Shear-Induced Conformational Ordering in the Melt of Isotactic Polypropylene

**Haining An,[†,‡] Baijin Zhao,[‡] Zhe Ma,[†,‡]
Chunguang Shao,[‡] Xiao Wang,[‡] Yapeng Fang,[‡]
Liangbin Li,*[,‡] and Zhongming Li[†]**

College of Polymer Science and Engineering and State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu, China, and National Synchrotron Radiation Lab and Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, China

Received May 5, 2007
Revised Manuscript Received May 23, 2007

Introduction. Flow-induced order and crystallization of polymers are fundamental (but poorly understood) nonequilibrium properties of these systems. As moreover flow fields are inevitably applied during polymer processing, the development of order under such conditions has attracted considerable interest.[1,2] Polymer ordering comprises intermolecular positional and orientational order as well as intramolecular conformational order. Unlike in the state of a perfect crystal, in general these ordering processes are not necessarily coupled to each other.[3] Conformationally disordered crystals provide well-known examples of intermolecular order without full conformational order.[4] In contrast, conformational order without accompanying intermolecular positional order is frequently found in natural polymers such as the α-helix of proteins rather than in synthetic polymers.[5,6] These two types of order can be properly studied independently during shear-induced crystallization of polymers, provided the intermolecular and intramolecular order can be decoupled.

During the past half a century, a great deal of research has been dedicated to shear-induced crystallization of polymers.[7−17] During the past decade time-resolved X-ray scattering at synchrotron facilities has led to new observations and insight.[18] In particular, information has been reported about precursors of crystallization both under shear and at quiescent conditions, which concerns intermolecular order like density fluctuation[19] rather than intramolecular order. The importance of intramolecular order has been emphasized in more recent models for polymer crystallization at quiescent conditions.[20−22] The idea of spinodal-assisted crystallization of polymers assumes that a liquid−liquid phase separation originates from differences in conformational order of various chain segments.[20] The multistage process proposed by Strobl[21] does not specifically rely on molecular information, but conformational ordering must be a necessary step for the proposed intermediate mesophase formation.

Flow or stretch-induced conformational order of natural polymers has gained considerable attention due to their characteristic structures and related biological functions, in contrast to their synthetic counterparts. Mechanical stretching can induce a coil−helix transition in a single molecule and in a network environment.[23−25] Tamashiro[26] and Buhot[27,28] formulated a theoretical framework based on a block copolymer model of a single molecule without cooperative interactions among the chains, while Terentjev's group presented experimental and theoretic work for the case of a network.[23,29] However, in spite of its importance for synthetic polymers a few theoretic and experimental contributions have been dedicated so far to shear-induced conformational order in the polymer melt.[30]

In this work, the typical synthetic polymer isotactic polypropylene (iPP) has been used as a model system to study the shear-induced coil−helix transition in the melt. In fact, iPP adopts a 3/1 helical conformation in the ordered (crystalline) state.[31] Because of its simplicity, the coil−helix transition of iPP is an ideal system to serve as "background" for biopolymers in which more complex interactions (hydrogen bonding, column interactions, hydrophobicity) take place. We have used Fourier-transform infrared (FTIR) spectroscopy to follow the coil−helix transition induced by shear because knowledge about the relationship between the helical length of iPP fragments and certain absorption bands in infrared spectra has been well documented.[32−34] Our results indicate that a shear field leads to an increase of both the concentration and the length of the helices in the iPP melt.

Experimental Section. High-molecular-mass iPP, supplied by SABIC-Europe, had a melt flow index about 0.3 g/10 min 230 °C/2.16 kg, ASTM D1238) and an average M_n and M_w of about 150 and 720 kg/mol, respectively. The melting point was around 165 °C. For the shear experiments iPP discs were prepared from the pellets as received as well as powder extracted and washed from xylene solution with acetone. No difference is found between these two starting materials.

To impose a shear field, a homemade parallel plate cell was employed driven by a servomotor. Two ZnSe plates were used as IR windows enclosing an iPP sample of 350 μm thickness. The samples were first heated up to 220 °C for 5 min to erase possible memory effects, then cooled down to the required temperature T_s, and held for 15 min before imposing the shear. The shear rate and strain were 14 s^{-1} and 1400%, respectively. In-situ IR spectra were collected over a wavenumber range of 750−1550 cm^{-1} using a Bruker IFS66V/S FTIR spectrometer with a resolution of 4 cm^{-1}. The intensities given refer to the peak height after baseline subtraction, and the relative intensity had been normalized.

