectively. The homogenized solution was poured into a stainless-steel dish and dried under a vacuum at 25°C for about 10 days. After TCE was removed from the films, the dried films, having similar thicknesses of 210 μm , were obtained.

Zone Drawing of Film

Zone drawing was carried out at several temperatures by moving a pair of narrow band heaters with dimensions of 7 cm length, 2.5 cm width, and 1 mm thickness (Fig. 1). The film used for zone drawing was of 210 μm thickness, 5 mm width, and 10 cm length, being drawn under tensions controlled by different dead weights, on an Instron Model 4201 (Fig. 2).^{20,24,33-36} The zone-drawing conditions are listed in Table I.

Hot Drawing of Film

The PVK film was drawn by tensile force in an air oven equipped with a tensile tester at the same drawing temperatures as in the case of zone drawing.



a. Upper jaw b. Specimen
 c. Band heater assembly d. Cross head
 e. Temperature controller f. Weight

Figure 2 Schematic representation of zone-drawing apparatus.

Characterization of Film

Birefringences were measured on a polarizing microscope with a senarmont compensator (Nikon, Optipot-Pol 104). The birefringence was determined by dividing the optical path length by the thickness.

Wide-angle X-ray diffractograms of PVK film, for determining crystallinity, were obtained with nickel-filtered CuK α radiation (40 kV, 200 mA) using an X-ray diffractometer (Mac Science, MXP-18). To measure the degree of crystallinity of the film, the X-ray diffraction patterns were recorded in the range of $2\theta = 5-65^\circ$ at a scan speed of $1^\circ/\text{min}$. The degree of crystallinity was

Table I Zone-drawing Conditions of PVK Film

Drawing stress (MPa)	0.32, 0.63, 0.95, 1.26
Drawing temperature ($^\circ\text{C}$)	120, 140, 160, 180
Heat band speed (mm/min)	1, 5, 10, 50

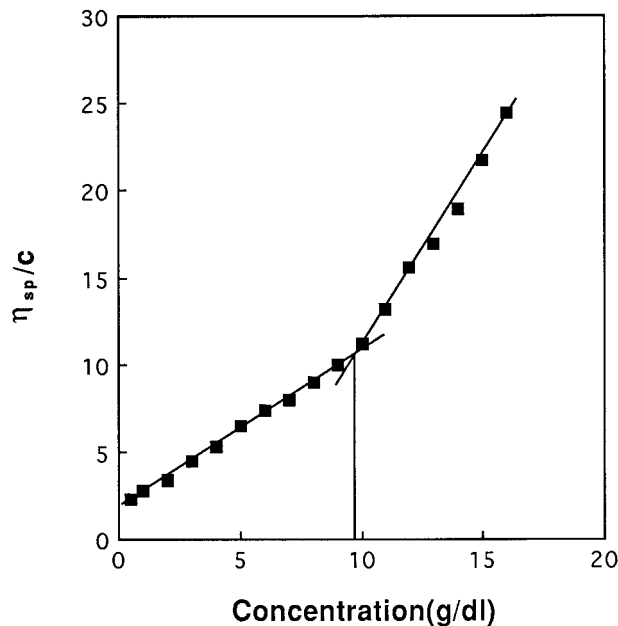


Figure 3 Reduced viscosity of PVK solution in TCE at 25°C with solution concentration.

calculated by using a basic method for diffraction between crystalline and amorphous scattering in diffraction intensity curves.³⁷

The lightness of the PVK film was measured by a color eye (I.D.I., Model C). Load-elongation curves were recorded on an Instron Model 4201 using a sample length of 2 cm and a crosshead speed of 100 mm/min. The tensile strength and modulus of the PVK film were each the average values of 20 samples.

