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Shear-Induced Smectic Order in Isotactic Polypropylene Revisited

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ABSTRACT: We provide evidence that earlier reported smectic ordering in the melt of isotactic polypropylene is not intrinsic to the system but results from the presence of small quantities of calcium stearate. No causal relation exists between this effect and the crystallization properties of iPP.

Introduction

As is well known, both the orientation and extension of the molecules in a polymer melt are affected if the system is subjected to external flow. As a result, the structure and morphology as well as the associated kinetics of subsequent crystallization will be strongly influenced. Recently, several reviews have appeared in this field.[1−3] The various models associated with these processes have in common that crystallization of polymers is assumed to be preceded by the formation of some form of ordered precursors,[4] which process has been the subject of intense research. In that context our group has published results indicative that isotactic propylene (iPP) forms weak smectic structures,[5−7] attributed to a coil−rod transition[8] under the influence of the applied shear. The increase in the speed of crystallization under shear was assumed to be related to this ordering. In this paper we report a revision of this interpretation. It turns out that the X-ray peak associated with the smectic ordering is due to the presence of small concentrations (about 0.1−0.2%) of the additive calcium stearate, which was not recognized at that time. In the following we report experimental results leading to this conclusion in the context of the role of additives on crystallization.

Experimental Section

Commercial iPP was obtained from Sabic Europe, Borealis, and Yanshan Petrol Co., with properties as given in Table 1. Calcium stearate was obtained in pure form from Fluka and of industrial quality from Borealis. Small-angle X-ray scattering (SAXS) was performed employing an in-house setup as described before,[5] equipped with a modified Linkam CSS450 temperature-controlled shear system as sample stage. Some additional results were obtained at beamline ID2 of the European Synchrotron Radiation Facility (ESRF, Grenoble).

Results and Discussion

Calcium stearate belongs to the classical metal soaps that have been extensively studied for their lyotropic liquid crystalline ordering in solution. The relevant phase transitions of pure calcium stearate are as follows.[9] Between 100 and 110 °C the aliphatic chains of the crystalline lamellar structure melt while the head groups form an orthorhombic structure of disks. This situation can be described in an approximate way as a lamellar smectic phase. Between 170 and 180 °C additional hexagonal reflections appear, indicating a rearrangement of the head groups of the calcium stearate into a two-dimensional hexagonal lattice. Figure 1 displays how these phase transitions are reflected in the smectic layer period of calcium stearate. These variations are mirrored in the smectic periodicity observed in iPP, pointing strongly to a common origin. The discrepancy in the period can be attributed to differences in hydration and/or purity.[10] Figure 2 confirms this interpretation: only if calcium stearate has been added to iPP, the smectic peak is found. For this peak to be observable the calcium stearate must be poorly dispersed, leading to relatively large clusters of at least 20 smectic layers.

Table 1. Characteristics of the Samples Used

sample	source	calcium stearate	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n	melt index (g/10 min)
IPPhp	Sabic	+	150	720	4.8	0.3
DM55pharm	Borealis	−	92	540	5.9	2.8
	Yanshan	+	100	370	3.7	1.1

The presence of additives in commodity polymers like iPP is known to be quite common but is seldom properly specified. This is due to a lack of control/knowledge about these details, which is often related to industrial secrecy about recipes. In our case we had been explicitly informed that the iPP as received contained only stabilizer (antioxidant) without which high-temperature studies are difficult if not impossible. Only in a much later stage it became clear that with the stabilizer small quantities (0.1−0.2%) of calcium stearate had been included. The function of the calcium stearate is to act both as release

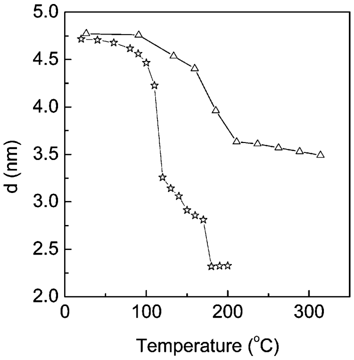

Figure 1. Temperature dependence of the smectic layer period of calcium stearate (top curve) and of iPP (Yanshan) with calcium stearate additives (bottom curve).

