

Combined Processing of Polypropylene Film by Coextrusion and Zone-Annealing

TOSHIO KUNUGI,*¹ YUKO YONEYAMA,¹ AKIHIRO SUZUKI,¹ and ROGER S. PORTER²

¹Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Yamanashi University 4-3-11 Takeda, Kofu 400 Japan and ²Polymer Science and Engineering Department and Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003

SYNOPSIS

In order to improve the mechanical properties of polypropylene film, a new processing combining extrusion and zone-annealing has been applied. It was found that there are suitable conditions for each step in the combined processing. When the coextrusion draw ratio was low, the total draw ratio and modulus could be increased by the zone-annealing subsequently done. The highest modulus was obtained when the film was coextruded at extrusion draw ratio 4 and then zone-annealed at 120°C under 7 kg/mm². The value was 12 GPa in Young's modulus or 17 GPa in dynamic modulus. The peak temperature of α_c dynamic dispersion for the combinedly processed film was 109°C, which is higher by 10°C than that for the as-coextruded film. Four drawing methods were compared in dynamic viscoelasticity. These methods are the coextrusion, zone-drawing/zone-annealing, two-step coextrusion, and the combined processing by coextrusion and zone-annealing. The highest dynamic modulus for each method was arranged in the above order. The combined processing indicated the most effective improvement in mechanical properties, because it is believed that lamellae in the original film were broken by cooperating interaction of shear stress, compression, and tension on coextrusion and then the superstructure with a high crystallinity and a high molecular orientation was formed on zone-annealing.

INTRODUCTION

The coextrusion method was developed by Porter and his co-workers and has been applied to a variety of polymers, such as polyethylene,¹ poly(ethylene terephthalate) (PET),² polystyrene,³ nylon,⁴ and poly(vinylidene fluoride).⁵ Further, Kanamoto et al.^{6,7} developed the two-step drawing method, in which a film was first coextruded and then was hot-drawn. In particular, it was an outstanding contribution to high-modulus polymer science that the Kanamoto and Porter groups⁶ had reached an ultrahigh modulus of 222 GPa from an ultrahigh molecular weight polyethylene single-crystal mat by this method. Afterward, they successfully applied this technique to some polymer films.

We also developed the zone-drawing/zone-annealing method⁸ in 1979. The method has remarkable effects in improving mechanical properties and increasing dimensional stability. The method has been applied to many kinds of polymers, e.g., flexible chain polymers, such as nylon 6,⁹⁻¹¹ polyethylene,^{12,13} PET,¹⁴⁻¹⁶ and poly(vinyl alcohol),¹⁷ and heat-resistant polymers, such as poly(ether ether ketone)¹⁸⁻²¹ and polyimide²¹ in both fiber and film forms. We reported on the applications of zone-drawing/zone-annealing²² and coextrusion²³ to polypropylene fiber and film.

In the present study, we have combined both methods and have examined the superstructure and mechanical properties of the films obtained at each step.

EXPERIMENTAL

The original material was as-extruded and unstretched polypropylene film of about 90 μm thick-

* To whom correspondence should be addressed.

ness supplied by Toray Co. Ltd. The film has a crystallinity of 53.5% and a birefringence of 14×10^{-5} .

The coextrusion was carried out at 120°C and at a plunger speed of 1 mm/min on a strip of 2 mm width and 90 mm length that was cut from the original film. The strip was interposed between half-cut billets of polyethylene. The dies with various ratios of inlet-diameter-to-outlet-one were used. The extrusion draw ratio is here abbreviated as EDR. In this study, the dies of EDR 2, 3, 4, 5, 6, 7, 8, 9, and 10 were used. Figure 1 shows schematically the coextrusion apparatus and the zone-annealing apparatus.

The zone-annealing was carried out on the coextruded film by moving a narrow heater along the film under a tension of 7 kg/mm². The temperature and moving speed of the heater were 120°C and 100 mm/min, respectively. The zone-annealing was repeated six times under the same conditions. Only the films coextruded at EDR 2 and 3 were zone-drawn before zone-annealing, because these films were still soft and severed on zone-annealing. The conditions used were at 70–110°C under 1 kg/mm², at 100 mm/min. Birefringence, density, X-ray diffraction pattern, tensile properties, and dynamic viscoelasticity were measured.

