

Rolling and Roll-Drawing of Ultrahigh Molecular Weight Polyethylene Reactor Powders

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SYNOPSIS

Ultrahigh molecular weight polyethylene (UHMWPE) reactor powders have been found to be processable in the solid state by the techniques of rolling and roll-drawing. Plates of compacted UHMWPE reactor powder were prepared below their melting points. These plates were then rolled at 124°C. The maximum uniaxial draw ratio (DR) obtained by multiple rolling was about 10. In additional experiments, rolled plates of a DR of 6 were further drawn by tensile stretching at a temperature of 135°C. The specimens prepared by rolling and by the two-stage draw were characterized by tensile measurements, differential scanning calorimetry (DSC), and X-ray diffraction. Results show that, on rolling alone, the tensile modulus and tensile strength achieved were 3 GPa and 42 MPa, respectively, at a DR of 9.6. The rolled plates were effectively drawn further to a total DR of 86. Such highly drawn films exhibited tensile moduli and tensile strength up to 81 and 1.3 GPa, respectively. A high crystallinity and high crystal orientation were also obtained by the two-stage draw.

INTRODUCTION

The deformation of polyethylene (PE) has been an extensively studied process. This is because its mechanical properties in draw directions are superior to those of the isotropic state. The tensile modulus and strength of a polymer chain depend on its force constants for bond-stretching and bending. These values can be calculated theoretically and estimated experimentally. For PE, the single-chain elastic modulus has been calculated using complex field theory to be 340 GPa.^{1,2} The experimental values for PE crystals are reported to be 290 GPa by Raman^{3,4} and 235 GPa by X-ray techniques.⁵ It is also known experimentally that the achievable optimum draw ratio increases with PE molecular weight.^{6,7}

With the goal of achieving improved properties, polyethylene of ultrahigh molecular weight (UHMWPE) has been subjected to study. The melt index of UHMWPE approaches zero, limiting its

processing by the usual methods, such as melt injection molding and extrusion. Independently, we have demonstrated that a commercial UHMWPE reactor powder can be drawn by solid-state coextrusion^{8,9} even in a single step at 110°C up to a draw ratio (DR) of 56.⁸ In contrast, extrusion draw of melt-crystallized UHMWPE proceeds only up to a DR 5, even at temperature as high as 136°C, which approaches the PE melting point.

Kanamoto et al. have reported that, by a two-stage drawing technique, UHMWPE reactor powder can be drawn up to a ratio of 77 at 120–135°C.¹⁰ Such drawn films exhibited tensile moduli up to 107 GPa. A limitation of this technique is the difficulty in producing samples of large dimensions.

Rolling is known to affect the physical and mechanical properties of polymers. Its advantages over extrusion are scale and speed. Several studies have been published on the rolling of UHMWPE.^{11–15} The mechanical properties, the crystal orientation, and the microstructure of hot-rolled and quench-rolled UHMWPE have been investigated by Kaito et al.¹² It was found that the tensile strength of rolled UHMWPE sheet increases with DR. Later in 1985, a roller draw method was reported for a high-density PE of conventional molecular weight. The Young's

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modulus and tensile strength attained reached 43 and 0.67 GPa, respectively, at the highest DR.¹⁵ Han et al. reported their results on rolling Hercules 1900 PE powder. The modulus and strength increased in the rolling direction. The maximum tensile modulus was 8.5×10^4 psi, corresponding to 0.58 GPa.¹⁴

Evolving from our solid-state coextrusion techniques,¹⁶ a new approach for processing UHMWPE, a solid-state roll-drawing method, has been developed. UHMWPE films with a Young's modulus of 81 GPa and tensile strength of 1.3 GPa have been prepared by processing at temperatures lower than their melting point.

EXPERIMENTAL

The as-received UHMWPE (Hercules, Inc., Hifax 1900 $M_v = 3.96 \times 10^6$) reactor powder was compression molded into plates of 1 mm thick at 150 kg/cm² at 110°C for 10 min. This is 30°C below the DSC melting peak temperature. Plates were cut into strips 10 mm wide and 65 mm long in preparation for the rolling experiment.

