

Improvement in the Mechanical Properties of Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) by Preorientation

Mohamed K. Hassan,¹ Samir A. Abdel-Latif,^{1,2} Omar M. El-Roudi,^{1,2} Mohamed A. Sharaf,^{1,2} Isao Noda,³ James E. Mark¹

¹Department of Chemistry and the Polymer Research Center, University of Cincinnati, Cincinnati, Ohio 45221-0172

²Department of Chemistry, Helwan University, Ain Helwan, Cairo 11795, Egypt

³Procter & Gamble Company, 8611 Beckett Road, West Chester, Ohio 45069

Received 5 January 2004; accepted 24 May 2004

DOI 10.1002/app.20992

Published online 22 October 2004 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Preoriented poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (Nodax™) films were obtained via the drawing of films to prestretching ratios ranging from 200 to 1000%. As expected, preorientation resulted in substantial improvements in the mechanical properties of the films from the corresponding increases in the amount and nature of the crystallinity present. Stress-strain curves in elongation showed a yield peak, which was relatively broad for the unoriented samples but became sharper, with a well-defined neck, as the extent of preorientation was increased. In addition,

the preoriented films had higher modulus, toughness, yield stress, and tensile strength values. The attribution of these changes in the mechanical properties to changes in the crystallinity was supported by X-ray diffraction measurements. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 2257–2262, 2004

Key words: modulus; strain; strength; stress; toughness; WAXS; poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)

INTRODUCTION

Anisotropic polymeric materials have a wide range of applications in many branches of industry, primarily because of their attractive mechanical properties. There have been many methods used to obtain the required segmental orientation of the polymer chains, such as flow-induced orientation, the placement of polymers in a liquid-crystalline medium, and orientation induced by an imposed strain (which seems to be the most promising technique for obtaining materials with the desired anisotropy).^{1,2} The degree of orientation can be easily controlled by this last technique, and it should be possible to drive the system into a highly oriented material with excellent high-performance properties because the modified products will retain much of their orientational order. Of particular interest is a novel orientation technique proposed by Erman et al.^{3,4} for the preparation of high-strength, high-modulus films and fibers from lyotropic main-chain liquid-crystalline polymers. The technique involves crosslinking the polymer, swelling it with a solvent,

stretching it in the swollen state, and then drying it in the stretched state. In contrast to conventional orientation techniques, this procedure should give controlled degrees of orientation among the anisotropic domains containing the liquid-crystalline chains and orderings persisting after the mechanical force inducing them is removed.^{5–7} This article is part of a series that stresses the use of the preorientation technique developed by Erman et al.^{3,4} Because of some experimental difficulties, however, it has not yet been possible to obtain crosslinked materials suitable for the required swelling and drying under strain. For this reason, alternative procedures have been employed.

The material of interest here is poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (Nodax™), a biodegradable, semicrystalline, aliphatic polyester initially produced only by microorganisms.^{8,9} This copolymer provides a unique combination of properties, such as full anaerobic degradability, moisture resistance, barrier properties, shelf stability under distribution and home-storage conditions, processability on conventional equipment, and dyeability. Its planned applications include the manufacture of storage bags, shopping bags, slip covers for automobiles and furniture, and chemical and mechanical protective coatings for food bags. This copolymer has the advantage of biodegradability, but its strength has not yet been fully optimized.

The mechanical properties of homopolymeric poly(hydroxyalkanoate)s range from brittle to flexible to

Correspondence to: J. E. Mark (markje@email.uc.edu).