Table I Draw Ratios on Coextrusion and Zone-Annealing and Total Draw Ratios at Each EDR Film

EDR Used	Real Draw Ratio on Coextrusion	Draw Ratio on Zone-Annealing	Total Draw Ratio
2	1.80	6.55	11.79
3	2.76	4.09	11.29
4	3.66	3.15	11.53
5	4.54	2.49	11.30
6	5.44	1.97	10.72
7	6.18	1.53	9.46
8	7.00	1.44	10.08
9	7.76	1.14	8.85
10	8.78	1.16	10.18

RESULTS AND DISCUSSION

Draw Ratio

The coextruded films were prepared using dies of EDR 2–10, namely, nine kinds. Above EDR 11, the original film broke into flakes. Real draw ratios on coextrusion are always smaller than the EDR used, because the deformation of the films did not follow

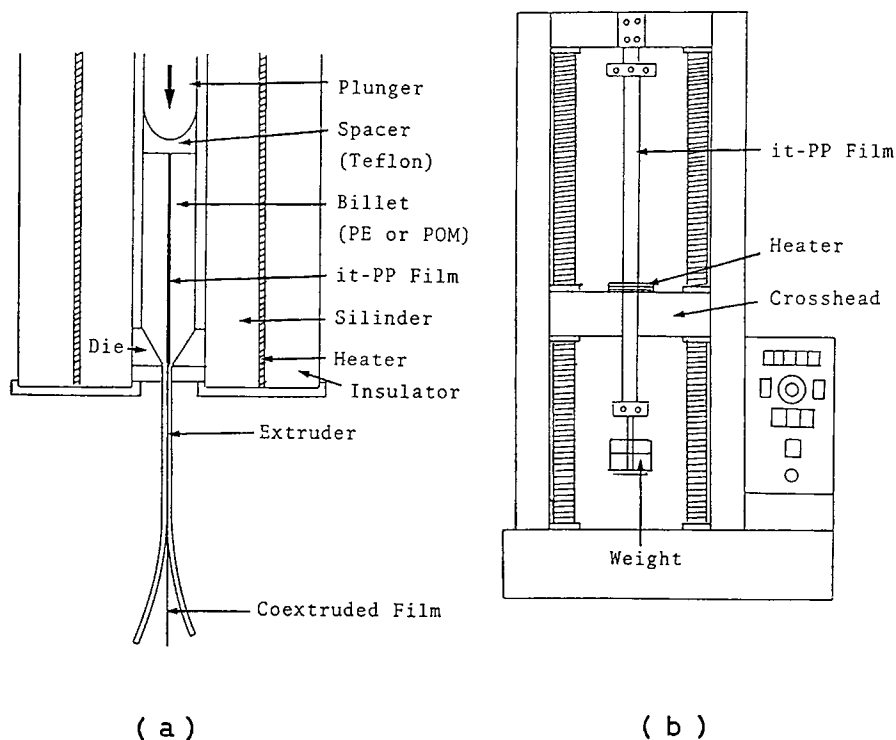


Figure 1 Schematic pictures of the apparatus for coextrusion (a) and zone-annealing (b).

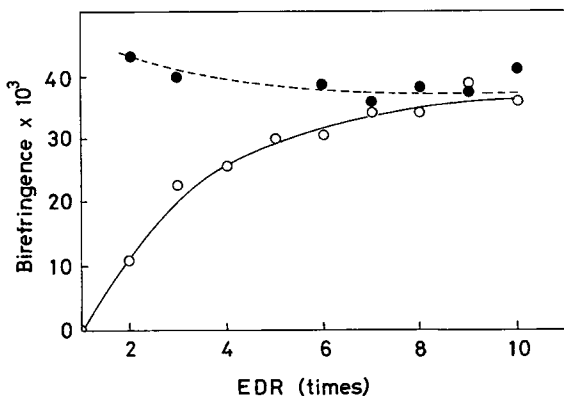


Figure 2 Birefringence of the coextruded films (\circ) and the coextruded and zone-annealed films (\bullet).

the flow of billets. When the coextruded films were zone-annealed, the draw ratios were further increased. Total draw ratio is the product of the real draw ratio on coextrusion and the draw ratio on zone-annealing. These draw ratios are listed in Table I.

