Uniplanar deformation of isotactic polypropylene: 2. Phase structure

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The phase structures of uniplanar-drawn isotactic polypropylene (iPP) have been investigated. Three phases (α-crystal, smectic and amorphous) are found to coexist in the uniaxially compressed samples. From thermal analyses and density measurements, the fractions and densities of these phases have been evaluated. At a compression draw temperature of 50°C $< T_s$ (the upper smectic phase stability limit), the amount of α-crystal decreased significantly and the smectic phase increased on developing a compression ratio up to ~10. The transition energy for smectic to crystal phase was found to be ~5.5 cal g^{-1}. At a draw temperature $> T_s$, decrystallization without smectic phase stability proceeded during the deformation. No draw-induced crystallization was observed. At all deformation temperatures, the density of the amorphous phase increased in the initial stage of deformation reaching a limit on further draw.

(Keywords: planar deformation; smectic phase; isotactic polypropylene)

INTRODUCTION

Uniaxial drawing of flexible chain polymers has been extensively studied to enhance their mechanical and physical properties[1,2]. Among thermoplastics, isotactic polypropylene (iPP) has been drawn uniaxially to high levels[3–5]. The consequent properties in the transverse direction, however, are less than those of the unoriented polymer. Biaxial deformation, on the other hand, can lead to enhancement of properties in two directions. A simple uniplanar compression can create a perfect equibiaxial field in the plane perpendicular to the compression axis[6].

In this study, iPP has been uniaxially compressed by a forging (uniplanar) process. The resultant sample consisted of two or three phases (α-crystal and amorphous, or α-crystal, amorphous and smectic), depending on the draw temperature. The phase structures have been characterized by thermal analyses and density measurements. The amount of the smectic phase was found to increase as deformation proceeded at a draw temperature of 50°C $< T_s$ (the smectic phase stability temperature). The amorphous density increased with increasing compression draw ratio. Based on these results, the deformation mechanism for the compressive uniplanar draw of iPP is discussed.

EXPERIMENTAL

Moulded iPP sheet was uniaxially compressed under a constant compression speed of 0.254 cm min^{-1} using an INSTRON model 1333. A detailed description of iPP and the compression test have been given[7,8]. Thermal analyses were performed on a Perkin–Elmer DSC7 calorimeter. All scans were recorded at a heating rate of 20°C min^{-1}. Density measurements were made on a density gradient column, using ethyl alcohol and a sodium bromide aqueous solution as a mixed miscible solvent pair. Wide-angle X-ray scattering (WAXS) patterns were obtained with a Statton camera using Ni-filtered Cu Kα radiation.

RESULTS AND DISCUSSION

On uniaxial compression of iPP, the smectic phase is induced at draw temperatures (T_d) below the upper temperature limit for smectic phase stability (T_s). The T_s for deformation under this experimental condition is ~120°C[7]. Therefore, the compression drawn samples prepared at $T_d < T_s$ consist of α-crystal, amorphous and smectic regions. No smectic phase is observed in samples prepared at $T_d > 70$°C, since the smectic phase induced under deformation reverts back to α-crystals[7,9]. In this study, a T_d of 50, 100 and 140°C was taken. To characterize the fraction and density of the phases, a two-phase model can be applied for the T_d of 100 and 140°C using equation (1). For the T_d of 50°C, at least a three-phase model is required; thus, equation (2) may be used for estimations:

$$\frac{1}{\rho} = \frac{X_c}{\rho_c} + \frac{1 - X_c}{\rho_a} \tag{1}$$

$$\frac{1}{\rho} = \frac{X_c}{\rho_c} + \frac{X_s}{\rho_s} + \frac{1 - (X_c + X_s)}{\rho_a} \tag{2}$$

where ρ is the density of the sample, and the subscripts c, s and a represent the crystal, smectic and amorphous phases, respectively. X_c, X_s and $1-(X_c+X_s)$ are weight fractions of the crystal, smectic and amorphous phases, respectively.