Contract grant sponsor: National Science Foundation; contract grant numbers: INT 0111334 (U.S.–Egypt International Program) and DMR-0075198 and DMR-0314760 (Polymers Program, Division of Materials Research).

elastic, depending on the contents and lengths of their side chains.¹⁰ Polymers with short side chains, such as poly(hydroxybutyrate), have high crystallinity and thus can be very brittle. However, copolymers of hydroxybutyrate (HB) and 3-hydroxyvalerate have somewhat better mechanical properties.¹¹ Copolymers consisting of HB and 3-hydroxyhexanoate (3HH) have mechanical properties even better than those of poly(hydroxybutyrate-co-hydroxyvalerate),¹² which make them comparable to conventional plastics, such as polypropylene and polyethylene. Doi et al.¹² studied the dependence of the degree of X-ray crystallinity for poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) films prepared by microbial synthesis on their contents of 3HH. They reached the conclusion that the degree of crystallinity decreased from 60 to 18% as the 3HH fraction was increased from 0 to 25 mol %, and they suggested that 3HH units were excluded from the poly(3-hydroxybutyrate) crystalline phase. Also, the isothermal radial growth rates of spherulites of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) were markedly reduced with an increase in the amount of 3HH.¹²

This article focuses on the use of preorientation induced by prestretching as a possible method for improving the mechanical properties of this commercially important polymer.

EXPERIMENTAL

Materials

The Nodax samples were provided by Procter & Gamble Co. (West Chester, OH). Nodax is a random copolymer consisting of 87–89 mol % 3-hydroxybutyrate and 11–13 mol % 3HH (according to NMR analysis). It has a number-average molecular weight of 500,000–600,000 g mol⁻¹ and a weight-average molecular weight/number-average molecular weight ratio of 1.9–2.1 according to polystyrene standards.

Differential scanning calorimetry (DSC) measurements

DSC measurements were carried out on a Mettler-Toledo (Columbus, OH) DSC 821e with nitrogen as the purging gas. The experiments were performed from 25 to 180°C at a heating rate of 10°C/min, cooled rapidly to -100°C, and then heated again from -100 to 180°C at the same rate. The second-heating DSC data are the data reported here.

Preparation and preorientation of the films

Films were prepared by the press molding of the polymer into Teflon-coated aluminum molds at 130°C. The preorientation of the films was performed by the heating of the samples at 130°C for about 10 min,

annealing for 5 min, and uniaxial stretching to the desired length. Stretched samples were then air-cooled to room temperature in the stretched state. The stretching was done with a home-built apparatus. The resulting prestretch ratio percentage was defined as $100(L - L_0)/L_0$, where L is the final length of the sample and L_0 is its initial length.

Stress-strain measurements

The values of the modulus and tensile strength of 30 mm × 5 mm × 1 mm samples were measured with a fully computerized Instron 1122 mechanical tester. The crosshead speed was varied to obtain the desired strain rate, with the initial gauge length being 30 mm. Both the displacement and load (kN) were recorded. The values of the toughness were calculated as the areas under the stress-strain curves.

X-ray diffraction (XRD) measurements

Wide-angle diffraction patterns (wide-angle X-ray scattering) from unoriented and oriented Nodax films were collected at room temperature on a Bruker AXS GmbH (Karlsruhe, Germany) D500 diffractometer with monochromatized Cu K α radiation (30 mA, 40 kV). Data were collected from $2\theta = 1^\circ$ to $2\theta = 30^\circ$ (where θ is half of the diffraction angle) with a step size of 0.05° and a time per step of 1 s.

RESULTS AND DISCUSSION

Thermal properties of Nodax

A representative DSC trace of Nodax is given in Figure 1(a,b). The DSC scans show a glass-transition temperature (T_g) of approximately -0.21°C, followed by a small endothermic peak at 59.6°C and a more pronounced peak around 106.3°C.

Preorientation of the films

The orientation of the samples via swelling in chloroform, stretching, and evaporation of the solvent while the samples were stretched⁵⁻⁷ was attempted for some of the samples. Because of problems with crosslinking and achieving high preorientation ratios in the swollen state, however, this more elaborate technique was temporarily abandoned. The remainder of the study was, therefore, focused on the simple preorientation of uncrosslinked, unswollen samples in the amorphous state. This simpler approach involved heating each film to 130°C, stretching it to the desired extension (%), and then quenching it to room temperature while it was in the stretched state. This procedure was done with a home-built uniaxial stretcher but could also be done simply with one's hands. This procedure en-