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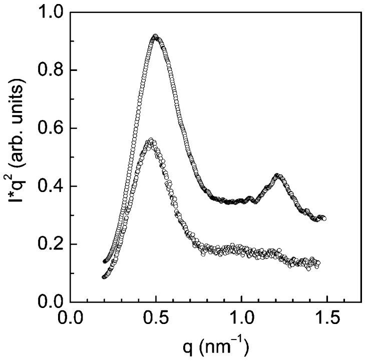

Figure 2. SAXS results of a crystallized iPP sample (Borealis) at room temperature with only stabilizer (bottom curve) and with additionally 0.16% calcium stearate mixed in (top curve).

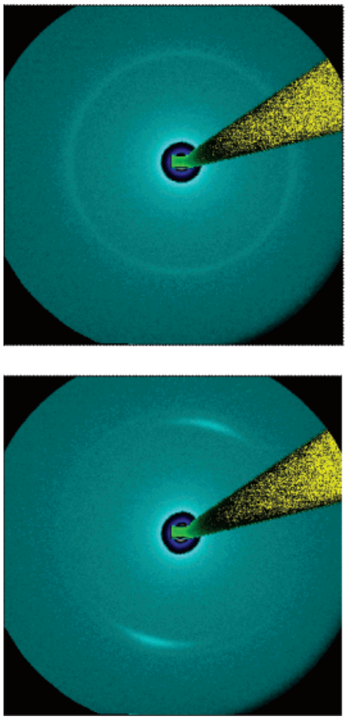

Figure 3. iPP pellets (as received from Sabic): (a, top) heated up to 219 °C showing in the melt a ring corresponding to smectic layers of ~4 nm; (b, bottom) after subsequent shearing in a Couette cell with 0.1 s^{-1} for 6 s.

agent and as acid scavenger catching acid parts left over from the catalyst that could affect the metal of the extruder.

Figure 3 shows some synchrotron SAXS measurements of pellets of iPP as received that evidently show a ring at the smectic position. After heating into the melt and shearing, alignment of the smectic regions is observed as reported before. At lower X-ray intensity the ring can easily be missed, and the smectic peak after shearing could be attributed to the shear itself. In our previous work this idea was supported by the observation in infrared spectroscopy of an increased length of local rodlike helical structures in iPP.[11] The latter result evidently still holds and should probably be attributed to a shear-induced shift of the random-coil to helical-rod equilibrium in iPP. As demonstrated in Figure 4, the calcium stearate as such hardly influences the speed of crystallization under quiescent conditions. The observed speeding up of the crystallization upon shearing can be attributed to alignment of the iPP itself.

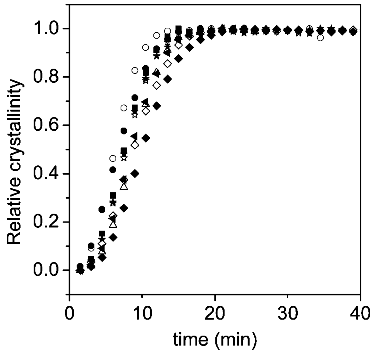

Figure 4. Quiescent crystallization of iPP (Borealis) at 129 °C after 5 min annealing at 212 °C: open symbols, iPP with only stabilizer added; filled symbols, with additionally 0.16% calcium stearate.

The misinterpretation of our studies of crystallization in iPP is an extreme example of the general problem of lack of detailed information on the properties of commercial polymers. The literature in this field contains many data that are difficult to compare because of a considerable variation of experimental parameters like molecular mass and its distribution and the possible presence of various additives. Also, any change in the molecular mass distribution during annealing at relatively high temperatures has hardly been investigated, though the high-molecular-mass tail of the distribution is known to have an appreciable influence on shear-induced crystallization.[1,2] Essentially there are two ways out of this dilemma, which are only beginning to be explored. The first is the use of well-characterized model materials.[12] Alternatively, one can start from completely pure commercial materials and systematically mix in various additives.[13]

In conclusion, the earlier reported changes under shear in both the speed of crystallization of iPP and the intensity of a smectic X-ray peak are only correlated because both originate from the same applied shear. However, there is no causal relation between the two effects.

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