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Figure 1 shows the heat of fusion (ΔH) of drawn samples as a function of compression draw ratio (CR) for the samples prepared at a T_d of 100 and 140°C. The crystallinity (α-crystal content) decreases as the deformation proceeds. For $T_d = 140$°C, the ΔH of the drawn sample is higher than that of original sample; that is, the samples are annealed at 140°C. However, ΔH decreased with draw. This suggests that decrystallization also proceeds during deformation. This is in contrast to uniaxially drawn iPP with no significant change in crystallinity[10] or with an increase in crystallinity[11,12]. *Figure 2* shows ρ as a function of CR; for all T_d, the value of ρ decreased with CR. As shown in *Figure 3*, the crystal modification of deformed and subsequently heat-treated samples was found by WAXS to be of the α-form and the lattice constant did not change significantly, indicating no change in the α-crystal density during the deformation.

There seem to be two effects on ρ in the experimental range studied. The first is decrystallization during the early stage of deformation (see *Figure 1*), and the second is an increase in amorphous density due to the compression deformation. For samples prepared at a T_d of 100 and 140°C, and for the subsequently heat-treated (140°C for 30 min) samples at a T_d of 50, 100 and 140°C, the amorphous densities (ρ_a) can be estimated using equation (1), since these samples must consist of only α-crystal and amorphous phases. After the heat treatment, ΔH of the samples at a T_d of 100 and 140°C increased by ~3 and ~1 cal g^{-1}, respectively. X_c (α-crystal content) was evaluated from $\Delta H/\Delta H_c^\circ$, where ΔH_c° is the heat of fusion of a perfect iPP crystal. In the calculation, it is necessary to select ΔH_c° and the density for the perfect α-crystal.

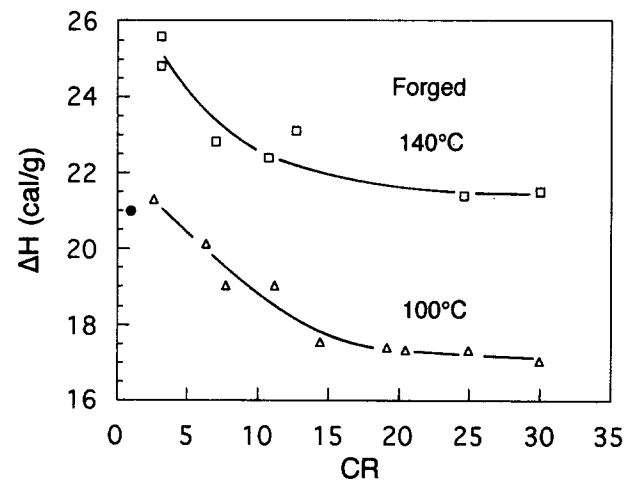

Figure 1 ΔH *versus* CR for samples prepared at 100 (△) and 140°C (□); original undeformed sample (●)

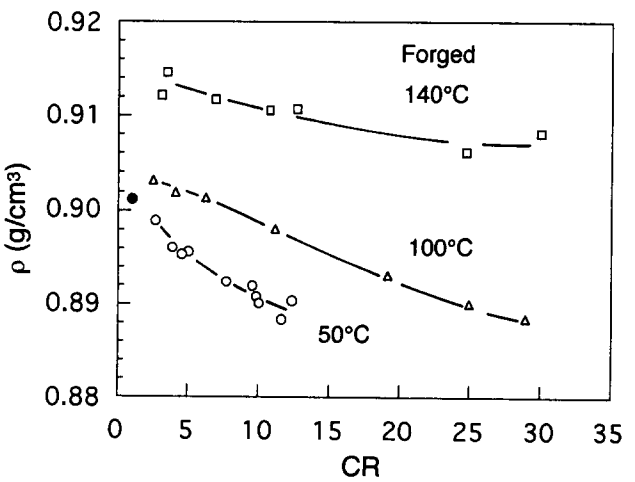

Figure 2 Density *versus* CR for samples prepared at 50 (○), 100 (△) and 140°C (□); original undeformed sample (●)