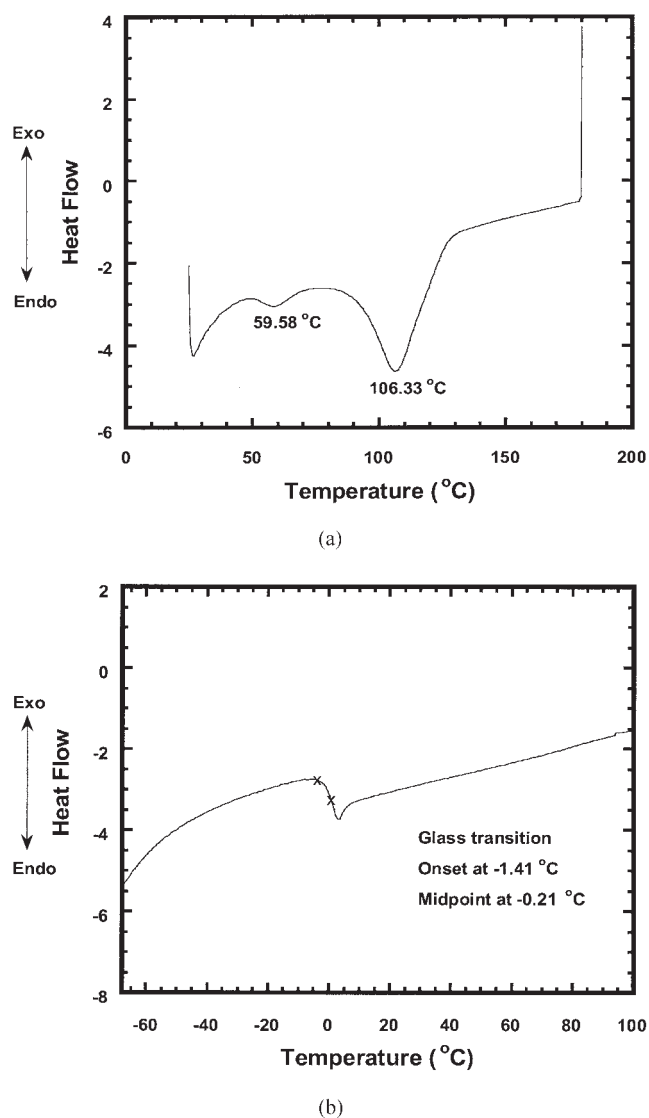


Figure 1 DSC traces of the polymer showing (a) the melting peaks and (b) T_g .

abled the stretching of these uncrosslinked films to extensions of up to 2000%. This good drawability was probably due to the high molecular weight of the samples.

The morphology of the initial undrawn material presumably had a folded-chain lamellar structure, with the coherence between individual lamellar crystals being provided by trapped entanglements.¹³ At the high draw ratios attained, the drawing process should involve the unfolding of the chains in the direction of completely extended chains. The high draw ratios could also have been due to the annealing of the samples before they were stretched. This could have given a higher level of cohesion between the lamellar crystals through trapped entanglements. Also, during the hot pressing, some of the nascent or virgin structures proposed by Smith et al.¹⁴ might

have formed. This would be consistent with wide-angle and small-angle XRD patterns for poly(β -hydroxybutyrate-co-hydroxyvalerate) films.¹³ The patterns of the undrawn film implied that the film was composed of lamellar structures with their surface normal oriented perpendicularly to the film surface. The patterns for oriented films, however, indicated that some of the chains had become oriented to a considerable extent in the draw direction, whereas at the same time, some of them were still perpendicular to the film surface.¹³ Thus, drawing inducing the formation of a new periodic structure in which the chain axis was parallel to the draw direction. These results were supported by birefringence results for the molecular orientation functions for the chains. It would be more meaningful to measure the molecular orientation functions and relate them to the macroscopic preorientation extent, but this was behind the scope of this study. Similar measurements carried out for drawn crosslinked starch-ether films supported the same conclusions regarding the orientation of the chains during the stretching of swollen samples before the removal of the solvent in the stretched state.⁷

