

Shear-Induced Smectic Ordering in the Melt of Isotactic Polypropylene

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(Received 16 October 2003; published 20 February 2004)

We report an unusual shear-induced smectic phase of high-molecular-mass isotactic polypropylene at temperatures well above its melting point. The necessary stiffness in the polymer chain is provided by shear-induced coil-helix transitions. Coupling between the conformational ordering and the density generates the smectic layering. The periodicity of about 4 nm is built up from a rigid helical sequence of at least 11 monomers and a random-coil part of about 1.4 nm. These results also provide new clues to the question of preordering before polymer crystallization.

DOI: 10.1103/PhysRevLett.92.075506

PACS numbers: 61.41.+e, 87.15.Nn

The rich phase behavior of macromolecules subjected to flow brings us an increasing number of diverse products varying from Chinese noodles to textiles, medical implants, and flexible displays [1], even though the flow-induced phase behavior is still poorly understood. Stiff macromolecules often assemble into liquid-crystal phases characterized by one- or two-dimensional order, while in general flexible-chain polymers only form three-dimensionally ordered crystals [2,3]. Nevertheless, theories of flexible-chain polymers show that rigidity induced by the coil-helix transition could provide the necessary stiffness to meet the conditions of an isotropic-nematic transition [4]. Many examples can be found in biopolymers such as DNA and proteins, in which hydrogen bonds stabilize the helices [5]. However, thus far liquid-crystal phases have not been observed in the melt of synthetic flexible-chain polymers. In this Letter, we show that, unexpectedly, a smectic phase (rather than a nematic one) can be induced by shear flow in the melt of the flexible-chain polymer isotactic polypropylene. This result demonstrates a physical means to “create” liquid crystallinity and also provides new insight into the debate about preordering before the onset of polymer crystallization [6,7].

Isotactic polypropylene (iPP) is a typical flexible-chain crystallizable polymer. Three crystal modifications α , β , and γ have been found, which all show a threefold helical conformation of the chains [8]. A mesophase has been reported in rapidly quenched samples [9]. Though its nature is still a matter of controversy, it is generally accepted that it is metastable and readily transforms into a crystalline phase at temperatures above 80 °C [10]. Because flow-induced phase transitions are fundamental (but poorly understood) properties of nonequilibrium systems and flow fields are inevitably applied during polymer processing, the ordering process under such conditions has attracted considerable interest [11].

The high-molecular-mass iPP, supplied by SABIC-Europe, had a melt flow index about 0.3 g/10 min (230 °C/2.16kg, ASTM D1238) and an average M_n and M_w of about 150 and 720 kg/mol, respectively. The melt-

ing point was around 165 °C. X-ray scattering measurements were carried out using an in-house small-angle (SAXS) and wide-angle x-ray scattering (WAXS) setup [12]. A Linkam CSS450 shear system was used as sample stage *a* in which a Couette cell was incorporated as shown in Fig. 1 [13].

Figure 2(a) gives a typical SAXS picture of the shear-induced smectic peak at 200 °C; an accompanying smectic WAXS peak may be hidden in the amorphous halo of the corresponding pattern in Fig. 2(b). At this temperature, no crystallization is expected at all, as confirmed by the absence of any crystalline reflections in both SAXS and WAXS. The smectic SAXS peak intensity is weak, due to a small volume fraction and limited density contrast (of the order of 7%). The smectic peak is sharp, giving a correlation length of the order of several tens of nm. The smectic phase can be obtained at a wide temperature range up to the order by applying the same shear field. It disappears at 225 °C after about 1 h but can survive longer than overnight at 170 °C. Its lifetime not only depends on thermodynamic stability but also may be negatively influenced by possible high-temperature degradation. At temperatures below 170 °C, the shear-induced smectic ordering is followed by crystallization [12]. By applying the weak shear field for longer times, almost perfect alignment of the smectic layers parallel to $\dot{\gamma}$ is obtained. Note that in a conventional two-plate shear

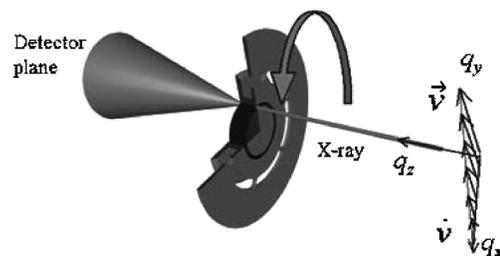


FIG. 1. Scattering situation in the shear geometry used with reciprocal space picture of the scattering wave vector \vec{q} , where $q = 4\pi \sin\theta/\lambda$, $\lambda = 0.154$ nm is the x-ray wavelength, and 2θ is the scattering angle.