Several values of ΔH_c° have been reported. Roy *et al.*[13] reported that the percentages of crystallinity based on heat of fusion ($\Delta H_c^\circ = 33$ cal g^{-1}) and on density measurements were very consistent; that is, the relation between $1/\rho$ (specific volume) and X_c is linear if the amorphous density and crystal density are constant. *Figure 4* shows $1/\rho$ *versus* X_c for data from *Figures 1* and *2*. In *Figure 4*, X_c was calculated from two reported ΔH_c° values of 33 and 50 cal g^{-1} [14,15]. The extrapolated crystal densities from undeformed samples are 0.938 and 0.996 g cm^{-3} for 33 and 50 cal g^{-1}, respectively. The reported values[15] for α-crystal density are ~0.932–0.946 g cm^{-3}. In the calculation using equation (1), values of $\Delta H_c^\circ = 33$ cal g^{-1} and $\rho_c = 0.938$ g cm^{-3} were taken for the perfect crystal. The results for calculation of ρ_a are shown in *Figure 5*. It can be seen that the value of ρ_a increases with CR up to ~10, independent of T_d. This result, combined with information in *Figure 1*, indicates that the compression of the amorphous region and decrystallization proceed simultaneously during the initial stage of deformation ($CR < 10$). For $T_d = 100$°C, the ρ_a seems to be relatively low and goes down at high CR (>20). At 100°C, the smectic phase is induced during the deformation, but then reverts back to the α-crystal. However, the sample may have a small amount of smectic phase (but unmeasurable by d.s.c.) especially for a high CR. The existence of the smectic phase lowers ρ since the density of the smectic phase is lower than that of the α-crystal. In this case, ρ_a is calculated as a lower value using equation (1). When samples are subsequently annealed at 140°C, the residual smectic phase should revert back to the α-crystal. In fact, the estimated ρ_a of the annealed sample is higher than that of the unannealed one for $T_d = 100$°C. The data in *Figure 5* are scattered. This may be due to the lower accuracy of the density measurement and/or the d.s.c. measurement. In our prior study[16], the sample densities were estimated using a density gradient column with an organic solvent pair (carbon tetrachloride and hexane), which reduced data scatter. However, some solvent was taken up by the samples. Therefore, the ρ_a values in the prior study were a few per cent higher than those in *Figure 5*. It should be noted that this increase in amorphous density with compressive draw is a new finding.

Figure 6 shows the d.s.c. thermogram for the sample at $T_d = 50$°C and $CR = 10$. The exotherm for formation of the smectic phase (ΔH_s) was observed at around 80°C. The smectic phase reverts back to the α-crystal after the exotherm (since the exothermic process is a transition from smectic to α-crystal), followed by the crystal-to-melt transition. Therefore, the heat of fusion (ΔH) indicated in *Figure 6* consists of X_c plus X_s, i.e. $\Delta H = (X_c + X_s)\Delta H_c^\circ$, where ΔH_c° is the heat of fusion for the α-crystal. ΔH_s and ΔH as a function of CR are plotted in *Figure 7*. ΔH_s decreased with CR, suggesting that the amount of smectic