Results. Isothermal crystallization of iPP has been studied with IR to investigate the evolution of helical sequences. Figure 1a gives the IR spectra of the iPP sample measured at different times when the sample was isothermal crystallized at 140 °C. This relatively high temperature was chosen because of the long induction period before crystallization. This allowed following at the same temperature also the IR bands after shear. The IR bands at 940, 1220, 1167, 1303, 1330, 841, 998, 900, 808, 1100, and 973 cm^{-1} correspond to helical structures with degree of order from high to low, and the minimum n values for appearance of bands at 973, 998, 841, and 1220 cm^{-1} are 5, 10, 12, and 14 monomers in helical sequences, respectively.[32,33]

Before the onset of crystallization, some regular bands (in particular those at 973, 1100, 998, 808, and 900 cm^{-1}) are present, indicating the existence of short helices in the melt. Upon crystallization the length of the helices grows with time while the corresponding IR intensity also increases. As soon as the 841 cm^{-1} band appears ($n \approx 12$), also other bands corresponding to long helices emerge successively (1330, 1303, 1167, 1220, and 940 cm^{-1}). Figure 1b gives the variation with

---

* Corresponding author. E-mail: lbli@ustc.edu.cn.
[†] Sichuan University.
[‡] University of Science and Technology of China.

10.1021/ma071021h CCC: $37.00

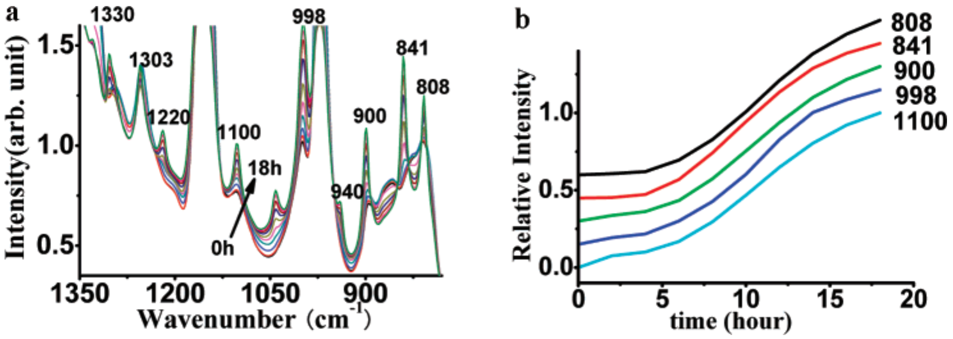

Figure 1. (a) IR spectra of iPP during crystallization at 140 °C at quiescent condition and (b) normalized relative intensities of different conformational bands vs crystallization time.

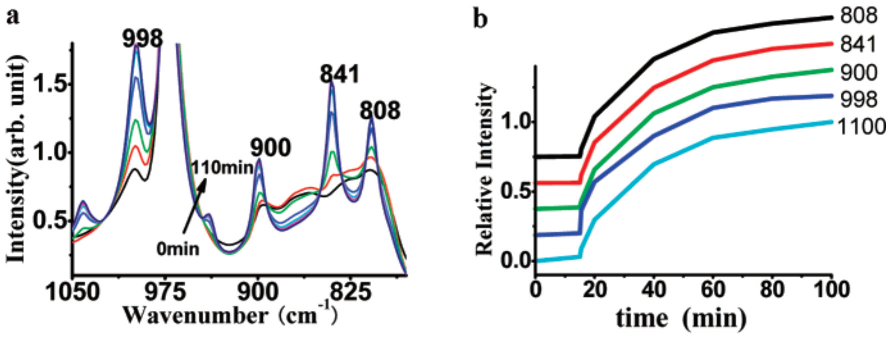

Figure 2. (a) IR spectra of iPP before and after shear at 140 °C and (b) normalized relative intensities of different conformational bands vs crystallization time.

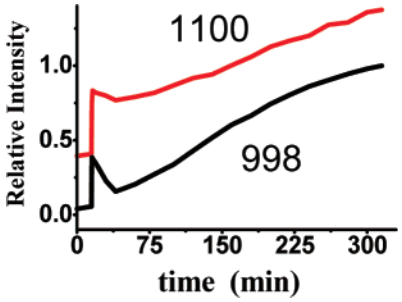

Figure 3. Normalized relative intensities of different conformational bands vs crystallization time at 156 °C.