The rolling was done on a Stanet calendar with two 26 cm diameter rollers, each of which rotates in the opposite side with equal speed. On rolling, there was only a small increase of sample width. The uniaxial DR for rolling of a strip was determined from the displacement of an ink mark preimprinted transversely on the strip surface.

For rolling, a strip of the compacted UHMWPE powder plate is sandwiched in aluminum foil. The plate is then inserted into the slit between the rollers. The turning speed of the rollers was set at 30 cm/min. The rollers were preheated to 124°C, 16°C below the peak melting point of the PE strip. To obtain a high DR, the rolling was repeated many times in the same direction with reduction of the slit width after every pass. For the purpose of getting possibly even a higher DR for the specimen, the rolled strip was further second-stage drawn; that is, the rolled films of 40 mm length were stretched in tension in an Instron tester Model 1321, equipped with a temperature control chamber. This second-stage drawing was done at a constant temperature of 135°C and a strain rate of 200%/min. The total draw ratio (TDR) was calculated by multiplying the DR by the subsequent DR achieved at the second-stage stretch.

The mechanical properties of deformed samples were characterized by the tensile modulus and strength that were measured at room temperature at a strain rate of 1×10^{-3} /s and 1×10^{-2} /s, respectively. The moduli were determined from the slope of the stress-strain curve at low (0.1%) strain.

The thermal behavior of samples were studied by a DSC-4 Perkin-Elmer differential scanning calorimeter (DSC) at a low heating rate of 5 K/min to avoid superheating effects.

RESULTS AND DISCUSSION

Rolling Process

The compacted UHMWPE reactor powder was successfully rolled to relatively high DRs, resulting in tapes with varying degrees of orientation. The uniformity of the rolled tapes was significantly affected both by the rolling temperature and turning speed of the rollers. At temperatures higher than their peak melting point, the samples after passing through rollers release a fraction of elastically stored energy. In consequence, the thickness of the tape increased. A high DR was thus not obtained directly. At much lower roll temperatures, say 90°C, the chain orientation achieved was negligible due to the slow rearrangement of molecular chain, as compared with samples of the same nominal DR prepared at 124°C. Samples rolled at this low temperature with a broken edge were obtained. The rate of deformation at the lower temperature was apparently too rapid to achieve the desired morphological conversion on draw. The turning speed of rollers is also important for getting a uniform sample. When the turning speed of the rollers was increased up to about 100 cm/min at 124°C, corrugations and broken samples resulted. The oriented molecular chains in the rolled sample relaxed more when processed at too low a speed.

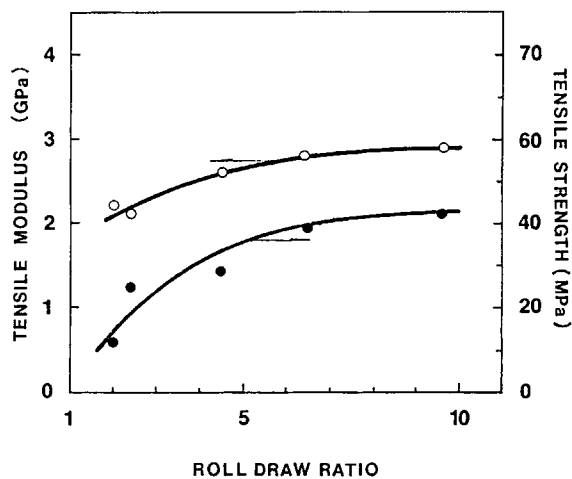


Figure 1 The tensile modulus (open circles) and tensile strength (solid circles) as a function of DR for plates of rolled UHMWPE reactor powder plates.

Under the experimental conditions selected, the rolling limit for compacted UHMWPE reactor powder was a DR of 9.6, maximized at an intermediate temperature of 124°C. An increase in transparency was noted as the DR was increased and as thinner tapes were produced.

Figure 1 shows the tensile modulus as a function of DR for rolled plates of compacted UHMWPE reactor powder. The modulus increases gradually with DR, reaching 2.9 GPa. The value is higher than that reported for UHMWPE prepared by the same technique of rolling,^{12,14} but lower than that for samples prepared by solid-state coextrusion.⁸ The tensile strength increases with DR of rolling, as shown in Figure 1. The maximum is 42 MPa, which is lower than that achieved by Kaito et al.¹² This is because, at this stage of rolling, the molecular chains have insufficient coherency to exhibit high strength. This is confirmed by the shrinkage study discussed in the following paragraph.