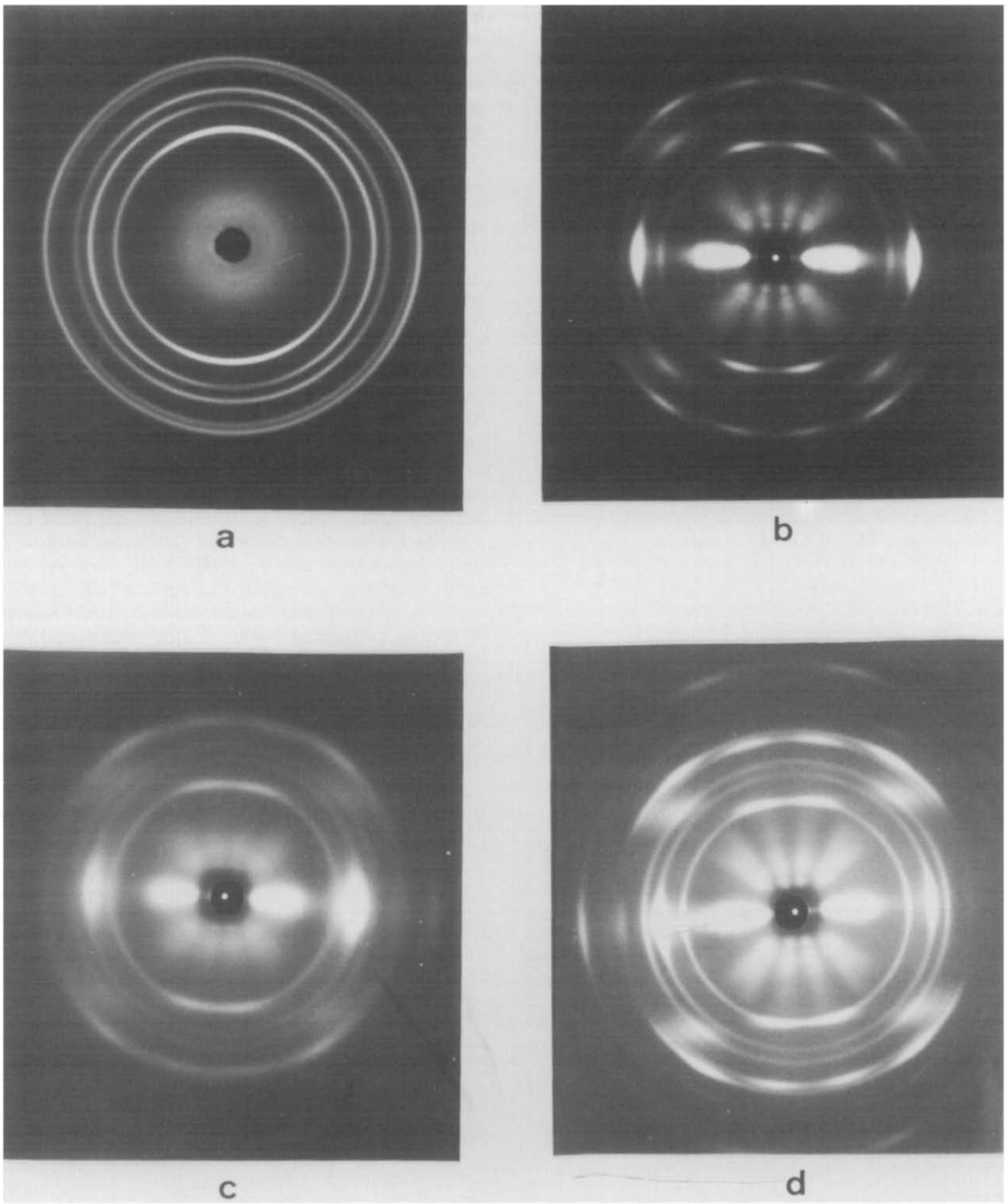

Figure 3 WAXS patterns of samples prepared at different CR and T_d; (a) $CR=3.9$ at 140°C, (b) $CR=50$ at 140°C, (c) $CR=12$ at 50°C, (d) sample c subsequently heat treated (140°C for 30 min). The incident X-ray beam is parallel to the plane direction. The plane direction is vertical on the photographs

phase increased during the deformation. On the other hand, ΔH is almost constant at $CR<4$, suggesting only an α-crystal-to-smectic transition in the initial stage of deformation. Subsequently, on draw, the smectic-to-amorphous transition may occur in addition to the α-crystal-to-smectic transition. Although a qualitative estimation of the smectic-phase content has been reported[7], the fraction of smectic phase could not be directly calculated from the exotherms, since the absolute heat for smectic-to-α-crystal transition is unknown. Since the peaks of ΔH and ΔH_s differ by ~80°C, X_c+X_s can be estimated approximately from $X_c+X_s=\Delta H/\Delta H_c^\circ$, although the exotherm and endotherm probably overlap. As such, the above estimation combined with equation (2) gives X_s:

$$X_s=\frac{1/\rho-X_t(1/\rho_c-1/\rho_a)-1/\rho_a}{1/\rho_s-1/\rho_c} \quad (3)$$

where $X_t=X_c+X_s$, and a value of $\rho_s=0.916\ \mathrm{g\,cm^{-3}}$ is taken[17]. The ρ_a for $T_d=50$°C is still unknown. The ρ_a for $T_d=50$°C was estimated from the dotted line in *Figure 8* (data are from *Figure 6*) since the values of ρ_a