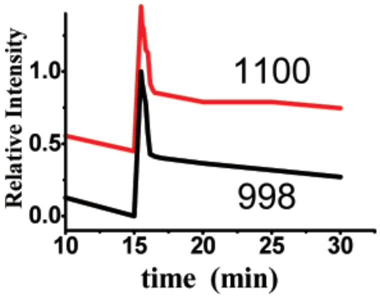

Figure 4. Normalized relative intensities of different conformational bands vs crystallization time before and after shear at 185 °C.

time of the normalized absorption intensities of some selected conformational bands.

Now we come to the effect of shear, which is introduced 15 min after reaching the crystallization temperature of 140 °C. From Figure 1b we know that during this period hardly any change occurs: crystallization does not appear until after 240 min. Figure 2a gives the IR spectra before and directly after shearing and Figure 2b the resulting normalized absorption intensities of several selected bands. Shear leads to a sharp increase in intensity of these bands, revealing a strong enhancement of the corresponding long helices by imposing the flow field. The increase of intensity is attributed to the increase of helical population rather than helical orientation, since the conformational bands with a polarization direction parallel and perpendicular to helix axis all show an increase of intensity after shear.[35] Following this stepwise shear-induced increase of intensities, a further increase of absorption indicates the onset of crystallization. The longer helices induced by the shear serve as the precursor structures for crystallization, resulting in a shortening of the crystallization time from 20 h (quiescent) to 100 min (shear).

Shear-induced conformational order is also observed at higher temperatures but with a somewhat different behavior. Figure 3 gives the variation of the normalized intensities of two bands (1100 and 998 cm^{-1}) with time before and after shear at 156 °C. They were chosen because of the possibility of a quantitative analysis, which was less evident for other conformational bands. The intensity of the vibration bands shows an inflection point that can be understood on the basis of the competition of "melting" of the helical structures and crystallization of the polymer. This phenomenon can be further extended to higher temperatures below the melting point. The induced structure relaxes at a time scale of tens of minutes. Before returning fully to the initial value, the intensity changes slope and increases again due to crystallization. The various conformational bands show somewhat different relaxation kinetics. Helices with about 6 monomers, represented by the 1100 cm^{-1} band, have a larger response to shear and a slower relaxation rate than the longer helix (10 monomers) conformational band at 998 cm^{-1}. It gives further evidence that intensity change upon shear is mainly arising from helical population rather than the helix orientation, as orientation of long helices has a larger response to shear and slower relaxation rate.

At temperatures above the melting point, shear can still induce conformational ordering. Figure 4 gives the normalized intensities of two bands before and after shear at 185 °C. A slightly

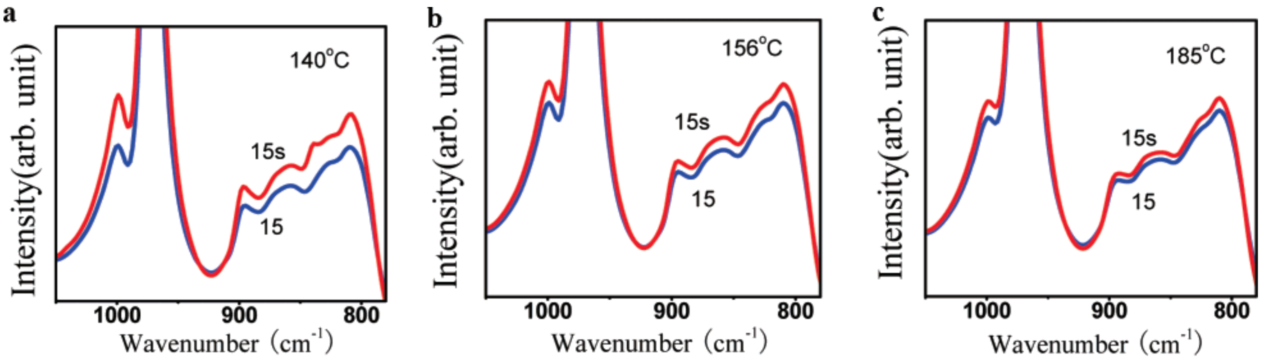

Figure 5. IR spectra of iPP in the range of 1050−780 cm^{-1} before and just after shear (15 min) at the temperature indicated.