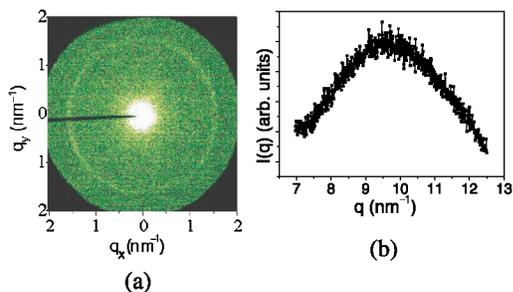


FIG. 2 (color online). Two-dimensional SAXS pattern of iPP displaying smectic ordering at 200 °C (a) and corresponding one-dimensional WAXS pattern (b) after a steady shear with shear rate 1 s^{-1} for 2 min.

cell configuration the x-ray beam will be parallel to the layer normal, preventing the observation of the layering. We also checked any possible layering without shear using a slow cooling process (0.05 °C/min), but no indication of smectic ordering was observed. However, it can already be induced when during sample preparation accidentally a weak shear is exerted. During a heating scan, the smectic phase also shows a higher melting temperature than its crystalline counterpart [see Fig. 3(a)].

How can a smectic ordering exist at high temperatures for a flexible-chain polymer such as iPP? The only possibility to create the necessary rigidity is conformational ordering [4]. In an ordered state, the molecular chain of iPP adopts in general a 3/1-helix conformation [8], which can supply the stiffness required to meet an isotropic to mesogenic transition. Figure 3(b) shows infrared (IR) spectra of an iPP melt that reveal after shear the presence of helical sequences of at least 14 and 12 monomers at 180 and 190 °C, respectively [14,15]. According to Doi *et al.* [16], the criterion for an isotropic to nematic transition is a critical persistence length:

$$l_p = \frac{4.19M_0}{bl_0\rho N_A}. \quad (1)$$

In this equation, b represents the diameter of a polymer

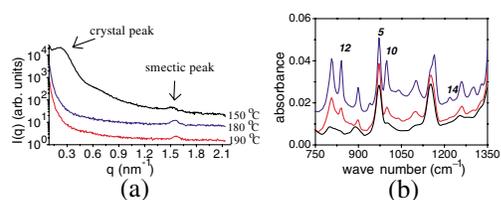


FIG. 3 (color online). (a) One-dimensional SAXS patterns of a sheared iPP sample as a function of temperature during heating from 150 °C to 190 °C, where the sample was sheared with a rate of 0.1 s^{-1} for 10 min and isothermally crystallized. (b) Infrared spectra of the same sample; from top to bottom, at 180 °C (top) and 190 °C (middle) and an unsheared sample at 190 °C (bottom); n indicates the number of monomers associated with a specific helical band.

segment, ρ the density, N_A Avogadro's number, and M_0 and l_0 the mass and the length of a monomer, respectively. Inserting values for the parameters into Eq. (1), we find $l_p \approx 2.38 \text{ nm}$, which is for a 3/1 helix equivalent to about 11 monomers [15]. Though the theory applies to rigid rods, it is gratifying that the rod length of iPP helices as obtained from IR meets this criterion.

The combination of SAXS and IR provides a picture of smectic layering that comprises a rigid helical sequence of at least 4 pitches ($\sim 2.6 \text{ nm}$) and a random-coil part of about 1.4 nm. Figure 4 schematically illustrates the process of shear-induced smectic ordering. Before the application of shear, the iPP chains are in a random-coil state [Fig. 4(a)]. The IR spectra at 190 °C [Fig. 3(b)] indicate that in the unsheared melt conformationally ordered helices with up to about ten monomers still exist locally, though the corresponding IR band is weak. The shear field increases the length of the ordered sequences as well as induces their alignment. As conformational ordering and density are coupled, we expect these two processes to occur simultaneously [Figs. 4(b) and 4(c)]. Evidently, the shear field has a crucial influence on the smectic ordering, but understanding this role precisely is more complicated than for systems with an intrinsic rigidity. In that case, both experimental and theoretical work indicates that a shear field can change the isotropic-nematic as well as the nematic-smectic transition [17,18]. For iPP, the shear flow induces simultaneously density changes and conformational ordering, leading to a complicated coupling process.

Our findings shed some new light on the ongoing discussion on polymer crystallization. Upon cooling a crystallizable polymer, some preordering has often been observed before crystallization starts, the nature of

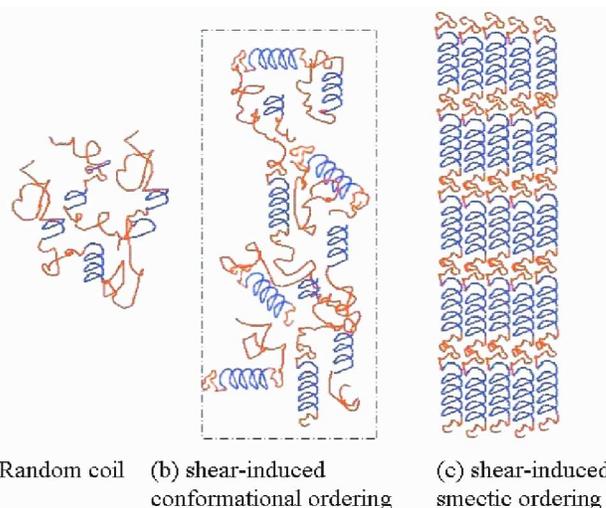


FIG. 4 (color online). Schematic picture of the process of shear-induced ordering of smectic bundles. The density modulation of the smectic layers consists of alternating rigid helices and flexible disordered segments.