It can be seen that when EDR is low the extruded film can be easily drawn on zone-annealing and the total draw ratio reaches above 11. On the other hand, when EDR exceeds 6, the total draw ratio is around 10. Kanamoto et al.^{6,7} also reported similar results in a two-step processing comprising coextrusion and

hot-drawing for several polymers. In the case of a single-crystal mat of ultrahigh molecular weight polypropylene, the film coextruded at EDR 6 indicated the highest drawability on subsequent hot-drawing. The film thus obtained had a high modulus of 33 GPa and a high strength of 1.5 GPa.

Birefringence and X-Ray Diffraction Pattern

Figure 2 shows the birefringence for the coextruded films and the coextruded and zone-annealed films as a function of EDR. As EDR became lower, the birefringence was clearly increased by zone-annealing. At above EDR 6, the increments of birefringence by zone-annealing were small. However, the birefringence values after zone-annealing are near or over 40×10^{-3} , which is higher than the maximum value of 36.9×10^{-3} for the zone-drawn/zone-annealed fiber.²² The value also is higher than the crystal intrinsic birefringence (33.1×10^{-3}) and close to the amorphous one (46.8×10^{-3}) that were reported by Sammuels.²⁴ This fact indicates that the combined processing has a fairly high effect on the molecular orientation.

Figure 3 shows wide-angle X-ray diffraction photographs for the original film, the films coextruded at EDR 2 and 8, and the films zone-annealed after the coextrusions. Because the film coextruded at

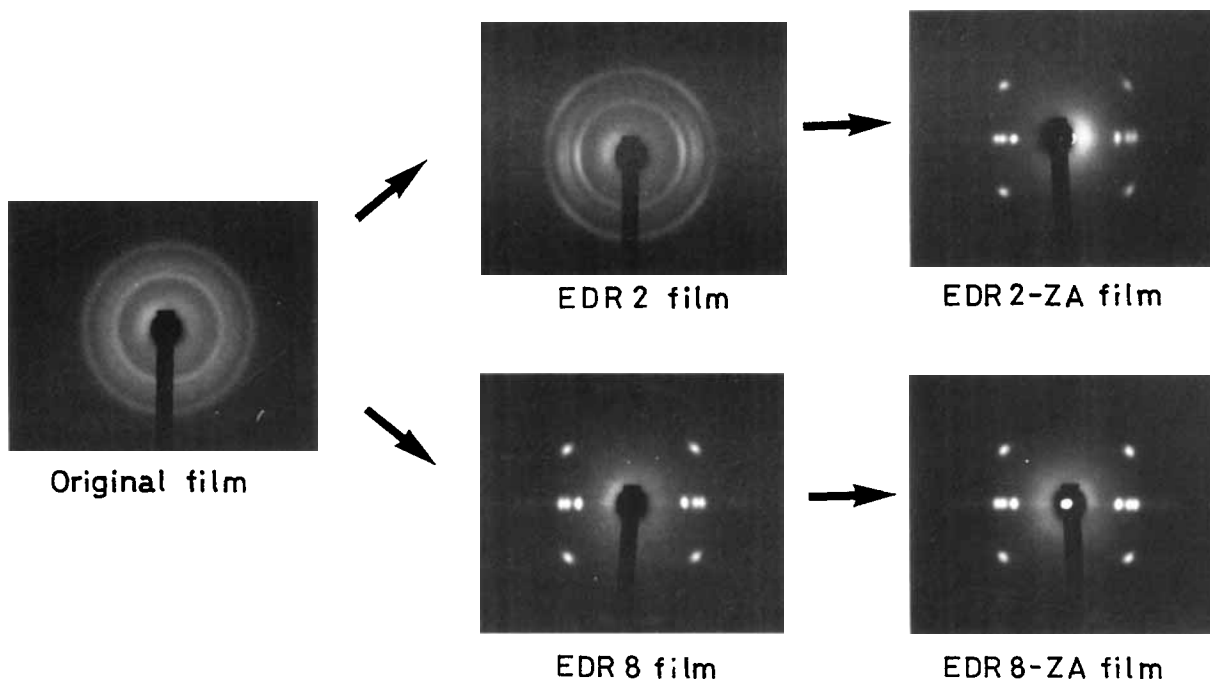


Figure 3 Wide-angle X-ray diffraction photographs of the coextruded films and the coextruded and zone-annealed films.