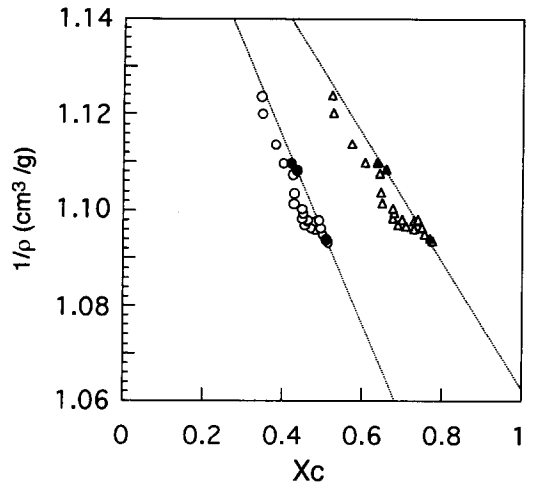

Figure 4 $1/\rho$ *versus* X_c calculated using ΔH_c values of 50 (○) and 33 cal g^{-1} (△). Filled symbols (●) for 50 and (▲) for 33 cal g^{-1} are for undeformed samples with different crystallinity

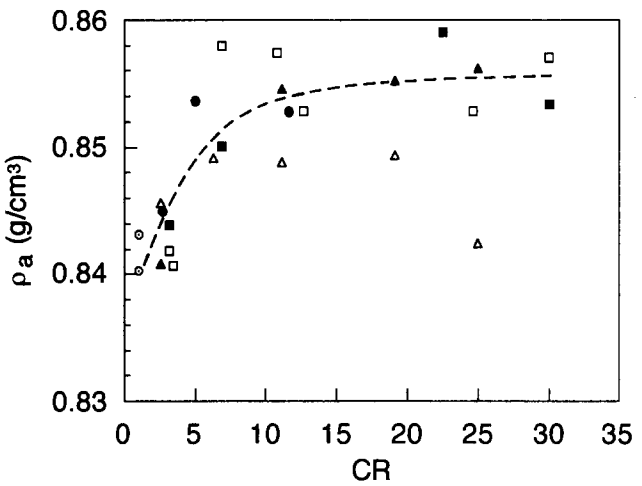

Figure 5 Amorphous density *versus CR* for samples prepared at 100 (△) and 140°C (□), and subsequently heat treated (140°C for 30 min) samples of T_d at 50 (●), 100 (▲) and 140°C (■)

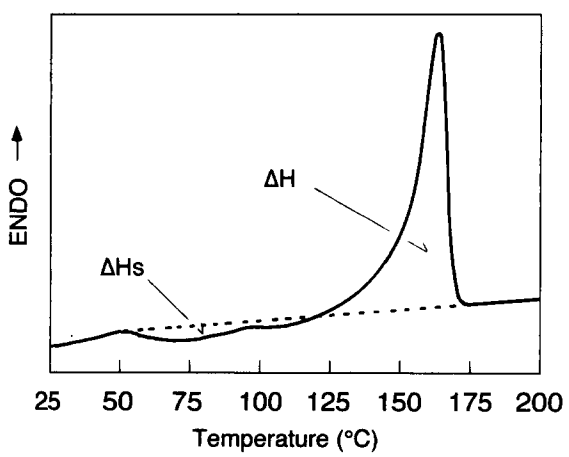

Figure 6 D.s.c. thermogram for the sample prepared at 50°C for $CR = 10$

estimated in *Figure 6* were a function of *CR* (independent of T_d). The calculated weight fractions X_s, X_c and X_a as a function of draw are shown in *Figure 9a*. For a *CR* up to 10, a large fraction of the α-crystal transforms to the smectic phase. This is confirmed by the broad and weak WAXS pattern of the sample drawn at 50°C (see *Figure 3c*). The average heat of transition for smectic to α-crystal estimated from *Figures 7* and *9a* was ~5.5 cal g^{-1}. This value is quite low compared with that for an α-crystal-to-melt transition because the smectic phase is a disordered form of the α-crystal, and smectic and α-crystal involve a one-three helix[18]. Thus, the smectic phase can easily revert back to the α-crystal on heating.