which is still a matter of controversy. As, by definition, crystallizable polymers can adopt certain ordered conformations, the induced rigidity may be a common property. Ordered conformations with a short sequence length couple to the density, which may lead to preordering before the onset of crystallization. Recently Muthukumar *et al.* [7] proposed, on the basis of computer simulations, the concept of smectic pearls as a nucleation model. A single chain connects many “baby nuclei” with a size much smaller than the final lamellar thickness. After incorporating in this model the high molecular mass and the shear alignment, it may well be in agreement with our observation of smectic bundles. Finally, we note that during shear-induced crystallization of polymers high-molecular-mass species forming threadlike precursors are known to give an important contribution to the enhanced nucleation rate [11]. Our work provides a possible microscopic explanation of this effect. The long chains stabilize the smectic bundles, which, in turn, ensure the formation and survival of threadlike precursors. In a similar way, the smectic ordering above the melting point provides a natural explanation of the memory effect in polymer crystallization [19].

In conclusion, we have shown that smectic ordering can be induced by shear in the flexible-chain polymer iPP at temperatures well above its melting point. Its formation is attributed to rigidity induced by coil-helix transitions. Though the existence of a smectic phase rather than a nematic one goes beyond the theoretical predictions, the length of the rigid part as obtained by IR measurements agrees roughly with the theoretical requirements. The mobility and orientation effects associated with the liquid crystallinity and its influence on the crystallization process could provide new opportunities to improve processing-property relations in the iPP industry.

The authors thank D. Frenkel and D. Lambrea (Amsterdam) for fruitful discussions, M. Soliman (SABIC-Europe) for supplying the iPP, and Z. Chen (Eindhoven) for performing the IR measurements. This work is part of the research program of the “Stichting voor Fundamenteel Onderzoek der Materie” (FOM), which is financially supported by the “Nederlandse Organisatie voor Wetenschappelijk Onderzoek” (NWO).

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- [1] See, for example, A. I. Nakatani and M. D. Dadmun, *Flow-Induced Structures in Polymers* (American Chemical Society, Washington, DC, 1995).
- [2] A. M. Donald and A. H. Windle, *Liquid Crystalline Polymers* (Cambridge University Press, New York, 1992).
- [3] G. Strobl, *The Physics of Polymers* (Springer-Verlag, Berlin, 1996).
- [4] P. G. De Gennes and P. Pincus, *Polym. Prepr.* **18**, 161 (1977); P. J. Flory and R. R. Matheson, *J. Phys. Chem.* **88**, 6606 (1984).
- [5] S. S. Plotkin and J. N. Onuchic, *Q. Rev. Biophys.* **35**, 111 (2002).
- [6] For a recent review, see E. L. Heeley *et al.*, *Faraday Discuss.* **122**, 343 (2002).
- [7] M. Muthukumar, *Philos. Trans. R. Soc. London, Sect. A* **361**, 539 (2003).
- [8] B. Lotz, J. C. Wittmann, and A. J. Lovinger, *Polymer* **37**, 4979 (1996).
- [9] G. Natta, M. Peraldo, and P. Corradini, *Rend. Accad. Naz. Lincei.* **26**, 14 (1956).
- [10] Z. G. Wang, B. S. Hsiao, S. Srinivas, G. M. Brown, A. H. Tsuo, S. Z. D. Cheng, and R. S. Stein, *Polymer* **42**, 7561 (2001).
- [11] P. Jerschow and H. Janeschitz-Kriegl, *Intl. Polym. Proc.* **7**, 72 (1997); M. Seki, D. W. Thurman, J. P. Oberhauser, and J. A. Kornfield, *Macromolecules* **35**, 2583 (2002); R. H. Somani *et al.*, *Macromolecules* **35**, 9096 (2002); A. Elmoumni, H. H. Winter, A. J. Eaddon, and H. Fruitwala, *Macromolecules* **36**, 6453 (2003).
- [12] L. B. Li and W. H. de Jeu, *Macromolecules* **36**, 4862 (2003).
- [13] A brass cylinder with an inner diameter of 8 mm replaced the original bottom plate of the Linkam shear cell, while the upper plate was changed into a rod with a diameter of 7 mm. Both have a height of 4 mm. Setting the gap at 1 mm, all the other parameter settings remain the same.
- [14] The IR measurements were taken under nitrogen atmosphere using an Excalibur FTIR Spectrometer (Excalibur Series BIO RAD, FTS3000MX) with the ATR technique.
- [15] X. Zhu, D. Yan, and Y. Fang, *J. Phys. Chem. B* **105**, 12 461 (2001).
- [16] M. Doi, T. Shimada, and K. Okano, *J. Chem. Phys.* **88**, 4070 (1988).
- [17] P. D. Olmsted and P. M. Goldbart, *Phys. Rev. A* **46**, 4966 (1992).
- [18] R. F. Bruinsma and C. R. Safinya, *Phys. Rev. A* **43**, 5377 (1991).
- [19] G. C. Alfonso and A. Ziabicki, *Colloid Polym. Sci.* **273**, 317 (1995).