Effect of preorientation on the stress-strain curves

The stress-strain curves obtained at a strain rate of 40 mm/min (Fig. 2) show some of the characteristics typical of semicrystalline polymers.^{15,16} For polymers with low degrees of crystallinity, there is no neck or yield maximum. Polymers of low crystallinity may consist of small crystallites randomly distributed in a matrix of disordered chains that are in liquidlike conformations and subject to few constraints. When a stress is applied to such a system, the disordered regions are preferentially deformed in a recoverable manner by passing the crystallites that are not sensibly affected.^{17,18} For polymers with higher degrees of crystallinity, which could be the case for our unoriented Nodax samples, lamellar crystallites can form, and the thickness of the disordered region between the crystallites can decrease.

Some relevant results are given in Figure 2(a,b). The ease of deformation of the chain segments in this region is reduced; in other words, it is no longer possible for the disordered regions to elastically deform independently of the crystalline regions. As a result, the initial modulus is influenced by the crystalline regions acting in parallel with some of the disordered regions. This results in an increase in the initial modulus as the crystallinity and ordering of lamellae develop.^{17,18} At this stage, crystallites are constrained to deform cooperatively over a complete cross section. Thus, we can observe the beginnings of neck formation (as visually observed during these measurements). The limited flexibility of surrounding disordered chains permits a certain diffuseness of the neck.

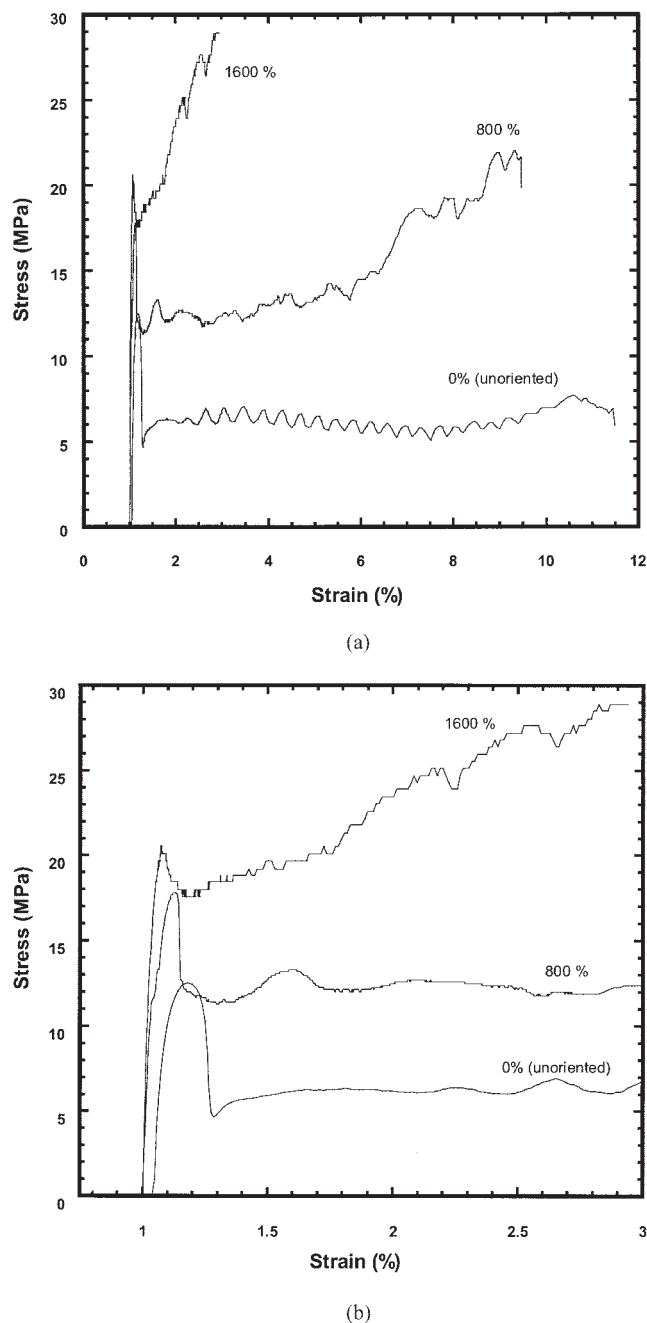


Figure 2 (a) Effect of preorientation on the stress-strain curves of Nodax films and (b) expanded versions of those curves.

