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Structural transitions during the cold drawing of aliphatic ketone terpolymers

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Abstract

Cold drawing of aliphatic ketone terpolymers with CH_3 substituents is shown to promote production of the high density α crystal phase. The quantity of the minor α component decreases with increasing CH_3 content and the solid–solid α → β phase transition temperature is shown to be lower compared with the unsubstituted polymer. Draw rate affects the amount of α phase produced: low draw rate favours α phase. This is explained in terms of strain-induced heating effects: high rates increase the temperature above the $T_{\alpha\rightarrow\beta}$ transition. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Aliphatic polyketone; Copolymer; Crystallization

1. Introduction

Poly aliphatic ketones are a relatively new family of semi-crystalline thermoplastics formed by two repeating units of the following chemical formula:

$[(CH_2CH_2CO)_n–(CH_2CRHCO)_m]$

which is currently being developed by BP-Amoco Chemicals under the tradename "Ketonex" and which has also been marketed by Shell Chemicals. The distribution of the two components along the chain is random. Chemically, this actually consists of units of three components: carbonyl units, ethylene and a second substituted olefin.

Consequently, this material has come to be termed a "terpolymer". Applications for this are to include barrier films, blend and electrical applications. The melting point, T_m, of the unsubstituted polymer (i.e. the copolymer, $R = H$) can be reduced from ~260°C by using CH_3 (addition of propylene monomer) or CH_2CH_3 (addition of butylene monomer) as the R group. For $R = CH_3$ some authors have found a continuous fall in T_m with CH_3 content [1]. However, after considering various results from a range of sources, we previously concluded that this fall in melting point is linear up to an upper-bound value at which ~9 mol% of the olefins are substituted [2]. At this point, the melting point stabilizes at ~190°C. A major consequence of substitution for the structure of the crystalline phase is that at relatively low levels of substitution, the usual room temperature, high density α phase is forced to adopt the lower density β structure (usually only found above ~100°C in the copolymer [3]). There is evidence that both this change in structure and the fall in T_m are consequences of incorporation of R groups within the lattice, according to the Inclusion Model of copolymer crystallization of Sanchez and Eby [4].

Upon orientation, the 6.6% CH_3 terpolymer, which forms almost exclusively β phase in the unoriented case, manifests significant levels of α phase. This has been reported when orientation is imposed in a number of ways. For example, gel spun fibres [5] and high-speed injection mouldings [6] both contain conspicuous levels of α phase. Also, our own earlier work has shown that modest cold drawing leads to formation of substantial α phase material [2]. Recent work has also shown the presence of α phase in isotropic material at modest substitution [1]. This was the starting point for the present work in which the focus is on cold drawing of CH_3 terpolymers and the associated structural changes. Not only is this of interest from a "fundamental" standpoint, but this is also of potential practical value.

2. Materials

Compression moulded films of terpolymers and copolymer of thickness 170 μm were supplied by BP-Amoco Chemicals. The CH_3 content in the terpolymers ranged

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Table 1
Materials characteristics of polymers used

Mol% CH_3	Nominal T_m (°C)	Moulding temperature (°C)
2.0	248	270
6.6	223	245
8.8	215	230
10.0	209	230
14.6	198	220

from 2.0 to 14.6 mol%. Table 1 shows the material identification and characterization (supplied by BP/Amoco).

3. Experimental

3.1. X-ray diffraction

The most convenient method of analysing the phase structure of crystalline materials is using wide angle X-ray diffraction (WAXD). This was carried out using pin-hole collimated, monochromated CuK_α radiation. Patterns were collected with a GADDS detection system (Brucker). Small angle X-ray scattering (SAXS) was used to investigate the larger scale lamellar structure. This was done using a Rigaku SAXS camera with a GADDS detection system using Ni filtered CuK_α radiation.

Drawn films were examined with the incident beam both normal and parallel (i.e. edge-on) to the surface to assess possible in-plane orientation effects (“double orientation”).

3.2. Differential scanning calorimetry (DSC)

A second means of assessing the presence of α crystals in the room temperature material is the appearance of an endotherm at ~100°C associated with the $\alpha \rightarrow \beta$ transition upon heating [3]. Samples were scanned in a DuPont 2910 DSC at a heating rate of 10°C/min.