RESULTS AND DISCUSSION

Determination of Optimum Polymer Concentration

It has been known that the draw ratio of solution-cast film is influenced by the solution concentration and that the maximum molecular orientation can be obtained at a certain solution concentration. Moreover, in the vicinity of this concentration, the solution viscosity steeply increases. Thus, in this study, first, relative viscosity measuring experiments were tried in order to predict the optimum polymer concentration of PVK, as shown in Figure 3. From the fact that all the measured data were approximated to two different linear lines in Figure 3, it can be seen that a critical polymer concentration of 9.8 g/dL, showing an abrupt change in the solution viscosity, is

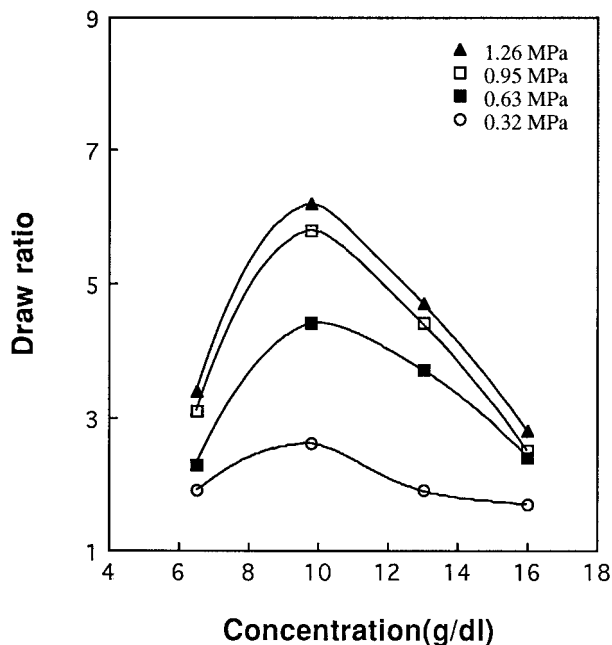


Figure 4 Zone draw ratio of PVK film drawn under various drawing stresses, a drawing temperature of 180°C, and a heat band speed of 1 mm/min with concentration of PVK solution

present. To confirm the viscometry data, we tried to determine the optimum polymer concentration of the PVK solution by the zone-drawing method. The structure and physical properties of zone-drawn film may vary with the conditions of preparation and drawing of the film; that is, first, the initial concentration of polymer solution during preparation of the film and also, second, processing parameters such as drawing stress, drawing temperature, and heat band speed during drawing of the film have a marked influence on the drawing behavior of the film. In this study, effects of those factors on the draw ratios of the films were investigated.

Figure 4 shows the zone draw ratios of PVK films drawn under various drawing stresses, a drawing temperature of 180°C, and a heat band speed of 1 mm/min as a function of the initial solution concentrations. The draw ratio increased with increasing drawing stress. Also, the maximum value of 6.2 could be obtained at a drawing stress of 1.26 MPa. This result can be explained as that deformation of molecular chains increases with increasing drawing stress above the glass transition temperature of about 130°C. At 1.26 MPa or above, a brittle breakage of the film occurred. The maximum value of the draw ratio appears at a solution concentration of 9.8 g/dL.

The draw ratio increases with increasing concentration up to 9.8 g/dL, but decreases above this concentration. This is attributed to a suitable number of entanglements for the film prepared at a solution concentration of 9.8 g/dL. Optimum initial concentrations of polymer solutions vary with the molecular weight, linearity, and stereoregularity of polymers and the type of solvent, etc. In this study, however, those effects were negligible because the same types of polymer, with the same molecular weight, and solvent were used in all the experiments. Therefore, it can be supposed that the initial concentration of 9.8 g/dL is the optimum concentration which contains suitable entanglements. The general viscometric method for a determination of the optimum solution concentration is time-consuming; thus, the zone-drawing method could be the better one.

The effect of the drawing temperature on the drawability is shown in Figure 5. The draw ratio increased for each film with increasing drawing temperature. This implies that as the drawing temperature reaches the melting temperature (180°C) of the undrawn PVK film the degree of freedom of the PVK chains increases. The largest value was obtained at a concentration of 9.8 g/dL, so this can be presumed to be the optimum concentration manifesting the highest draw ratio.