It has been shown that the elastic recovery of drawn PE can be a sensitive and quantitative measure for the efficiency of draw.^{17,18} The correlations of this property with morphology and tensile modulus have been discussed. We have thus measured the thermally induced elastic recovery for each sample rolled at 124°C. When a rolled specimen was immersed and freely floated in a silicon oil bath kept at 220°C, elastic shrinkage quickly occurred, being complete within seconds. The efficiency of rolling was evaluated in terms of the ratio of molecular draw ratio (MDR) to the macroscopic deformation defined previously^{17,18}:

$$EFF = \frac{L_t - (L_s - L_0)}{L_t}$$

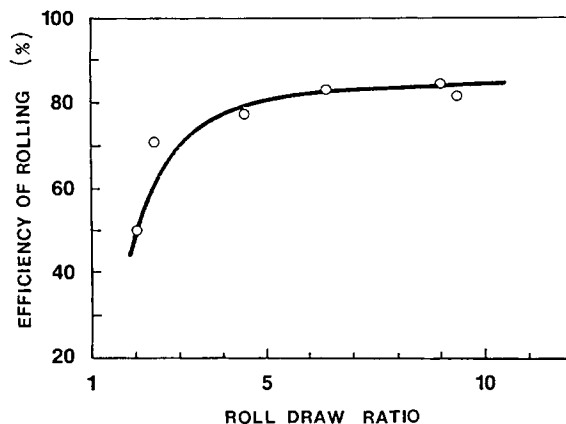


Figure 2 The efficiency of draw by rolling as a function of DR for rolled powder plates.

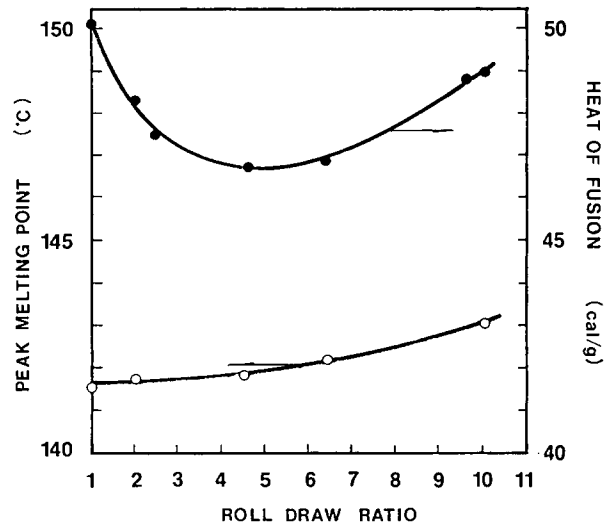


Figure 3 The peak melting temperature (open circles) and heat of fusion (solid circles) as a function of DR for rolled plates of reactor powder.

where L_0 is the sample length prior to draw, L_t is the total length after draw, and L_s is the shrunken length after recovery (see Fig. 2). At the lowest DR, molecular extension was about 50% of the macroscopic sample DR, reflecting an insufficient coherency of the reactor powder in the compression-molded plate. On increasing DR, the efficiency increased rapidly, plateauing at about 84%. This increase is attributed to the coherency of the particles during the roll deformation. This feature may be why the tensile strength of our sample is significantly lower than that obtained from melt rolling.¹²

The melting peak temperature and heat of fusion as a function of DR for compacted UHMWPE reactor powder measured by DSC are shown in Figure 3. The former increases gradually with DR, but the heat of fusion decreases to a minimum at a DR of 5 and subsequently slightly increases with advancing DR by rolling. This implies a change of crystallinity in the rolling process. Similar phenomena on drawing of PE have been reported.^{11,12} After roller-drawing, HDPE showed by X-ray that the intensities of the D_{200} and D_{020} reflections monotonically decreased with DR, suggesting that the cleavage of crystals occurred in the (100) and (010) planes. This trend also has been reported by Glenz et al.¹⁹ and by Chuah et al.^{20,21} in their studies of extrusion drawing of PE. The initial decrease in crystallinity in conventional drawing of UHMWPE is suggested to result from the partial distortion and subsequent destruction during transformation into a fibril structure of the less perfect original crystals.