A yield peak on the stress-strain curves is evident, but it is relatively broad. This observation is clear for the unoriented Nodax film, as shown in Figure 2(b) [which is simply a magnification of part of the entire curve given in Fig. 2(a)]. For prestretched samples with the highest levels of crystallinity, the intermolecular region containing the disordered structures is relatively small. In this case, the isotropic regions cannot be deformed independently of the crystallites. Consequently, the deformation will be conserved on

microscopic bases across a complete cross section. The resulting modulus will thus conform to a model in which the crystalline and noncrystalline regions are deformed in parallel, and the value of the modulus will be an approximate linear function of crystallinity. This is reflected by the existence of sharp yield points in the stress-strain curves and a well-defined neck during the measurements. This was particularly significant for samples that had been prestretched 800–1600%, as shown in Figure 2.

As can be deduced from Figure 2(a), the elongation at break decreased very much from 11.50 for an unoriented sample to 9.50 for samples prestretched to 800% and finally to 2.90 for samples prestretched to 1600%. At the relatively high molecular weight of the polymer used in this study, numerous entanglements could severely reduce the deformability of the noncrystalline sequences between lamellae.¹⁷ They then served as the weak point of the total system. Rupture could then occur among these sequences before the full elongation benefits of the melting-recrystallization process could be realized.¹⁷

Effect of preorientation on the toughness and the modulus

As expected, the preorientation resulted in much tougher films with higher values of the modulus, in comparison with the original unoriented films. This was particularly significant for samples that had been prestretched 200–1000%, as shown in Figure 3. Beyond 1000% pre-extension, the toughness decreased, whereas the modulus continued to increase. For all values of the pre-extension, a plateau developed after a yield point similar to that observed for the unoriented sample. Finally, for a sample preoriented to 800%, there was a sharper yield point (at ca. 17.8 MPa),

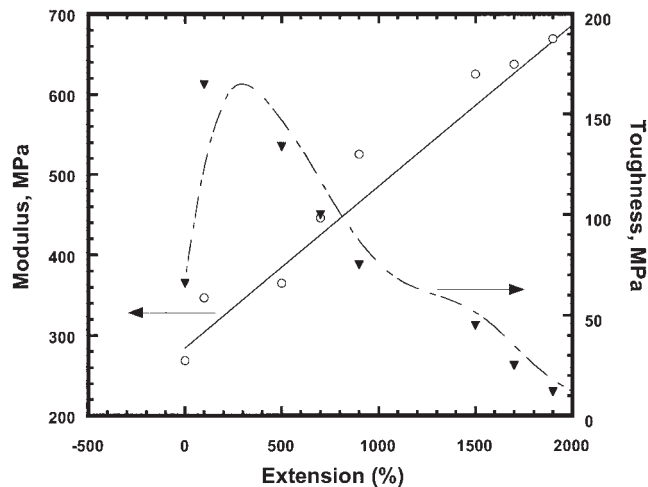


Figure 3 Effect of preorientation on the tensile modulus and toughness.

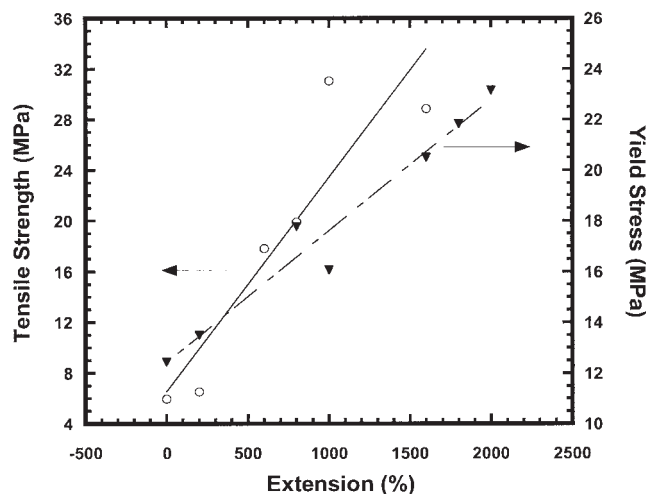


Figure 4 Effect of preorientation on the tensile strength and yield stress.