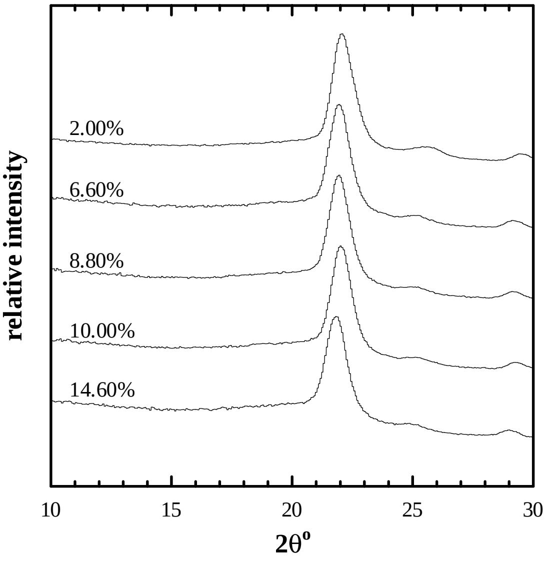

Fig. 1. Plot of WAXD data: relative intensity vs. 2θ for isotropic terpolymers. CH_3 content increases towards bottom of figure.

Table 2
Unit cell parameters and principal reflections from α and β structures. Spacings calculated from the cell parameters given in Refs. [5] and [7], respectively

	α(5)	β(7)
a (Å)	6.91	7.97
b (Å)	5.12	4.76
c (Å)	7.60	7.57
Calculated spacing (Å)		
hkl	α cell	β cell
011_β		4.02
110_α	4.11	
110_β		4.09
200_β		3.99
002_α	3.80	
002_β		3.79
111_α	3.62	
111_β		3.59
200_α	3.46	
210_α	2.85	
210_β		3.06
211_β		2.83
212_β		2.38
113_α	2.16	
203_β		2.13
113_β		2.15

3.3. Drawing

Materials were initially drawn by hand at room temperature to draw ratios (DRs) of ~3–6. At a later stage, selected samples were drawn at controlled rates in an Instron 4411 tensile testing device.

4. Results

4.1. X-ray diffraction

4.1.1. Structure of undrawn film

By WAXD, the “as received” terpolymer films all appeared isotropic in both projections. Fig. 1 shows plots of intensity against 2θ, integrated over the whole azimuth angle, for the terpolymer materials. Table 2 lists the principal WAXD reflections from the two crystal structures [5,7]. These traces are characterized by three peaks at 2θs of ~22, 26 and 29°. The main reflection at ~22° corresponds to the mixed $110_\beta/200_\beta$ (see Table 2). The peak at ~26° corresponds to the position of both the characteristic 200_α and the 111_β and cannot be used to indicate the presence of α material in isotropic samples. Only after orientation are these signals separated into different parts of the Debye ring. However, most of this maximum must be 111_β because the traces are all dominated by β reflections. Nevertheless, since this maximum is particularly well developed in the

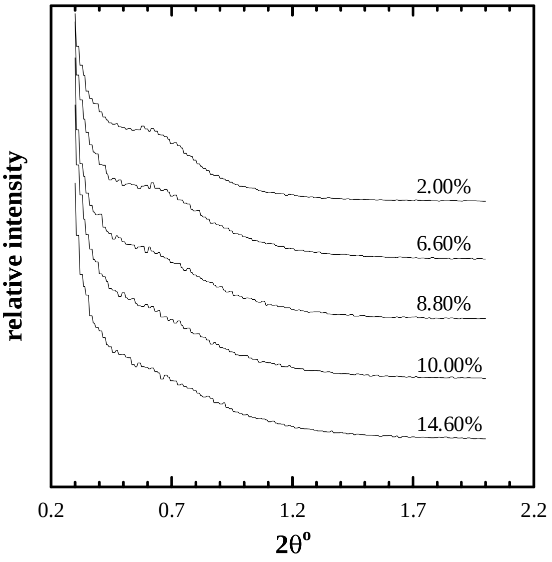

Fig. 2. Plot of SAXS data: relative intensity vs. 2θ for isotropic terpolymers. CH_3 content increases towards bottom of the figure.

2.00 mol% sample, the possible presence of some additional 200_α component in this specimen is also suggested. The peak at ~29° can be unambiguously assigned as the 210_β.

The SAXS profiles, also integrated over the whole azimuth angle, all show a single maximum at 2θ ~0.6°, giving long periods of ~150 Å (Fig. 2). This maximum becomes progressively less defined with increasing CH_3 content and no higher order signals are apparent, even in the sample with lowest CH_3 content. Morphologically, this is consistent with a progressively looser and variable fold surface with CH_3 content.