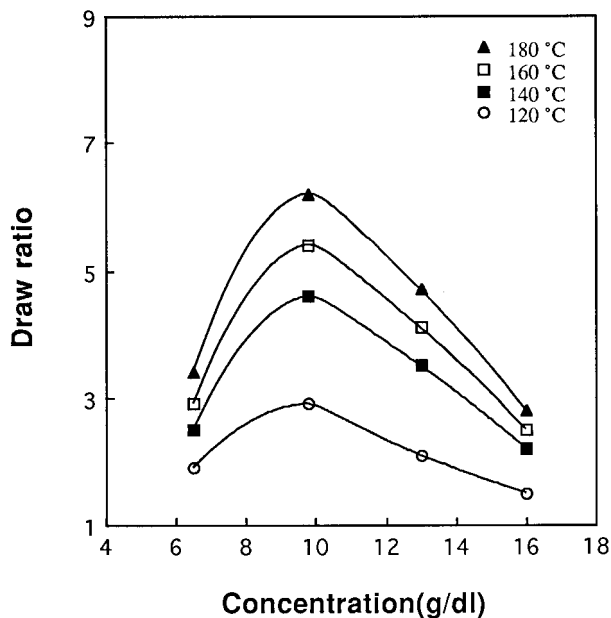


Figure 5 Zone draw ratio of PVK film drawn under various drawing temperatures, a drawing stress of 1.26 MPa, and a heat band speed of 1 mm/min with concentration of PVK solution.

Figure 6 shows the zone draw ratios of PVK films drawn under various heat band speeds, a drawing stress of 1.26 MPa, and a drawing temperature of 180°C as a function of the initial solution concentrations. It was shown that the slower the heat band speed the larger is the draw ratio. This may point to the softening of the film becoming easier owing to a longer residence time for the film between two heat bands; that is, a more uniform heat transfer to the sample of a slower heat band speed had a great effect on the draw ratio of the PVK film. As shown in Figures 4–6, the zone draw ratio of the film prepared at a concentration of 9.8 g/dL was the largest value among all the films prepared at different concentrations. Thus, it was supposed that the film prepared at this concentration had suitable entanglements to attain the maximum draw ratio. Conclusively, it can be predicted that the present method of determining the optimum initial concentration of the PVK solution by the zone draw ratio is correct and suitable.

Dependence of Physical Properties of Film on the Initial Concentration and Draw Ratio

The effect of the initial polymer concentration on the birefringence of the PVK film zone drawn

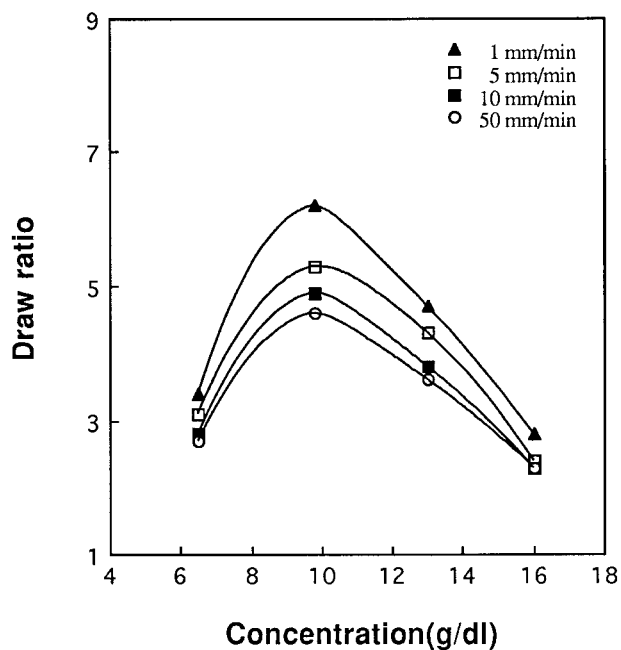


Figure 6 Zone draw ratio of PVK film drawn under various drawing stresses, a drawing stress of 1.26 MPa, and a drawing temperature 180°C with concentration of PVK solution.