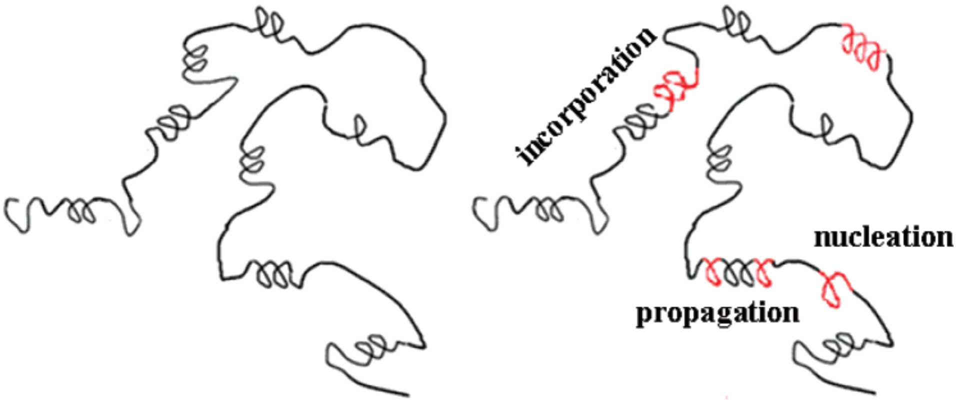

Figure 6. Schematic picture of the three different aspects of the shear-induced coil−helix transition.

decrease in intensity is observed in the first 15 min, which may be due to thermal degradation at the high temperature as evidenced by the appearance of C═O absorption band at 1716 cm^{-1}. Imposing shear leads to an increase of intensity followed by a relatively fast relaxation. The temperature effect on the shear-induced conformational ordering is further illustrated in Figure 5, in which intensities before and just after imposing shear are highlighted for the range of 1050−780 cm^{-1} at 140, 156, and 185 °C. At 140 °C enhancement of the intensity after shear is clearly observed at 998 cm^{-1} ($n \approx 10$) and 841 cm^{-1} ($n \approx 12$), which effect becomes increasingly smaller at 156 and 185 °C. The difference between low and high temperatures shows that shear increases the concentration of long helices, which effect is weaker at higher temperatures.

Discussion. The experimental results clearly demonstrate that shear can induce an increase of both the length and the concentration of helices in the melt of iPP. How does this process occur? Three possible mechanisms of shear-induced conformational ordering are schematically illustrated in Figure 6. Theoretical considerations concerning the coil−helix transition[36] distinguish two elementary steps: the rate-limiting formation of the first helical turn (nucleation) followed by fast addition of helical residues to its ends (propagation). As some short helices already exist in the iPP melt, the first possibility to form of long helices by shear is direct growth on the short ones. The helical structure can propagate from both sides of the short helices without primary nucleation. The second possibility is to generate helices through nucleation and growth. Without such primary nucleation the short helices would be consumed by the formation of longer ones, leading to a decrease of their concentration. As all conformational bands show an increased intensity after shear, we can safely conclude that nucleation does happen. In addition to nucleation and growth and subsequent propagation, a third possibility for the formation of long helices is by merging two shorter ones (incorporation), which can diffuse along molecular chain without energy barrier.[37] Short helices with the same chirality can do so easily without the need of reversing their direction. Combining right- or left-handed helices would be more difficult because of the energy barrier that must be overcome.[38] Shear field drives the molecular chains deviated from the ideal random coil state and consequently reduces the entropy to promote the coil−helix transition through the above three approaches.

The molecular picture of the shear-induced conformational ordering given above can also be understood following Terentjev's theory for stretching-induced coil−helix transition in a network, which is an extension of the description for a single chain,[26−29,39] as a transient network exists in the polymer melt through chain entanglement. The essential idea is that an external field reduces the entropy of random coil segments by extending the chains and subsequently shifts the balance of the coil−helix equilibrium in the direction of helix formation. However, this is a thermodynamic approach, which may not be fully appropriate for the hydrodynamic issue of shear. The thermodynamic approach may be adequate to explain two (nucleation and propagation) of the three mechanisms for the shear-induced coil−helix transition, while the hydrodynamic effect certainly plays an important role in the incorporation of two short helices.

Once induced by the shear, the long helixes can (i) relax back to initial state or (ii) grow and align, inducing subsequent crystallization. Figure 5 indicates that for the same shear field the shear-induced conformational ordering is more pronounced at low temperatures. As the long helices are obtained through a nonequilibrium process, they will naturally relax back to their original state after withdrawing the external field. Higher temperatures corresponding to a larger superheating drive faster melt kinetics of the long helices (see Figures 3 and 4). The relaxation time of the long helices varies from tens of minutes at 156 °C to several minutes at 185 °C. In the melt (185 °C), the time scale is significantly larger than the Rouse time of iPP but of the same order of the reptation time. The relaxation time in the supercooled melt is even longer than the reptation time, which may be related to the lifetime of shear-induced precursor for crystallization. The shear-induced conformational order with the involvement of enthalpy may explain the precursor with the lifetime beyond the reptation time which is driven by entropy alone.