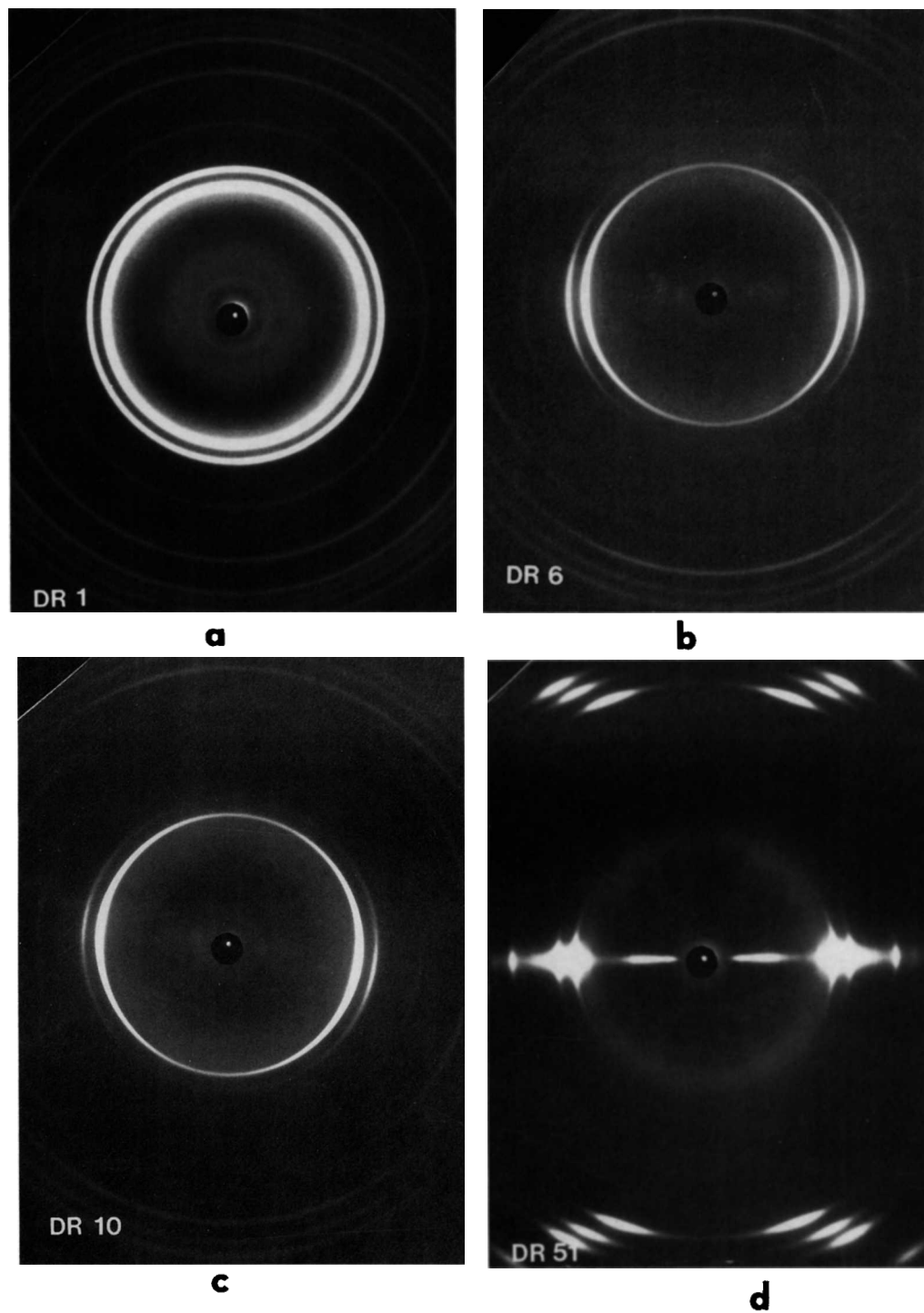


Figure 4 X-ray diffraction patterns of UHMWPE drawn to three different DR: (a) original compacted powder; (b) DR 6.4; (c) DR 10; (d) TDR 51.