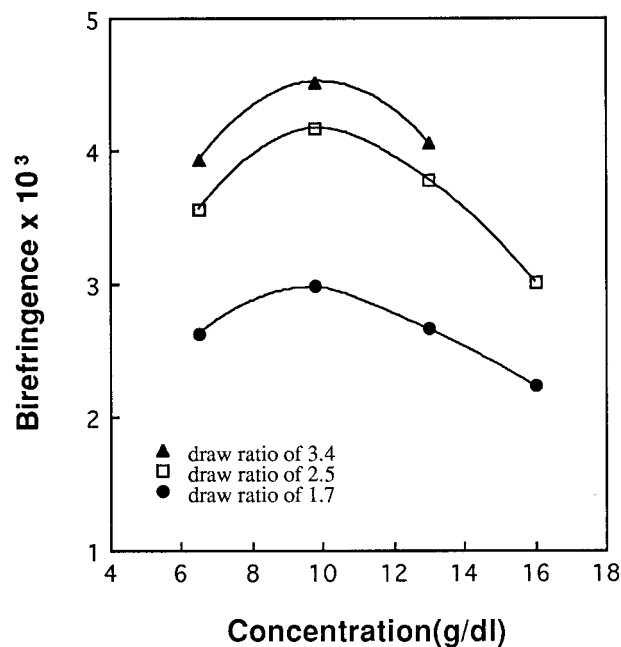


Figure 7 Birefringence of PVK film zone-drawn under various drawing stresses, a drawing temperature of 180°C, and a heat band speed of 1 mm/min with draw ratio.

under various drawing stresses, at a drawing temperature of 180°C, and a heat band speed of 1 mm/min with draw ratios is shown in Figure 7. Nevertheless, specimens having similar draw ratios of about 1.7, 2.5, and 3.4, the effect of the concentration on the birefringence is obvious. It was shown that the maximum birefringence appeared at a solution concentration of 9.8 g/dL. The birefringence increases with the concentration up to 9.8 g/dL, but decreases above this concentration. This demonstrates that the degree of overall orientation of the PVK film cast at 9.8 g/dL, the concentration of maximum drawability, is the highest value among those cast at the other concentrations. Moreover, birefringence of the film increased with increase in the draw ratio. It was thought that much more heat transfer to the sample at a longer drawing time had a great effect on the increment of the birefringence of the film.

Figure 8 compares the crystallinities of PVK films zone-drawn with those hot-drawn under the same drawing conditions with the draw ratios. As the draw ratio increased, crystallinity increased in both the zone and the hot drawings. However, it is interesting to see that the crystallinities of the zone-drawn PVK films were much lower than were those of the hot-drawn PVK films of similar

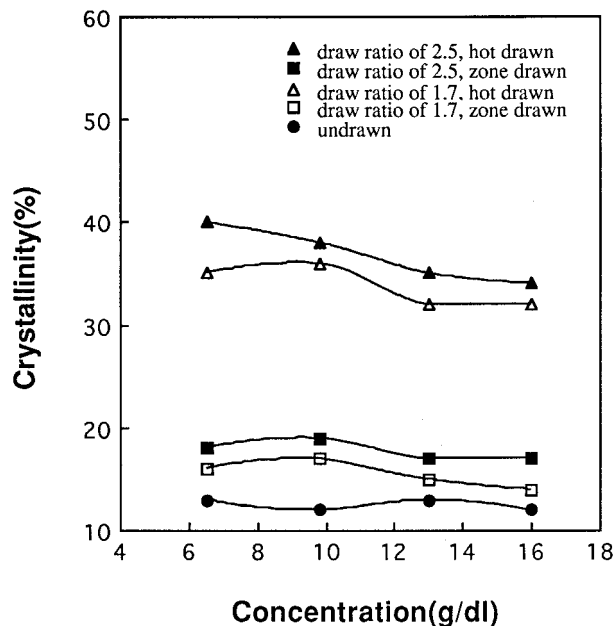


Figure 8 Crystallinities of PVK films zone-drawn and hot-drawn, respectively, with draw ratio.

draw ratios. In Figure 9, it can be seen that this fact is important.

Figure 9 shows the effects of the drawing methods and draw ratios on the degree of lightness of the PVK film. The lightness of the PVK film decreased with an increase in the draw ratios of the films prepared by both drawing methods. This may be explained by the fact that, as the draw ratio was increased, crystallinity also was increased, resulting in a decrease of the lightness of the PVK film. In addition, the lightness of the hot-drawn PVK film was much lower than that of the zone-drawn PVK film. This was because hot-drawing methods have problems such as higher probabilities of microcrystallite formation and crystallization and of back-folding of molecular chains than for the zone-drawing method. Because PVK film is used mostly for photorefractive base materials,⁹⁻¹³ higher lightness of the PVK film for these uses is necessary. Therefore, from the results that the zone-drawing method produces PVK film with a higher lightness, it is expected that the zone-drawn PVK film is a promising base material for photoreactive polymers.