4.1.2. Cold drawn films

Fig. 3 shows example WAXD patterns from drawn films, in this case for the 2.0 mol% material. The upper and lower figures are in the beam-normal and beam-parallel projections, respectively. Orientation has separated the reflection at 2θ ~26° into two identifiable components: on the equator and on the first layer line (although the first layer line reflection is not expected to reproduce well). From this, the equatorial component at ~26° can be uniquely indexed as 200_α, indicating the presence of substantial α phase material. Therefore, some 110_α must also be mixed in with the main $110_\beta/200_\beta$ reflection. With the beam edge-on, the 200_α is far stronger than before (Fig. 3(b)), implying that the material is oriented with $(100)_\alpha$ within the plane of the sheet. Fig. 4(a) and (b) are plots of intensity vs. 2θ taken through the equatorial regions of the patterns (integrated over an azimuth range about the equator) of all the CH_3 containing materials in the normal and edge-on projections, respectively. A word of caution should be added regarding the precision of the 2θ scale on Fig. 4. The nature of the experimental instrumentation lent itself to possible introduction of non-systematic errors in camera length; accordingly small differences in peak 2θ may not be significant.

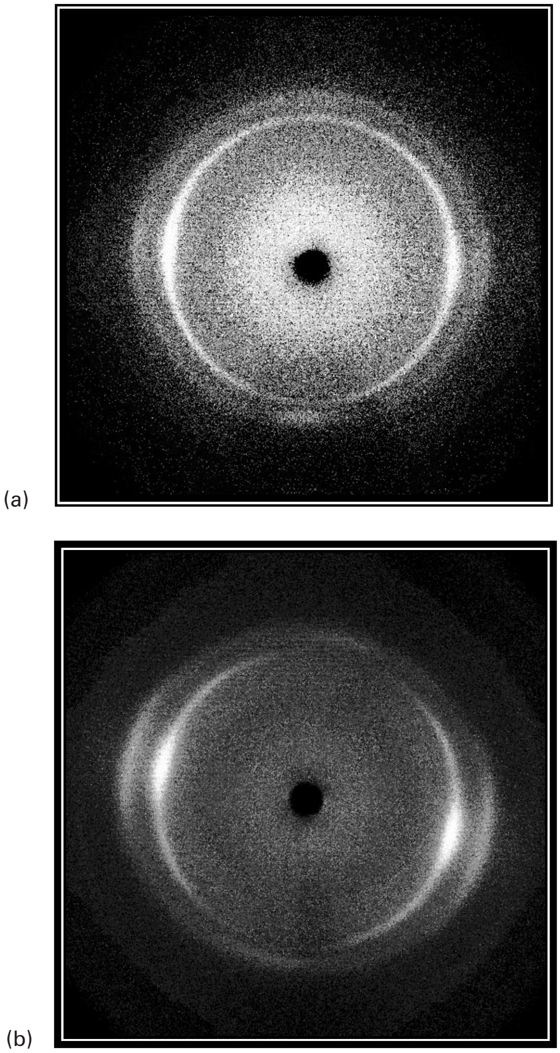

Fig. 3. WAXD patterns of cold drawn film with 2.0 mol% material (DR ~3): (a) beam along normal; (b) beam edge-on.

With increasing CH_3 content, four features are evident (Fig. (4)):

1. The intensity of the 200_α decreases.
2. In all materials the FWHM of the main peak is larger than in the undrawn materials, Fig. 1, (~1.6° cf. ~1.0°, excluding the effect of instrumental broadening, which can be expected to be constant).
3. The 210_β at ~29° is better defined before drawing, Fig. 1.
4. As already mentioned, where the terpolymers show the presence of α phase, the 200_α is stronger in the edge-on projections, Fig. 4(b). Note that the films were isotropic before drawing. Therefore, the anisotropy in 200_α is a consequence of drawing.

4.2. Effect of strain rate

The effect of strain rate on phase structure was explored.