When at low temperatures after shearing subsequently crystallization occurs, the long helices are obviously stabilized. What kind of relationship could exist between the shear-induced coil−helix transition and shear-induced crystallization? As mentioned in the Introduction, comparisons of intermolecular ordering and shear-induced intramolecular ordering are scarce in the literature. Conformational ordering is a necessary step for polymer crystallization. Zhu et al.[32] suggested that helical sequences with monomer numbers of at least 12 are critical for the onset of shear-induced crystallization. At large supercooling (140 °C) imposing shear immediately indeed leads to the creation of such long helices (represented by the 841 cm^{-1} band). Crystallization follows this ordering process within 1 min. Hence, at this temperature shear-induced conformational ordering seems to trigger subsequent crystallization. However, from our results we cannot distinguish between any effect on crystal nucleation of longer helices and of a larger concentration of shorter helices.

At higher temperatures (156 °C), after imposing shear the intensity enhancement of the 841 cm^{-1} band is not as clear as that at 140 °C, though some effect cannot be excluded (Figure 5). Subsequently, the long helices relax for about 13 min before crystallization picks up the ordering process. At this point the concentration of long helices (10 monomers) is still larger than under quiescent conditions at the same temperature. This implies that shear-induced conformational ordering still plays a role at the crystallization. However, if concentration and length of the helical sequences were the only critical parameters for crystallization, one would expect iPP crystallization to occur directly after shearing when these parameters are larger than after some relaxation. The occurrence of crystallization after some relaxation of the shear-induced helices suggests that a rearrangement of the helices is necessary (see Figure 3). This observation leads to two interesting points: (i) Evidently, the conformational ordering alone is not enough for nucleation, which requires coupling between intramolecular and intermolecular ordering. (ii) In the nucleation and growth approach to polymer crystallization,[40] shear-induced precursors may not constitute the appropriate nuclei for crystal growth. Evidently, the relationship between conformational precursors and nuclei for crystallization is not clear yet.

Conclusions. In-situ FTIR measurements reveal that conformational order can be induced in the iPP melt by shear. The effect is more pronounced at temperatures below the melting point of iPP than above. Three different mechanisms are proposed to be involved in the shear-induced coil−helix transition. Of these, a propagation process is kinetically favorable because short helices already exist in the melt before shearing. Following the shear-induced conformational ordering, relaxation as well as crystallization occurs, which effects strongly depend on temperature. The competition of conformational relaxation and crystallization suggests that conformational ordering alone is not sufficient to induce crystallization.

Acknowledgment. L.B.L. thanks Prof. Wim de Jue (AMOLF) for fruitful discussion and careful reading of the manuscript. This work is supported by the National Science Foundation (50503015) as well as the "One hundred talent scientist" program of the Chinese Academy of Science and the "985" program from the Minister of Education. The research is also in part supported by the Opening Project of the State Key Laboratory of Polymer Materials Engineering (Sichuan University).