The effect of the initial polymer concentration on (a) the tensile strength and (b) the tensile modulus of the PVK films zone-drawn under various zone-drawing conditions is shown in Figure 10. It is clear that the tensile strength and tensile modulus of the PVK film increased significantly

with the draw ratio. It is also noted from Figure 10 that the tensile strength and tensile modulus of the PVK film showed the maximum value at 9.8 g/dL. The maximum tensile strength and tensile modulus obtained in the PVK film with the maximum draw ratio were 0.48 and 4.3 GPa, respectively. In general, the fact that the film represents a high tensile strength and tensile modulus means that the polymer has a suitable length of tie molecules and a uniform length distribution. The tensile strength and tensile modulus of the PVK film cast at 9.8 g/dL were higher than those of the PVK films cast at other concentrations because the film had suitable tie molecules and a uniform length distribution. The PVK films cast at higher concentrations had too many tie molecules which prevented orientation of the chains, so the tensile strength and the tensile modulus were lowered. The PVK films cast at lower concentrations had fewer tie molecules, so the tensile strength and tensile modulus were lowered due to slippage of the molecular chains. In the case of undrawn PVK film, shattering and crack-formation phenomena, which are undesirable for photorefractive base materials, occurred frequently during the tensile experiments. This was attributed to a lack of toughness of the undrawn film. In contrast, these bad problems disappeared after zone drawing. From the fact that zone-drawn PVK film has a tensile strength and tensile mod-

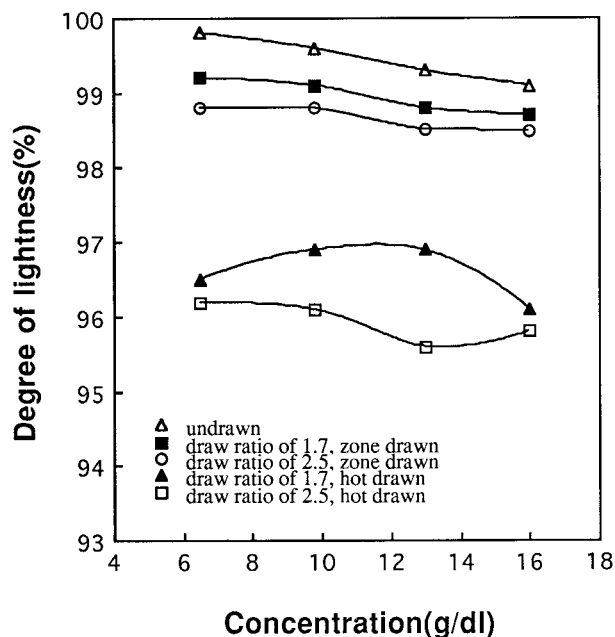


Figure 9 Degree of lightness of PVK films zone-drawn and hot-drawn, respectively, with draw ratio.