Table II Tensile Properties of Coextruded with Various EDR and Subsequently Zone-Annealed Films

Sample	Young's Modulus (GPa)	Strength at Break (kg/mm ²)	Elongation at Break (%)
Original film	1.1	—	—
Coextruded (2)-ZD, ZA	11.1	68.5	12.2
Coextruded (3)-ZD, ZA	12.3	74.5	9.5
Coextruded (4)-ZA	11.5	81.3	11.8
Coextruded (5)-ZA	11.3	70.0	11.2
Coextruded (6)-ZA	11.1	65.5	15.8
Coextruded (7)-ZA	11.5	74.1	20.4
Coextruded (8)-ZA	7.8	61.6	12.3
Coextruded (9)-ZA	8.0	69.3	13.6
Coextruded (10)-ZA	8.8	55.8	11.7

EDR 8 had already reached a high orientation level, the crystallite orientation scarcely increased by zone-annealing. However, the film coextruded at EDR 2 is rapidly increased in crystallite orientation by zone-annealing. It is of importance for improving mechanical properties, as described below, that the superstructure before zone-annealing is moderately loose.

Tensile Properties

Table II shows Young's modulus, tensile strength, and elongation at break for the original film and the films that were zone-annealed after coextrusion at various EDR. In the same manner as the total draw ratio, the films coextruded with the dies of low EDR, i.e., 2–7, have high Young's moduli of 11–12 GPa after zone-annealing. However, the dependencies of tensile strength and elongation at break on the EDR used on coextrusion are not clear. The highest strength value of 81.3 kg/mm² is superior to the 75.8 kg/mm² for the zone-drawn/zone-annealed fiber²² and is fourfold greater than the 14–24 kg/mm² for commercial films.

In Figure 4, Young's moduli for the films before and after zone-annealing are compared as a function of EDR. Up to EDR 7, Young's modulus was greatly increased by zone-annealing and kept at a constant value of 11–12 GPa. Because Young's modulus of the as-coextruded films is increased with increasing EDR, it can be said that the increments of Young's modulus by zone-annealing are decreased as EDR becomes higher. However, above EDR 8, Young's modulus was suddenly restricted to around 8 GPa. This restriction results from the formation of a fairly rigid superstructure on coextrusion with too high EDR. The tensile strength also had changed in a similar feature to Young's modulus just described.

The elongation at break for as-coextruded films decreased with increasing EDR, but the values of the films after zone-annealing were restricted in the range of 10–20% at any EDR.

Dynamic Viscoelasticity

Figure 5 shows the temperature dependence of dynamic modulus E' and loss modulus E'' for the coextruded and zone-annealed films. In the case of as-coextruded films that were reported in the previous paper,²³ E' was increased with increasing EDR. However, when the coextruded films were further zone-annealed, the order of E' was reversed as seen in Figure 5. The E' value becomes larger as EDR is small in the range of EDR 4–10. Only the moduli of the films coextruded at EDR 2 and 3 are slightly smaller than that at EDR 4. In the case of EDR 10, the increment of E' by zone-annealing was only 3 GPa at room temperature. A crystalline dispersion

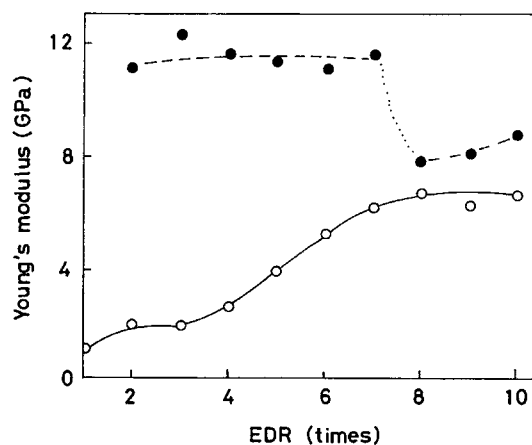


Figure 4 Young's modulus of the coextruded films (○) and the coextruded and zone-annealed films (●).