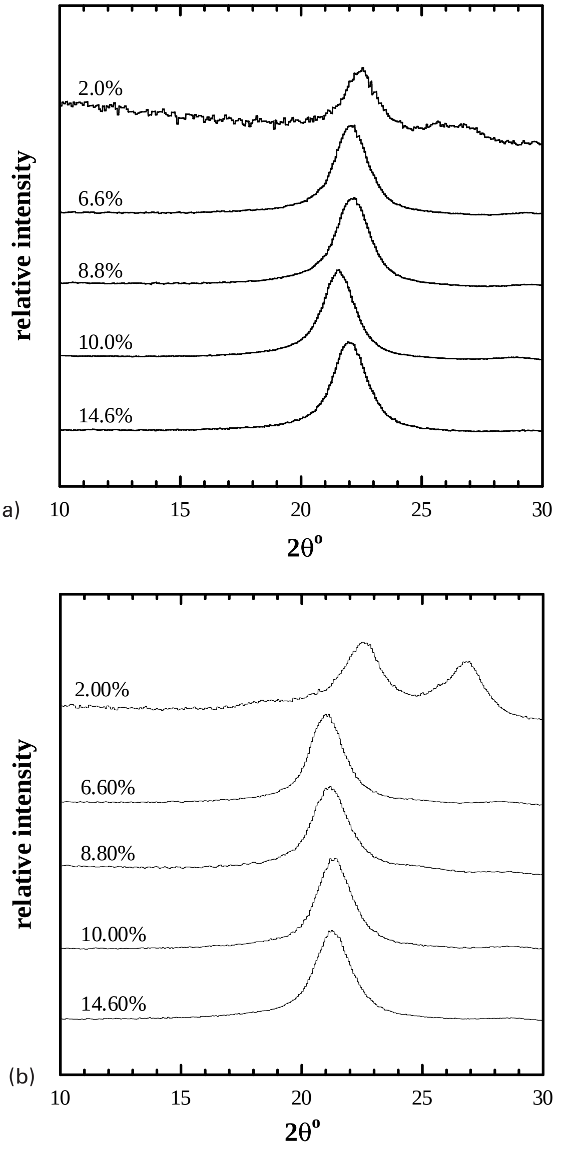

Fig. 4. Equatorial WAXD intensities of drawn terpolymers: (a) beam in normal projection; (b) beam in edge-on projection. CH_3 content increases towards bottom of the figures.

Films with 8.8 mol% CH_3 content were drawn to DRs of ~3–5 at controlled speeds in an Instron at rates covering two decades (5–500 mm/min).

The following points were apparent:

1. As is usual the degree of orientation increased with strain rate, evidenced by a narrowing of the azimuthal spread of the reflections.
2. At lower draw speeds (5 and 50 mm/min) 200_α was apparent, particularly in the edge-on projection, see Fig. 5. However, at 500 mm/min, no 200_α can be seen. This is despite a higher degree of orientation at higher draw rates. Clearly, α phase formation is favoured by low strain rates despite the higher overall orientation.

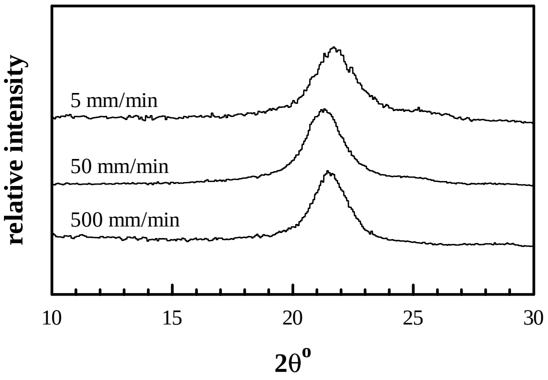

Fig. 5. Equatorial WAXD intensities of 8.8 mol% material drawn at controlled rates: beam edge-on. Draw speed increases towards bottom of figure.

4.3. DSC

The crystal phase behaviour can also be conveniently studied by taking advantage of the fact that, upon heating, the α crystal reportedly changes to the β modification in the region of 100°C (depending upon substituent content) [3] and can therefore be used to indicate the presence of this crystal form.

Fig. 6(a) and (b) shows DSC traces on heating for undrawn and drawn specimens, respectively. For comparison, the unsubstituted copolymer, which, by WAXD contained substantial α phase, is also shown. (In some cases insufficient drawn material could be obtained for DSC scans; in these cases the data for the undrawn material is also omitted from Fig. 6(a).) The undrawn copolymer shows two endotherms at ~255 and ~91°C. The larger of these, at ~255°C, is associated with the final β crystal melting, the lower with the α → β transition. Our value for $T_{\alpha\rightarrow\beta}$ of 91°C can be compared with that of 112°C reported by other workers [3]. After drawing, the copolymer shows a slight lowering in the final melting point to ~251°C and a substantial broadening in the low temperature endotherm, peaking around 64°C.