References and Notes

(1) Nakatani, A. I.; Dadmun, M. D. *Flow-Induced Structure in Polymers*; American Chemical Society: Washington, DC, 1995.
(2) Li, L. B.; De Jeu, W. H. *Adv. Polym. Sci.* **2005**, *181*, 75−120.
(3) Teramoto, A. *Prog. Polym. Sci.* **2001**, *26*, 667−720.
(4) Wunderlich, B.; Grebowicz, J. *Adv. Polym. Sci.* **1984**, *60*, 1−59.
(5) Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: New York, 1984.
(6) Schula, G. E.; Schirmer, R. H. *Principles of Protein Structure*; Springer-Verlag: New York, 1979.
(7) Kornfield, J. A.; Kumaraswamy, G.; Issaian, A. M. *Ind. Eng. Chem. Res.* **2002**, *41*, 6383−6392.
(8) Somani, R. H.; Yang, L.; Zhu, L.; Hsiao, B. S. *Polymer* **2005**, *46*, 8587−8623.
(9) Azzurri, F.; Alfonso, G. C. *Macromolecules* **2005**, *38*, 1723−1728.
(10) Jay, F.; Haudin, J. M.; Monasse, B. *J. Mater. Sci.* **1999**, *34*, 2089−2102.
(11) Na, B.; Zhang, Q.; Wang, K.; Li, L. B.; Fu, Q. *Polymer* **2005**, *46*, 819−825.
(12) Zhang, C. G.; Hu, H. Q.; Wang, X. H.; Yao, Y. H.; Dong, X.; Wang, D. J.; Wang, Z. G.; Han, C. C. *Polymer* **2007**, *48*, 1105−1115.
(13) Muthukumar, M. *Adv. Polym. Sci.* **2005**, *191*, 241−274.
(14) Hu, W. B.; Fenkel, D.; Mathot, V. B. F. *Macromolecules* **2002**, *35*, 7172−7174.
(15) Kume, T.; Hattori, T.; Hashimoto, T. *Macromolecules* **1997**, *30*, 427−434.
(16) Pogodina, N. V.; Siddiquee, S. K.; Van Egmond, J. W.; Winter, H. H. *Macromolecules* **1999**, *32*, 1167−1174.
(17) Eder, G.; Janeschitz-Kriegl, H.; Krobath, G. *Prog. Colloid Polym. Sci.* **1989**, *80*, 1−7.
(18) Somani, R. H.; Hsiao, B. S.; Nogales, A.; Srinivas, S.; Tsou, A. H.; Sics, I.; Balta-Calleja, F. J.; Ezquerra, T. A. *Macromolecules* **2000**, *33*, 9385−9394.
(19) Terrill, N. J.; Fairclough, P. A.; Towns-Andrews, E.; Komanschek, B. U.; Young, R. J.; Ryan, A. J. *Polymer* **1998**, *39*, 2381−2385.
(20) Olmsted, P. D.; Poon, W. C. K.; McLeish, T. C. B.; Terrill, N. J.; Ryan, A. J. *Phys. Rev. Lett.* **1998**, *81*, 373−376.
(21) Strobl, G. *Eur. Phys. J. E* **2000**, *3*, 165−183.
(22) Matsuba, G.; Kaji, K.; Nishida, K.; Kanaya, T.; Imai, M. *Macromolecules* **1999**, *32*, 8932−8937.
(23) Courty, S.; Gornall, J. L.; Terentjev, E. M. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 13457−13460.
(24) Varshney, V.; Carri, G. A. *Macromolecules* **2005**, *38*, 780−787.
(25) Tanaka, F. *Macromolecules* **2000**, *33*, 4249−4263.
(26) Tamashiro, M. N.; Pincus, P. *Phys. Rev. E* **2001**, *63*, 021909.
(27) Buhot, A.; Halperin, A. *Phys. Rev. Lett.* **2000**, *84*, 2160−2163.
(28) Buhot, A.; Halperin, A. *Macromolecules* **2002**, *35*, 3238−3252.
(29) Courty, S.; Gornall, J. L.; Terentjev, E. M. *Biophys. J.* **2006**, *90*, 1019−1027.
(30) Chai, C. K.; Dixon, N. M.; Gerrard, D. L.; Reed, W. *Polymer* **1995**, *36*, 661−663.
(31) Lotz, B.; Wittmann, J. C.; Lovinger, A. J. *Polymer* **1996**, *37*, 4979−4992.
(32) Zerbi, G.; Ciampelli, F.; Zamboni, V. *J. Polym. Sci.* **1963**, *C7*, 141−151.
(33) Zhu, X. Y.; Yan, D. Y.; Fang, Y. P. *J. Phys. Chem. B* **2001**, *105*, 12461−12463.
(34) Budevska, B. O.; Manning, C. J.; Griffiths, P. R.; Roginski, R. T. *Appl. Spectrosc.* **1993**, *47*, 1843−1851.
(35) Painter, P. C.; Colemman, M. M.; Koening, J. L. *The Theory of Vibrational Spectroscopy and Its Application to Polymeric Materials*; John Wiley & Sons: New York, 1982; p 382.
(36) Poland, D.; Scheraga, H. A. *Theory of Helix-Coil Transitions in Biopolymers*; Academic Press: New York, 1970.
(37) Hummer, G.; Garcia, A. E.; Garde, S. *Phys. Rev. Lett.* **2000**, *85*, 2637.
(38) Lotz, B. *Adv. Polym. Sci.* **2005**, *180*, 17−44.
(39) Zimm, B. H.; Bragg, J. K. *J. Chem. Phys.* **1959**, *31*, 526−535.
(40) Hoffman, J. D.; Miller, R. L. *Polymer* **1997**, *38*, 3151−3212.

MA071021H