The diffraction patterns of the (110) and (200) reflection of an original compacted powder, of a DR of 6.4 of rolled specimen, and of a rolled tape with DR of 10 are shown in Figure 4(a), (b), and (c), respectively. This shows that the orientation of crystals takes place on rolling, but the crystal orientation is lower compared with coextrusion at the same DR.¹⁰ When the DR of rolling was increased to 10, almost no further change in orientation was noted. This is the result of multiple pass rolling with free ends. This is consistent with that observed in the measurement of rolling efficiency: Beyond the DR of 6, the *EFF* reaches a saturated value.

Roll-Drawing Process

The rolled tapes were subjected to a second-stage tensile draw at an elevated temperature of 135°C. From Figures 1, 3, and 5, it can be seen that when DR by multiple rolling reaches 6, the rolling efficiency and mechanical properties reach saturation. So the rolled tape with a DR of 6 was chosen for second-stage tensile drawing.

Compared with the extrusion-drawing of UHMWPE powder, results of the increase of mechanical properties with the TDR are similar, only with lower efficiency.¹⁰ The incremental mechanical properties with TDR are shown in Figure 5. The highest tensile modulus and strength obtained at a TDR of 86 are 81 GPa and 1.3 GPa, respectively.

The tensile moduli of samples obtained both by roll-drawing and coextrusion-drawing may be compared at DR 50. The modulus was 36 GPa for the

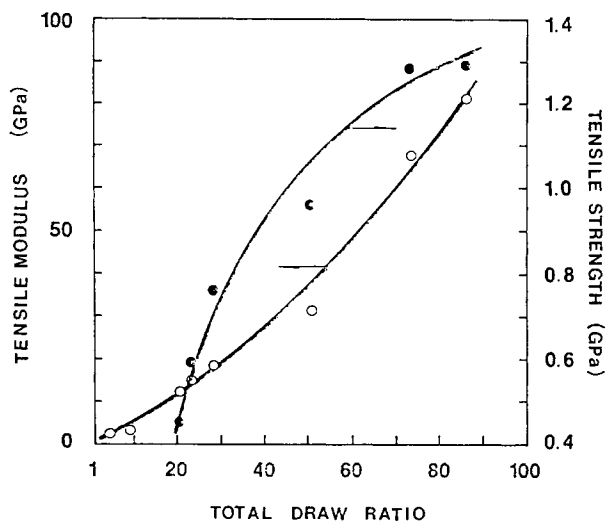


Figure 5 The increase of tensile modulus (open circles), and tensile strength (solid circles) with TDR by roll-drawing.

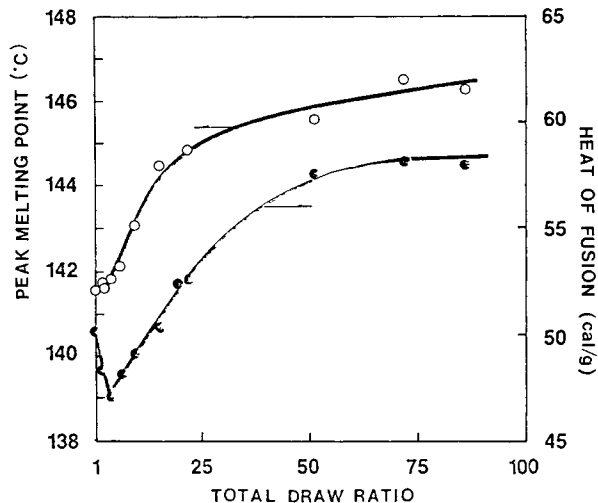


Figure 6 The change of peak melting temperature (open circle) and heat of fusion with TDR of UHMWPE reactor powder on roll-drawing.

former and 100 GPa for the later.¹⁰ This difference reflects the lower efficiency of deformation in the rolling stage of the process.