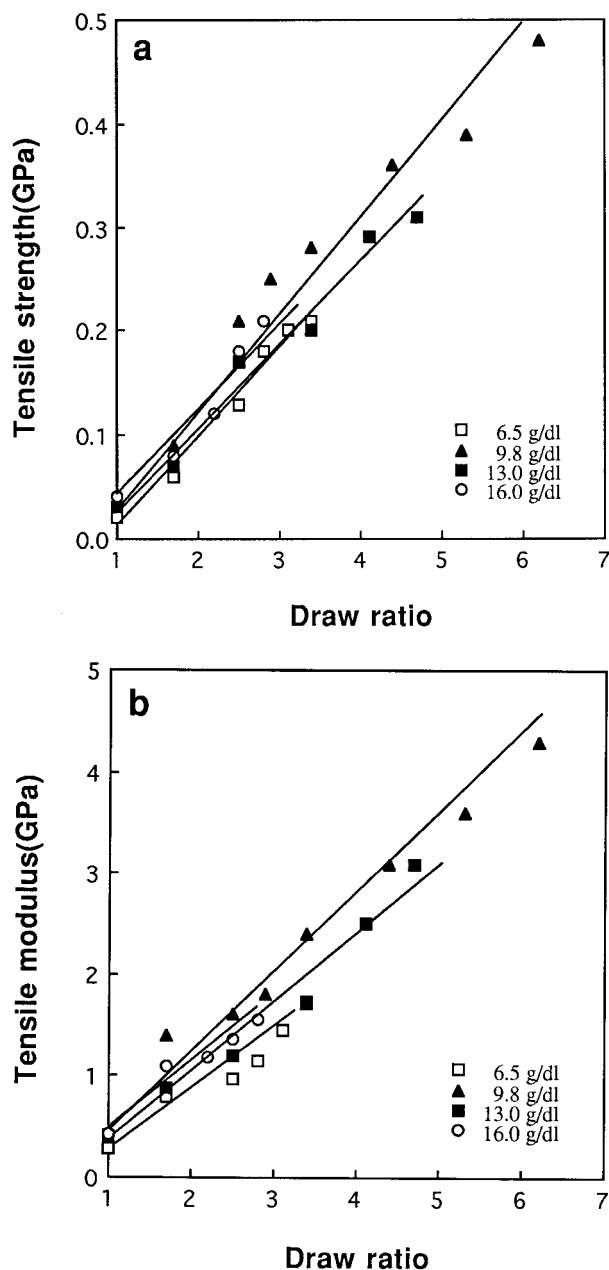


Figure 10 (a) Tensile strength and (b) tensile modulus of PVK film one-step zone-drawn under various zone-drawing conditions with draw ratio.

ulus of about 0.1–0.48 and 0.4–4.3 GPa, respectively, it is concluded that zone drawing and/or the zone-annealing technique is an effective method for preparing PVK film having higher lightness accompanied with good surface uniformity, high durability in high electric field, and suitable toughness, arising from increased mechanical properties.

CONCLUSIONS

The optimum processing conditions for the PVK film were investigated by measuring the birefringence, crystallinity, lightness, and tensile properties, in terms of the initial polymer concentration and draw ratio of the film. PVK films were prepared from TCE solutions with different initial concentrations of 6.5, 9.8, 13.0, and 16.0 g/dL, respectively. To investigate the drawing behavior of the PVK films with different solution concentrations, the films were drawn under various zone-drawing conditions. From several results, it was identified that the initial concentration of the PVK solution in TCE caused significant changes in the draw ratio of the PVK film, that is, the zone draw ratios and tensile properties of the film at the initial concentration of 9.8 g/dL exhibited maximum values and gradually decreased at higher or lower concentrations. The lightness of the zone-drawn PVK film was much higher than that of the hot-drawn PVK film, resulting from diminishing microcrystallite formation, crystallization, and back-folding of molecular chains by the zone drawing. Moreover, the mechanical properties of the PVK film were significantly improved by introducing the zone-drawing technique, maintaining the lightness of the zone-drawn film to a similar degree as to that of the undrawn film. Therefore, it is definitely possible to produce various PVK films having higher lightness and higher orientation accompanied with good surface uniformity, high durability in a high electric field, and high mechanical properties. In the near future, we will report on the preparation and the zone drawing of PVK thick film containing chromophores for photorefractive materials.

This study was supported by the RRC Research Fund. We acknowledge the support with appreciation.

REFERENCES

1. Block, H. *Adv Polym Sci* 1973, 33, 93.
2. Skompska, M.; Hillman, A. R. *J Electroanal Chem* 1997, 433, 127.
3. Touihri, S.; Safoula, G.; Bernede, J. C.; Leny, R.; Alimi, K. *Thin Solid Films* 1997, 304, 16.
4. Ma, D.; Wang, D.; Hong, Z.; Zhao, X.; Jing, X.; Wang, F. *Synth Met* 1997, 91, 331.
5. Adachi, A.; Manhart, S. A.; Okita, K.; Kido, J.; Ohshiya, J.; Kunai, A. *Synth Met* 1997, 91, 333.
6. Yang, Y.; Jiang, H.; Liu, S.; Zhou, X.; Wu, F.; Tian, W.; Ma, Y.; Shen, J. *J Synth Met* 1997, 91, 335.