followed by extensive elongation at an almost constant stress. This indicated a higher level of ordering from the higher stretch ratios.⁷

Also, Figure 3 demonstrates an increase in the modulus with an increasing level of preorientation. This was presumably due to increases in the crystallinity with orientation, as reported for random ethylene copolymers.¹⁸ The continuous increase in the modulus with increasing levels of crystallinity (as predicted from the increasing orientation level) for the copolymers indicated that both the crystalline and noncrystalline regions were major contributors to the initial deformation mechanism and the value of the initial modulus.¹⁸

Effect of preorientation on the yield stress and the tensile strength

Figure 4 shows that an increase in the prestretching percentage of the films resulted in an increase in the yield stress and the tensile strength (the stress at break).^{17–22} This result agreed with results previously reported for polyethylenes and polyamides. In these studies, there was a linear increase in the yield stress at room temperature with an increase in the density and thus with the degree of crystallinity.^{17–22}

XRD measurements

An examination of the diffraction patterns of the unoriented and oriented films showed a significant increase in the peak intensity due to preorientation. Typical results are given in Figure 5. The peak at $2\theta = 13.4^\circ$ increased with an increase in the extent of preorientation, and this confirmed the expected increase in the crystallinity. This supports the fact that chain orientation is a strong function of the draw

ratio.¹⁷ For the peak at $2\theta = 17^\circ$, samples that had been prestretched 800% had almost the same area under the peak as that of the unoriented samples. This could be a result of some of the chains becoming oriented to a considerable extent in the draw direction, whereas other chains were still oriented perpendicularly to the film surface.¹³ Also, this could indicate that some lamellar crystalline morphology of the copolymer was still retained even after drawing to 800%.^{13,23,24} These results explain the increase in the modulus, stress, and the decrease in the elongation at break with an increase in the prestretching ratio.

Finally, these improvements in the mechanical properties demonstrated the very desirable effects of preorientation techniques on mechanical properties. They were very similar to those observed earlier for other biodegradable starch-ether^{3,4,7} and poly(D,L-lactide) materials.²⁵ The preorientation of films yields chains that are nearly perfectly oriented in the stretching direction, but such materials are weak in the directions perpendicular to the stretching direction. A biaxial extension procedure applied to a film could give more useful materials that would be extremely strong in all directions. This is a subject of ongoing research on the polymer used in this study. Such improvements in the mechanical properties of Nodax will certainly be very important for industrial end-use applications.

CONCLUSIONS

Preorientation improved the modulus, tensile strength, and yield stress and increased or at least maintained the toughness of Nodax films. These improvements presumably resulted from increases in the crystallinity with orientation, and this was supported by increases in the intensity of the XRD patterns of the

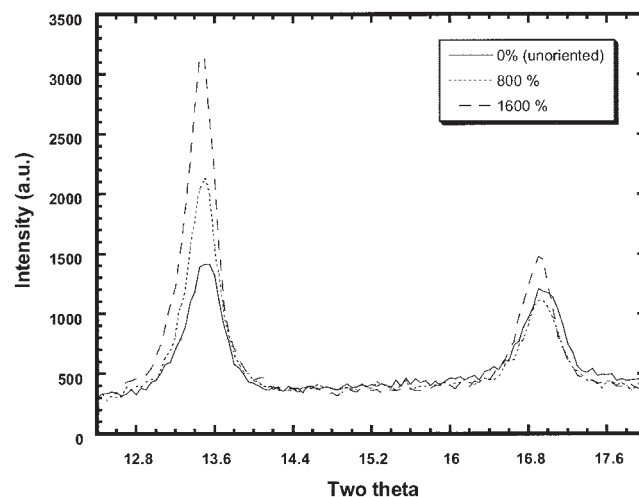


Figure 5 XRD patterns for the unoriented and oriented films.

preoriented samples with respect to those of the un-oriented ones. Preorientation techniques could, therefore, be very useful in processing such materials for industrial applications.