The peak melting temperature and heat of fusion as a function of TDR are shown in Figure 6. A trend similar to that attained by solid-state coextrusion-draw of the same reactor UHMWPE powder is observed.¹⁰ At the maximum TDR of 86, the peak melting point is 146°C and the heat of fusion achieved is 58 cal/g, corresponding to 85% crystallinity, using 69.2 cal/g as the enthalpy of fusion of pure crystalline PE.

The wide-angle X-ray diffraction patterns of a sample with a TDR of 51 is shown in Figure 4(d). No monoclinic structure is observed. Near-perfect orientation of the crystalline chain may be noted. This is consistent with the improved mechanical properties.

CONCLUSIONS

UHMWPE reactor powder has been successfully roll drawn. The most efficient process was found at 124°C. For further improvement of mechanical properties of samples, a two-stage draw technique was used, i.e., compacted powder plates were rolled to a DR of 6, followed by tensile drawing at 135°C. Under rolling, both the temperature and the turning speed of the roller influence the efficiency and uniformity of deformation. The efficiency of rolling, evaluated by the shrinkage technique, is found to be 85%. The highest tensile modulus and tensile

strength obtained for sample prepared by roll-drawing are 81 GPa and 1.3 GPa, respectively, at the maximum TDR of 86.

REFERENCES

1. T. Shimanochi, M. Asshira, and S. Enamoto, *J. Polym. Sci.*, **51**, 93 (1963).
2. R. F. Schantale and T. Shimanochi, *J. Chem. Phys.*, **41**, 3605 (1967).
3. J. L. Koenig and D. L. Tabb, *J. Macromol. Sci. Phys.*, **B9**, 141 (1974).
4. G. R. Strobl and R. Eckel, *J. Polym. Sci. Polym. Phys. Ed.*, **14**, 919 (1976).
5. I. Sakurada, T. Ito, and K. Nakamae, *J. Polym. Sci. C*, **15**, 75 (1966).
6. T. Kanamoto and R. S. Porter, *J. Polym. Sci. Polym. Lett. Ed.*, **21**, 1005 (1983).
7. B. Kalb and A. J. Pennings, *J. Mater. Sci.*, **15**, 2584 (1980).
8. G. T. Pawlikowski, D. J. Mitchell, and R. S. Porter, *J. Polym. Sci. Polym. Phys. Ed.*, **26**, 1865 (1988).
9. A. E. Zachariades, M. P. C. Watts, T. Kanamoto, and R. S. Porter, *J. Polym. Sci. Polym. Lett. Ed.*, **17**, 485 (1979).
10. T. Kanamoto, T. Ohama, K. Tanaka, and R. S. Porter, *Polymer*, **28**, 1517 (1987).
11. G. Meinel and A. Peterlin, *Kolloid Z. Z. Polym.*, **242**, 1151 (1970).
12. A. Kaito, K. Nakayama, and H. Kanetsuna, *J. Appl. Polym. Sci.*, **28**, 1207 (1983).
13. D. M. Bigg, E. G. Smith, M. M. Epstein, and R. J. Fioretino, *J. Eng. Ind.*, **106**, 109 (1984).
14. K. S. Han, J. F. Wallace, R. W. Truss, and P. H. Geil, *J. Macromol. Sci.*, **B19**, 313 (1981).
15. A. Kaito, K. Nakayama, and H. Kanetsuna, *J. Appl. Polym. Sci.*, **30**, 1241 (1985).
16. A. E. Zachariades, W. T. Mead, and R. S. Porter, *Chem. Rev.*, **80**, 351 (1980).
17. M. P. C. Watts, A. E. Zacharides, and R. S. Porter, *J. Mater. Sci.*, **15**, 426 (1980).
18. R. S. Porter, M. Daniels, M. P. C. Watts, J. R. C. Pereira, and A. E. Zacharides, *J. Mater. Sci.*, **16**, 1134 (1981).
19. W. Glenz, N. Morosoft, and A. Peterlin, *J. Polym. Sci. Polym. Lett. Ed.*, **9**, 211 (1971).
20. H. H. Chuah, P. E. DeMicheli, and R. S. Porter, *J. Polym. Sci. Polym. Lett. Ed.*, **21**, 791 (1983).
21. H. H. Chuah and R. S. Porter, *J. Polym. Sci. Polym. Phys. Ed.*, **22**, 1353 (1984).

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