The undrawn terpolymers show the final T_m and heats of fusion falling as the mol% of CH_3 increases, see Table 3. The decrease in heat of fusion is in line with falling crystallinity with CH_3 content. Although none of the undrawn

Table 3
Heats of fusion and final melting temperature in undrawn material from DSC

Mol% CH_3	ΔH_f (J/g)	T_m (°C)
0	121	256
2.0	106	247
6.6	87	231
8.8	79	217
10.0	85	220
14.6	63	205

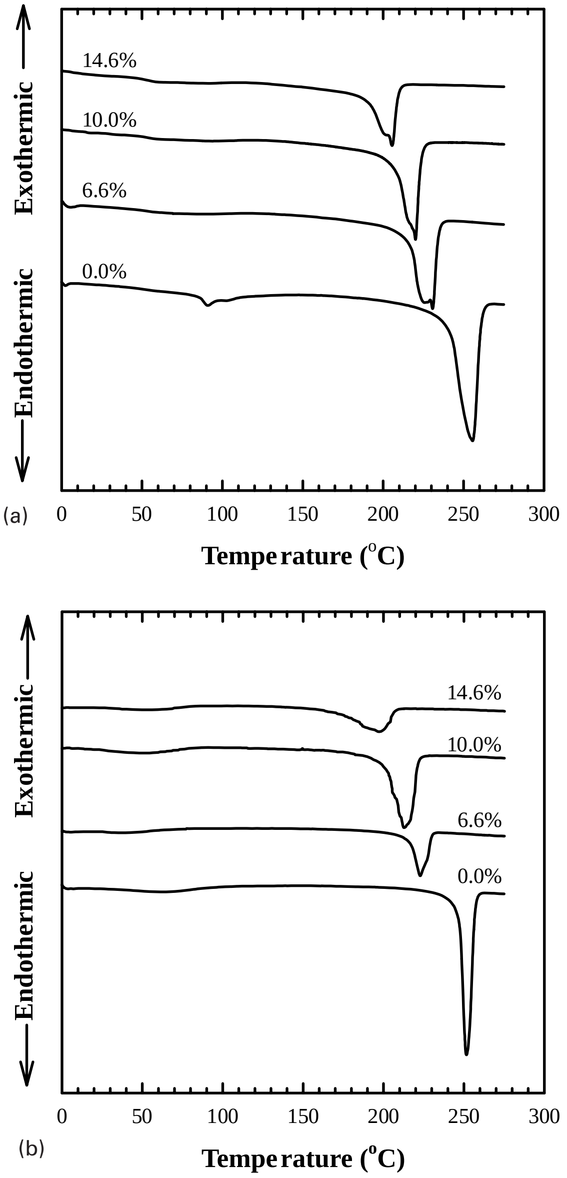

Fig. 6. DSC traces on heating for: (a) undrawn film; (b) drawn films.

samples shows a clear low temperature endotherm, the broad, weak maximum at ~60–80°C present in all the samples may possibly be associated with the presence of very small, imperfect crystals of α material.

Within the series of scans of drawn samples, there are clear trends. All samples examined show slightly lower final melting points than in the undrawn states and now display broad but identifiable endotherms at around 40–50°C. Note that this is lower than the temperature for the copolymer. This can be associated with the α → β solid–solid transition. Hence, there is evidence that, by DSC, even the material of highest CH_3 content contains an element of this second crystal phase after drawing. Note that only the materials of lower CH_3 content showed distinct α phase WAXD reflections. It is to be expected that, as CH_3 content increases, assuming equivalent degree of randomness, defect-free lengths will become shorter and hence it is reasonable to expect that the size of α phase crystallites will become smaller. Therefore, it is concluded that this effect is probably a consequence of size; WAXD in this case is unable to detect the smaller crystallite regions, which can be successfully recognized by the thermal technique.

5. Discussion

In the undrawn, isotropic state it has previously been shown that CH_3 terpolymers adopt the β structure rather than the α found in the unsubstituted copolymer because of the capacity for the β structure to accommodate the substituent groups [3]. In all the materials studied here, it has been found that the α content in the undrawn state is minimal.

The two possible α and β crystal cells are closely related. Both have identical extended chain conformations, form orthorhombic structures and have identical repeat lengths along *c* (7.60 Å). They differ in lateral cell dimensions (see Table 2) and in the details of lateral chain packing. The α cell has a smaller cross-sectional area and chains are arranged in a more sheet-like manner (parallel to the *ac* plane) than in β, which is near hexagonal. The high melting points of these materials also suggest secondary bonding rather than simple van der Waals interactions [3], e.g. via the carbonyl groups.