Figure 10 is a schematic of the phase changes on draw for $T_d < T_s$. At T_d (50°C) $< T_s$, it is thought that the crystal deformation proceeds through the generation of an intermediate smectic phase (Process I). *Figure 9a* shows that a large fraction of α-crystal is transformed to smectic by a *CR* of ~10. In this process, the molecular chains are pulled out from the lamellae (lamellae unravelling process). For $T_d = 100$°C, the smectic phase cannot be observed. However, Process I would also proceed since the smectic phase is produced during the deformation[7]. After compression, the smectic phase reverts back to the α-crystal (Process I′) because the smectic phase is unstable at >70°C and atmospheric pressure[7,19]. In addition to Process I, the smectic-to-amorphous transition (Process II) may also occur, but the process is not major (see *Figure 9a*). At T_d (140°C) $> T_s$, decrystallization and annealing proceed during the deformation. A small amount of α-crystal was totally decrystallized by $CR < \sim 10$ followed by no major decrystallization on further draw (see *Figure 9b*). At this temperature, however, the metastable smectic phase is not formed[7], so that the

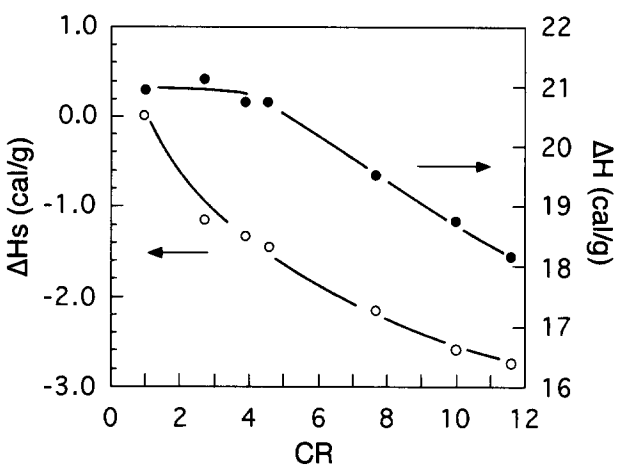

Figure 7 ΔH_s and ΔH *versus CR* for samples prepared at 50°C

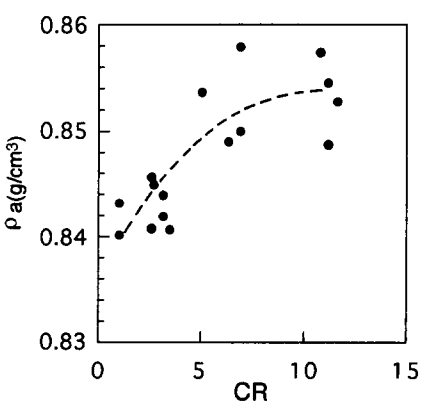

Figure 8 ρ_a *versus CR*: dotted line is expressed by $\rho_a = 0.836 + 3.40 \times 10^{-3} \times CR - 1.65 \times 10^{-4} CR^2$