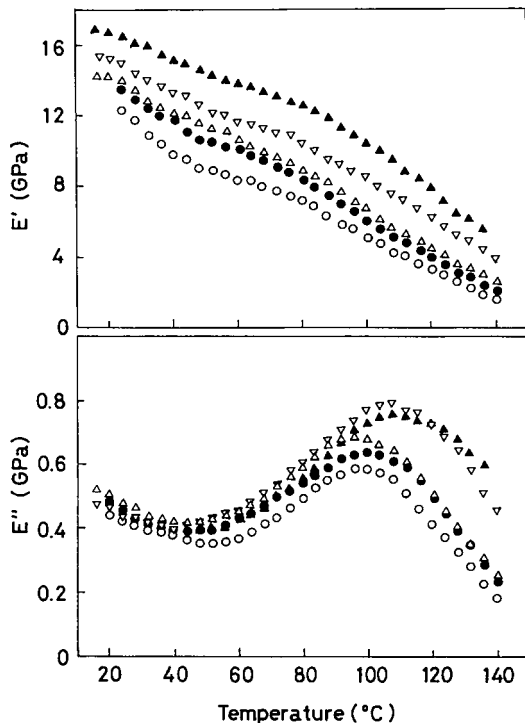


Figure 5 Temperature dependencies of dynamic modulus (E') and loss modulus (E'') for the coextruded and zone-annealed films: EDR 2-ZA (∇); EDR 4-ZA (\blacktriangle); EDR 6-ZA (\triangle); EDR 8-ZA (\bullet); EDR 10-ZA (\circ).

peak (α_c peak) occurs in the vicinity of 100°C in E'' -temperature curves. The intensity of the E'' peaks is arranged in a similar order to the E' , namely, the peak intensity becomes larger and the peak temperature also shifts to higher temperatures from 100 to 109°C with decreasing EDR from 10 to 4.

Furthermore, both the intensity and temperature of these E'' peaks are much larger than those for the as-coextruded films. In Figure 6, for example, the temperature dependencies of E' and E'' for the film coextruded at EDR 4 are compared with those for the film after zone-annealing. Both E' and E'' were greatly increased by zone-annealing. The E' for the film after zone-annealing is 17 GPa at room temperature, 10.5 GPa at 100°C , and 5 GPa even at 120°C . It must be noted that the modulus keeps to an exceedingly high level at elevated temperatures. In general, this is an important characteristic of zone-drawn and zone-annealed fibers or films. It is clear from Figure 6 that the α_c peak in the E'' -temperature curve was strikingly increased by zone-annealing. The α_c peak cannot be found in the curve for the as-coextruded film, but appeared at 109°C as a broad and large peak in the curve for the coextruded and zone-annealed film. The temperature

position is higher by 19°C than that of the zone-drawn and zone-annealed fiber (90°C).²² It is supposed that the crystallites formed by zone-annealing are made of rigid crystals and suppress molecular movements in the crystals.

Comparison of the Combined Processing with Three Other Drawing Methods

In Figure 7, the maximum E' values for the films obtained by four kinds of drawing methods are compared together with that of the original film. These films are the coextruded film, the zone-drawn/zone-annealed film, the two-step coextruded film, and the coextruded and zone-annealed film. The E' -temperature curves are aligned, increasing the E' in the order described above. These curves do not intersect each other in the whole temperature range measured. It is clear that the combined processing has the most outstanding effect on improving the mechanical properties. In the case of the combined processing, such as coextrusion and zone-annealing or coextrusion and hot-drawing, it is necessary that the coextrusion is always performed on the original films