Drawing, however, clearly promotes formation of the α phase in CH_3 terpolymers. Why drawing should lead to the development of a new phase is not readily obvious and we will return to this shortly. However, given the finding that α phase is produced on drawing, there is also the associated observation from WAXD that less α material forms as CH_3 content increases. Such suppression of draw-induced α phase formation by high CH_3 content is, of course, consistent with difficulty in accommodating such units in the α phase. Where α does appear in drawn materials this must correspond to crystallites of low substituent content. Therefore, it appears there are two competing effects: (a) the presence of substituents — which favours the β structure; and (b) drawing which tends to push the system towards the α phase.

To understand better why drawing should encourage the production of α phase the mechanism of drawing in semi-crystalline polymers must be considered. This has been a long discussed issue with views falling into two broad categories:

1. that drawing occurs in the solid state, without loss of the crystal order e.g. Ref. [8];
2. that drawing involves destruction of the initial crystal and formation of a new structure (akin to a melting and re-crystallization process) e.g. Refs. [9,10].

An obvious comment regarding the formation of the α phase is that it must originate from either the original β crystallites or from the original amorphous material. However, since the amorphous component is likely to contain segments with high defect (CH_3) concentrations it is considered that the probable source of the newly forming α material is the original crystalline β component. Formation of α crystals with low defect content is clearly only possible with substantial rearrangement, effectively rejecting CH_3s from the original lattice, which it will be recalled gave long periods of ~150 Å. Allowing for realistic values of crystallinities of approximately 30%, this gives a value of (roughly) 40 Å for the crystal core. It is difficult to envisage how such a transition, dependent upon the ejection of methyl groups, can occur in the context of a strictly solid–solid transition without the intervention of a disordered state. It is also apparent that the principal WAXD reflection (comprised essentially of *hk*0 signals from the β lattice) broadened substantially after drawing. In all cases before drawing the (albeit uncorrected) FWHM was ~1.0° compared with ~1.6° after drawing. Of course, a more disordered crystal can also cause such broadening, but if it is assumed that broadening is entirely due to size effects and, if instrumental broadening is ignored, the Scherrer equation can be used to estimate apparent lateral crystal sizes. Using a value of 0.9 as the Scherrer constant, this indicates apparent lateral crystallite sizes of 80 and 50 Å for the undrawn and drawn materials, respectively. This is consistent with very large scale break-up of the original β crystallite morphology on drawing. It is also noted that the 210_β is apparently more well defined in the undrawn than in the drawn materials. This is also consistent with smaller lateral crystallite sizes in the drawn materials.

Drawing also produces recognizable regions of α phase. Such crystallites must be sufficiently depleted in CH_3. Their presence implies the selective crystallization of sequence lengths of low CH_3 content during the draw. Such sequences will be progressively shorter and fewer in materials of increasing CH_3 content, explaining the loss of α material at high CH_3 content.

The finding that the α phase was only observed if drawing was conducted at low draw rates is entirely reasonable when it is recalled that the $\alpha \rightarrow \beta$ phase transition temperatures for the substituted materials were in the range of 50°C. Higher draw rates lead to higher local temperatures at the point of drawing due to the low thermal conductivity and high internal damping intrinsic in these polymers. If the temperature exceeds the $\alpha \rightarrow \beta$ transition temperature, then the α phase will be lost. Previous work has shown that substantial undercooling is required to reverse the transition [3] and hence it is to be expected that high draw rates will result in loss of α crystallites, beginning with the smallest, thermally least stable crystallites.

It may be noted that the $\alpha \rightarrow \beta$ phase transition temperature in the copolymer decreases after drawing. Also, $T_{\alpha\rightarrow\beta}$ is lower in the drawn terpolymer than in the drawn copolymer. The lowering of the transition temperature in the copolymer on drawing can be explained by the formation of smaller, less stable α crystals on drawing. To explain the lower transition temperatures in the drawn terpolymer compared to the drawn copolymer, we propose that the α crystallites in the terpolymer are smaller than in the copolymer as a result of the CH_3 groups being rejected from the forming α phase.

6. Summary

Cold drawing of CH_3 terpolymers leads to large scale break-up of the original β crystal population and produces α crystal phase from this population. The quantity of α material decreases as the CH_3 content increases and the $\alpha \rightarrow \beta$ phase transition temperature decreases in the CH_3 containing terpolymer compared to the unsubstituted material. High draw speeds lower the α content because of strain-induced heating above the $\alpha \rightarrow \beta$ transition temperature.

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