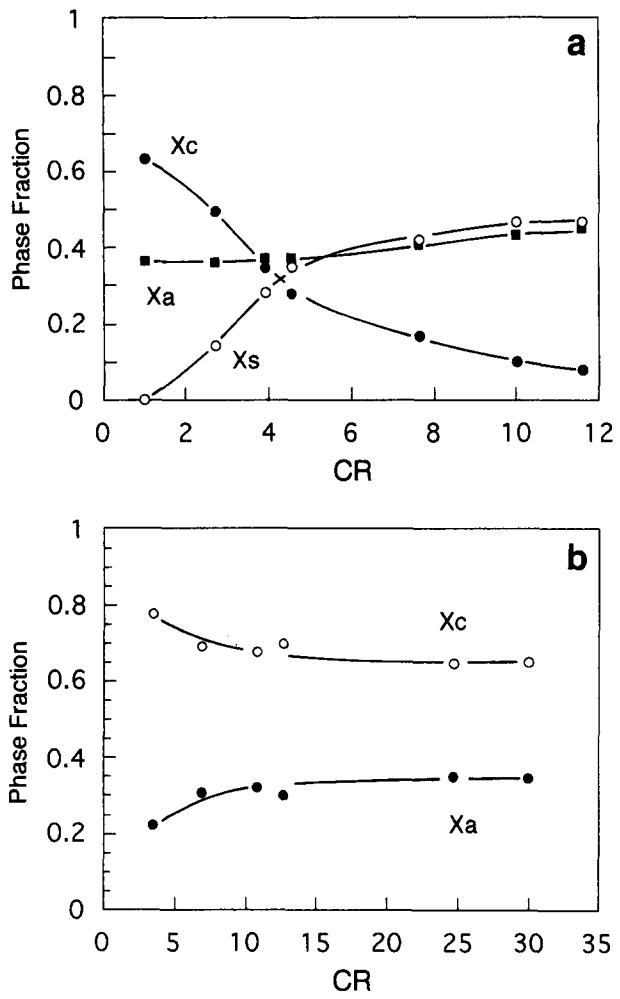

Figure 9 (a) X_c (●), X_s (○) and X_a (■) as a function of CR for samples prepared at 50°C; (b) X_c (○) and X_a (●) as a function of CR for samples prepared at 140°C

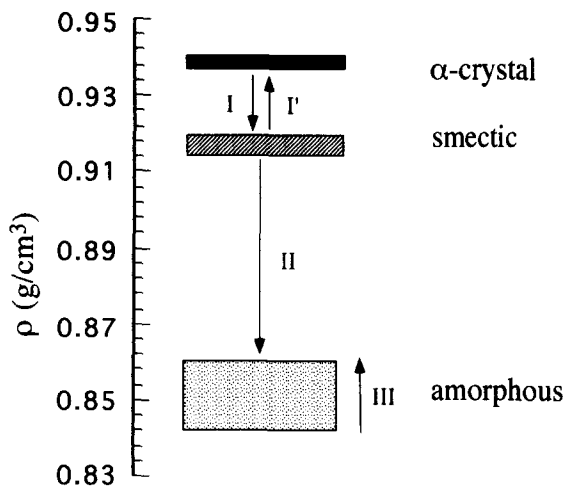

Figure 10 Schematic of phase changes on compression draw

pulled-out chains fall back into their α-crystal form during the deformation, prohibiting the lamellae unravelling process. We have reported[8] that the draw efficiency parallel to the uniplanar direction for $T_d < T_s$ was higher than that for $T_d > T_s$. It can thus be concluded that Process I apparently facilitates the efficient draw of the α-crystal phase.

The original undeformed iPP sample consists of about half amorphous chains. During the sample deformation, the amorphous chains are extended by the compressive force. Saraf and Porter[7] pointed out that the amorphous region might form a rubbery network with entanglement points as temporary crosslink junctions[20]. Furthermore, the network might behave like an ideal rubber for planar deformation up to ~4[7,21]. As shown in *Figure 5*, the amorphous density increased rapidly at low CR ($< \sim 5$). This indicates that the rubber-like deformation of the amorphous phase is accompanied by an increase in the density caused by the compressive force. Process III is independent of T_d. Therefore, there seems to be no relation between the increase in amorphous density and the formation of the smectic phase.

The uniplanar deformed iPP samples showed some interesting properties and morphology. For example, T_g increased with draw, the smectic phase reduced the tensile modulus, the transparency of the sample was improved with the existence of the smectic phase, and the deformed sample had a layer structure. The effects of structural change on the physical properties of iPP will be reported in a subsequent paper.

CONCLUSION

The uniaxially compressed iPP consisted of two or three phases (α-crystal and amorphous or α-crystal, amorphous and smectic), depending on the draw temperature (T_d). The percentage of each phase and amorphous density increase have been evaluated by thermal analysis and density measurements. At $T_d < T_s$, a large fraction of the α-crystal transforms to the smectic phase by a CR of ~10, without any major change in the amorphous fraction. This process facilitates lamellae unravelling, leading to a high molecular draw efficiency. At $T_d > T_s$, no measurable smectic fraction is observed. The density of the amorphous phase increases with increasing CR up to ~10, independent of T_d.

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