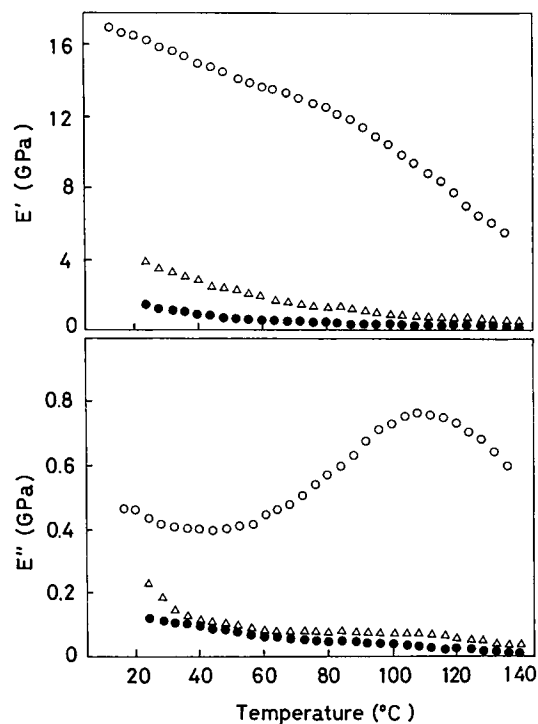


Figure 6 Effect of zone-annealing on the dynamic modulus in the case of the film coextruded with EDR 4: the original film (\bullet); the film coextruded with EDR 4 (\triangle); the film coextruded with EDR 4 and zone-annealed (\circ).

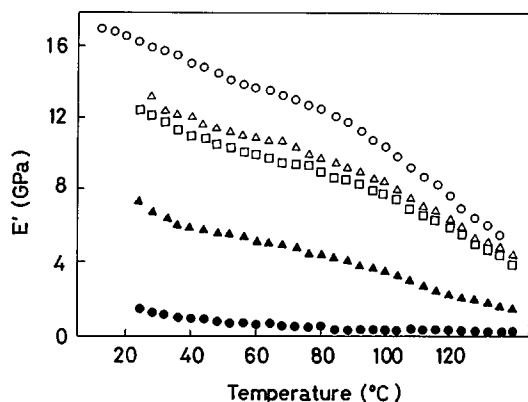


Figure 7 Comparisons between maximum dynamic moduli of the films that were prepared by four kinds of drawing methods: the coextruded film (EDR 10) (\blacktriangle); the zone-drawn/zone-annealed film (\square); the two-step coextruded film (EDR 7-EDR 2) (\triangle); the coextruded (EDR 4) and zone-annealed film (\circ); and the original film (\bullet).

before further drawing. If not so, the films are broken into small flakes. When the zone-drawn films are coextruded, the deformation of the films cannot follow the deformation of the billets. The coextrusion possesses a characteristic mechanism of the stretching deformation. As can be seen from Figure 1(a), the film interposing between the billets receives a strong combined force of compression, shear stress, and stretching stress during passing the die. Such a complicated force becomes stronger as the die diameter is decreased. The force acts on crystallites rather than on the amorphous phase, because their hardnesses differ greatly. The lamellae selectively deform, tilt, break, and partially unfold. The resulting structure is fairly homogeneous and more favorable to subsequent zone-drawing or hot-drawing. It is interesting that Kanamoto et al.^{6,7} obtained similar results for different combinations of coextrusion and hot-drawing.

CONCLUSIONS

The combined processing of coextrusion and zone-drawing has been applied to polypropylene films. The improvements in drawability, orientation, and mechanical properties were investigated, and the following conclusions were obtained:

1. As the EDR used on coextrusion is low, the drawability, orientation, and mechanical properties have been remarkably increased by subsequent zone-annealing.