The authors thank the Geology Department of the University of Cincinnati for the use of its X-ray diffraction machine.

References

1. Kloczkowski, A.; Sharaf, M. A.; Mark, J. E. *Comput Polym Sci* 1993, 3, 39.
2. Kloczkowski, A.; Sharaf, M. A.; Mark, J. E. *Chem Eng Sci* 1994, 49, 2889.
3. Erman, B.; Bahar, I.; Kloczkowski, A.; Mark, J. E. *Macromolecules* 1990, 23, 5335.
4. Erman, B.; Bahar, I.; Kloczkowski, A.; Mark, J. E. In *Polymer Solutions, Blends and Interfaces*; Noda, I.; Rubingh, D. N., Eds.; Elsevier: Amsterdam, 1992; p 221.
5. Yang, Y.; Kloczkowski, A.; Mark, J. E.; Erman, B.; Bahar, I. *Colloid Polym Sci* 1994, 272, 284.
6. Zhao, W.; Kloczkowski, A.; Mark, J. E.; Erman, B.; Bahar, I. *Macromolecules* 1996, 29, 2796.
7. Zhao, W.; Kloczkowski, A.; Mark, J. E.; Erman, B. *Chem Mater* 1998, 10, 794.
8. Tian, G.; Wu, Q.; Sun, S.; Noda, I.; Chen, G. *J Polym Sci Part B: Polym Phys* 2002, 40, 649.
9. Satkowski, M. M.; Melik, D. H.; Autran, J.-P.; Green, P. R.; Noda, I.; Schechtman, L. A. In *Biopolymers*; Doi, Y.; Steinbüchel, A., Eds.; Wiley-VCH: Weinheim, 2001; Vol. 3b, p 231.
10. Chen, G.; Wu, Q.; Xi, J.; Yu, P. H. *Prog Nat Sci* 2000, 10, 843.
11. Steinbüchel, A. In *Biomaterials: Novel Materials from Biological Sources*; Byrom, D., Ed.; Stockton: New York, 1991; p 124.
12. Doi, Y.; Kitamura, S.; Abe, H. *Macromolecules* 1995, 28, 4822.
13. Ito, H.; Marchessault, R. H.; St. John Manley, R. *Polym Commun* 1991, 32, 164.
14. Smith, P.; Chanzy, H. D.; Potzinger, B. P. *J Mater Sci* 1987, 22, 523.
15. Young, R. G. *Introduction to Polymers*; Chapman & Hall: London, 1981; p 287.
16. Peterlin, A. In *the Strength and Stiffness of Polymers*; Zachariades, A. E.; Porter, R. S., Eds.; Marcel Dekker: New York, 1983; p 97.
17. Popli, R.; Mandelkern, L. *J Polym Sci Part B: Polym Phys* 1987, 25, 441.
18. Peacock, A. J.; Mandelkern, L. *J Polym Sci Part B: Polym Phys* 1990, 28, 1917.
19. Sperati, C. A.; Franta, W. A.; Starkweather, H. W. *J Am Chem Soc* 1953, 75, 6127.
20. Starkweather, H. W.; Moore, G. E.; Hansen, H. E.; Roder, T. M.; Brooks, R. E. *J Polym Sci* 1956, 21, 189.
21. Williamson, G. R.; Wright, B.; Haward, R. N. *J Appl Chem* 1964, 14, 131.
22. Trainor, A.; Haward, R. N.; Hay, J. N. *J Polym Sci Polym Phys Ed* 1977, 15, 1077.
23. Cornibert, J.; Marchessault, R. H. *J Mol Biol* 1972, 71, 735.
24. Yokouchi, M.; Chatani, Y.; Tadokoro, H.; Teranishi, K.; Tani, H. *Polymer* 1973, 14, 267.
25. Grijpma, D. W.; Altpeter, H.; Bevis, M. J.; Feijen, J. *Polym Int* 2002, 51, 845.