7. Kusano, H.; Hosaka, S.; Shiraishi, N.; Kawakami, S.; Sugioka, K.; Kitagawa, M.; Ichino, K.; Kobayashi, H. *Synth Met* 1997, 91, 337.
8. Kusano, H.; Shiraishi, N.; Hosaka, S.; Kuruma, I.; Kitagawa, M.; Ichino, K.; Kobayashi, H. *Synth Met* 1997, 91, 341.
9. Sandalphon, J. F.; Wang, B.; Kippelen, N.; Peyghambarian, N. *Appl Phys Lett* 1997, 71, 873.
10. Hendrickx, E.; Volodin, B. L.; Steele, D. D.; Maldonado, J. L.; Wang, J. F.; Kippelen, B.; Peyghambarian, N. *Appl Phys Lett* 1997, 71, 1159.
11. Cheng, N.; Swedek, B.; Prasad, P. N. *Appl Phys Lett* 1997, 71, 1828.
12. Swedek, B.; Cheng, N.; Cui, Y.; Ziega, J.; Winiarz, J.; Prasad, P. N. *J Appl Phys* 1997, 82, 5923.
13. Hendrickx, E.; Wang, J. F.; Maldonado, J. L.; Wolodin, B. L.; Sandalphon, J. F.; Mash, E. A.; Persoons, A.; Kippelen, B.; Peyghambarian, N. *Macromolecules* 1998, 31, 734.
14. Ikawa, T.; Shiga, T.; Okada, A. *J Appl Polym Sci* 1997, 66, 1569.
15. Kamezawa, M.; Yamada, K. *J Appl Polym Sci* 1979, 24, 1227.
16. Kunugi, T.; Akiyama, I. *Polymer* 1982, 23, 1199.
17. Yamada, K.; Takayanagi, M. *J Appl Polym Sci* 1982, 27, 2091.
18. Kunugi, T.; Ohmori, S. *Polymer* 1988, 29, 814.
19. Ji, B. C.; Kim, E. K.; Lee, C. J.; Lyoo, W. S.; Yoon, W. S.; Han, S. S. *Polymer (Korea)* 1995, 19, 846.
20. Han, S. S.; Yoon, W. S.; Choi, J. H.; Kim, S. Y.; Ji, B. C.; Lyoo, W. S. *J Appl Polym Sci* 1997, 66, 1583.
21. Smith, P.; Lemstra, P. J.; Pijpers, J. P. L. *J Polym Sci Polym Phys* 1982, 20, 2229.
22. Garrett, P. D.; Grubb, D. T. *Polym Commun* 1988, 29, 60.
23. Hallam, M. A.; Cansfield, D. L. M.; Ward, I. M.; Pollard, G. *J Mater Sci* 1986, 21, 4199.
24. Lyoo, W. S.; Han, S. S.; Choi, J. H.; Cho, Y. W.; Ha, W. S. *J Kor Fiber Soc* 1995, 32, 1023.
25. Sawatari, C.; Okumura, T.; Matsuo, M. *Polym J* 1986, 18, 741.
26. Bastiaansen, C. W. M. *J Polym Sci Polym Phys* 1990, 28, 1475.
27. Liu, B. L.; Murakami, N.; Sumita, M.; Miyasaka, K. *J Polym Sci Polym Phys* 1989, 27, 2441.
28. Nunes, R. W.; Martin, J. R.; Johnson, J. F. *Polym Eng Sci* 1982, 22, 205.
29. Douglas, M. J. F.; Freed, F. *Macromolecules* 1983, 16, 741.
30. Ji, B. C.; Yoon, W. S.; Kim, S. Y. *J Kor Fiber Soc* 1993, 30, 379.
31. Kim, S. Y.; Han, S. S. *J Kor Fiber Soc* 1994, 31, 912.
32. Ji, B. C.; Yoon, W. S.; Kim, S. Y. *J Kor Fiber Soc* 1993, 30, 328.
33. Han, S. S.; Lyoo, W. S.; Cho, J. H.; Park, S. K.; Ji, B. C.; Ha, W. S.; Lee, C. J. *Polymer (Korea)* 1996, 20, 228.
34. Choi, J. H.; Cho, Y. W.; Ha, W. S.; Lyoo, W. S.; Lee, C. J.; Ji, B. C.; Han, S. S.; Yoon, W. S. *Polym Int* 1998, 47, 237.
35. Kwag, M. G.; Rhee, J. M.; Han, S. S.; Lyoo, W. S.; Kim, B. C.; Lee, C. J. *Polymer (Korea)* 1996, 20, 849.
36. Han, S. S.; Yoon, W. S.; Lyoo, W. S.; Lee, C. J.; Ghim, H. D.; Han, Y. A.; Ji, B. C. *Polymer (Korea)* 1996, 20, 1049.
37. Rabek, J. F. In *Experimental Methods in Polymer Chemistry*; Rabek, J. F., Ed. Wiley: New York, 1985.