2. Film that was coextruded at EDR 4 and then zone-drawn at a heater temperature of 170°C under a tension of 7 kg/mm² indicated a high draw ratio of 11 and a high birefringence of 40×10^{-3} .
3. The film has Young's modulus of 12 GPa, a tensile strength of 81.3 kg/mm², and an elongation at break of 11.8%. These mechanical properties are much better than are the maximum values of the as-coextruded films, i.e., 7 GPa, 52.1 kg/mm², and 62.5%, respectively.
4. The dynamic modulus of the film shows 17 GPa at room temperature, 10.5 GPa at 100°C, and 5 GPa at 120°C, indicating, especially, the excellent high-temperature performance.
5. The α_c peak in E'' -temperature curve of the film is high in both the intensity and temperature position. In particular, the peak temperature was 109°C, which is higher by 9°C than is the maximum peak temperature (100°C) of the as-coextruded films previously reported.²³
6. Such excellent effects of the combined processing on improving the mechanical properties result from the first deformation taking place during coextrusion. During coextrusion, the compression, shear stress, and stretching stress acts strongly and selectively on the lamellae in the original film. The coextruded film can be more easily zone-drawn than can the non-coextruded films.

The authors thank Toray Co. Ltd. for supplying the original films. This research was supported in part by a grant from the scientific research funds (B) of the Ministry of Education, Japan.

REFERENCES

1. P. D. Griswold, A. E. Zachariades, and R. S. Porter, *Polym. Eng. Sci.*, **18**, 861 (1978).
2. J. R. C. Pereira and R. S. Porter, *J. Polym. Sci. Phys. Ed.*, **21**, 1133 (1983).
3. A. E. Zachariades, E. S. Sherman, and R. S. Porter, *J. Appl. Polym. Sci.*, **24**, 2137 (1979).
4. A. E. Zachariades and R. S. Porter, *J. Appl. Polym. Sci.*, **24**, 1371 (1979).
5. T. Shimada, A. E. Zachariades, W. T. Mead, and R. S. Porter, *J. Cryst. Growth*, **48**, 334 (1980).
6. T. Kanamoto, A. Tsuruta, K. Tanaka, M. Takeda, and R. S. Porter, *Polym. J.*, **15**, 327 (1983).
7. T. Kanamoto, A. Tsuruta, and K. Tanaka, *Polym. J.*, **16**, 75 (1984).

8. T. Kunugi, A. Suzuki, I. Akiyama, and M. Hashimoto, *Polym. Prepr. Am. Chem. Soc.*, **20**, 778 (1979).
9. T. Kunugi, I. Akiyama, and M. Hashimoto, *Polymer*, **23**, 1193 (1982).
10. T. Kunugi, I. Akiyama, and M. Hashimoto, *Polymer*, **23**, 1199 (1982).
11. T. Kunugi, T. Ikuta, M. Hashimoto, and K. Matsuzaki, *Polymer*, **23**, 1983 (1982).
12. T. Kunugi, I. Aoki, and M. Hashimoto, *Kobunshi Ronbunshu*, **38**, 301 (1981).
13. T. Kunugi, S. Oomori, and S. Mikami, *Polymer*, **29**, 814 (1988).
14. T. Kunugi, A. Suzuki, and M. Hashimoto, *J. Appl. Polym. Sci.*, **26**, 213 (1981).
15. T. Kunugi, A. Suzuki, and M. Hashimoto, *J. Appl. Polym. Sci.*, **26**, 1951 (1981).
16. T. Kunugi, C. Ichinose, and A. Suzuki, *J. Appl. Polym. Sci.*, **31**, 429 (1981).
17. T. Kunugi, T. Kawasumi, and T. Ito, *J. Appl. Polym. Sci.*, **40**, 2101 (1990).
18. T. Kunugi, A. Mizushima, and T. Hayakawa, *Polymer Commun.*, **27**, 175 (1988).
19. T. Kunugi, T. Hayakawa, and A. Mizushima, *Polymer*, to appear.
20. T. Kunugi, in *First Pacific Polymer Conference, Hawaii*, Preprints, 1989, Vol. 1, p. 95.
21. T. Kunugi, in *Proceedings of the MRS International Meeting on Advanced Materials*, Tokyo, 1988, Vol. 1, p. 201.
22. T. Kunugi, T. Ito, and M. Hashimoto, *J. Appl. Polym. Sci.*, **28**, 179 (1983).
23. T. Kunugi, Y. Yoneyama, and R. S. Porter, *J. Appl. Polym. Sci.*, to appear.
24. R. J. Samuels, *J. Polym. Sci. A.*, **3**, 1741 (1965).

Accepted November 27, 1990