Some crystallization kinetics of isotactic polypropylene

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Infra-red evidence is presented that the building of helices in the crystallization process from the glassy (or smectic) phase or from the melt are second order or zero-th order respectively. The observation coupled with data from density and X-ray diffraction measurements is interpreted in molecular structural terms.

INTRODUCTION

Isotactic polypropylene is a polymer of considerable commercial importance and several studies have been made on its crystal structure, mode of crystallization and properties of the various solid phases. These studies are of relevance because the material can easily form a random phase which slowly converts to the crystalline forms causing dimensional instability. Further, shrinkage on cooling is considerable and to some extent also influences the usefulness of the polymer. Here, we concern ourselves with various aspects of the crystallization process.

The polymer adopts a chain conformation involving a 3^1 helix but crystallizes in a number of different ways. Three crystalline variants are frequently encountered together and are labelled α, β and γ. The α form, which predominates, is monoclinic, contains 4 chains per unit cell and has been described by Mencik[1] and Natta *et al.*[2]. The β form is less prevelant, is hexagonal and has been studied by Samuels and Yee[4]. Single spherullites usually contain both α and β variants in coexistence, with the α form predominating[3].

The third and rarest form γ, has been reported by Turner-Jones *et al.*[5]. It seems that the α form can be converted to γ by annealing at high pressures and temperatures (M. Hikosaka *et al.*[6]).

Like many other polymers, the structure and properties of polypropylene rapidly quenched from the melt are disordered and unlike its crystalline counterparts (at least for limited periods). The disordered phase so produced is relatively stable at room temperature and below. The X-ray diffractogram obtained from a quenched sample is diffuse in appearance and hence suggests a completely disordered phase[7]. Infra-red evidence exists, however, showing the presence of helices in the phase and hence a somewhat ordered structure[8,9]. It has been suggested by Miller[17] that the structure of the quenched phase is paracrystalline, i.e. essentially it is three-dimensionally ordered but with a high incidence of defects. Alternatively, Bodov *et al*[18] using X-ray evidence suggest that the structure is composed of microcrystallites of monoclinic (i.e. α) habit. Geil[11] agrees regarding the microcrystallinity but proposes a hexagonal habit. Another structural model to gain support is the 'frozen liquid' type of structure sometimes described as a 'smectic phase'[29]. McAllister *et al.*[19] have suggested that 60% of the material in this form of polypropylene is amorphous, with the remainder in microcrystalline arrays of cubic or tetragonal symmetry. It is clear that the nature of this paracrystalline phase may well be variable and is certainly not fully understood. For our purposes we need to refer to this phase (or phases) repeatedly and will describe it rather arbitrarily as a 'glass'.

The glass transition temperature T_g of isotactic polypropylene is most widely held to lie near 265K. However, values as low as 238K are to be found in the literature[10]. If the glass is annealed well above T_g crystallization occurs at a slow rate to produce exclusively the α form[11].

The kinetics of crystallization of isotactic polypropylene from the melt have been studied by several investigators[12–15] all of whom have concerned themselves with spherullite growth, nucleation and the effect of temperature on crystallization. Other papers refer to the effect of melt temperature and time in the molten state on subsequent crystallization processes. We will refer to specific items of information later in this paper as they are required.

The kinetics of crystallization from the glass (i.e. quenched phase) have been studied by Fichera and Zanneti[16]. Here also, the rate of crystallization (as observed from the plot of heat of fusion vs. time) was found to be dependent upon temperature (the higher the crystallization temperature, the higher the rate of crystallization). They suggested that as the quenched sample is heated, melting of the microcrystallites occurs and that this is followed by crystallization.

All the kinetic measurements referred to above, whether they be for the melt→crystal or glass→crystal transitions have been made using methods such as changes in specific volume, heat of fusion and crystal front propagation. None of these studies can be considered

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satisfactory from a molecular structure viewpoint. A range of methods now exist enabling us to monitor the helical content, degree of order and subtleties regarding lamellar core growth. These molecular level structural tools have been applied here to the kinetics of the crystallization of melt and glass of polypropylene. X-ray diffration methods[19] are basic to such work.

Density gives a 2-phase model estimate of order. Assuming additivity of amorphous and crystalline volumes, the crystallinity may be calculated using the parameters for isotactic polypropylene proposed by Natta *et al.*[20]. Infra-red spectroscopy is an excellent method for measurement of the helical content of the polymer. The principal bands in the spectrum of helical isotactic polypropylene are near 1220, 1163, 998, 900, 941 and 809 cm^{-1}. Of these, the band at 998 cm^{-1} has been widely used for estimating helical content. The critical minimum number of monomer units, arranged helically and necessary for the observation of this band is thought to be 10 or 11 [21]. Kissin[21] also established that the minimum number of monomer units necessary for observation of the band at 973 cm^{-1} is only four. Since this band is rather insensitive to the helical segment length it is widely used as an internal reference for measuring the intensities of 'helix bands'. Zerbi[22] *et al.* showed that the band at 998 cm^{-1} is present in the infra-red spectrum of isotactic polypropylene above its melting point. Using Raman spectroscopy, the frequency can be measured of an accordion-like motion in regular sequences of polymer chains whether they be cores of lamellae or regular runs of polymer buried in a random matrix. The vibration concerned is normally called the longitudinal acoustic (*LA*) mode whilst the relationship between the *LA* mode frequency and the length of regular chain segments derived from a simple elastic rod model is given by:

$$\nu = \frac{M}{2L}\left(\frac{E}{\rho}\right)^{\frac{1}{2}}$$

where E is the effective elastic modulus of the crystalline core, ρ is the density of the vibrating 'rod', L is the length of the regular segment*, M is the order of the vibration (in this case an odd integer), and ν is the frequency of the *LA* modes. Values of E and ρ deduced by Hsu *et al.*[24] from their experiments on polypropylene are: $E = (3.66 \pm 0.12) \times 10^{11}$ dyne cm^{-2} and $\rho = 0.936$ g cm^{-3}. The SI equivalent units are $E = 3.66 \times 10^{10}$ N m^{-2} and $\rho = 0.936 \times 10^{3}$ kg m^{-3}. Inserting these values in the equation above we find that: $L = 1625/\nu$ (Å), with ν expressed in cm^{-1}. A controversy exists regarding the precise relationship between *LA* mode frequencies and the core thickness of lamellae (or other sequence lengths) and as a consequence it is premature to claim that the values of L obtained above have any real physical significance. It is, however, widely accepted that the values of L deduced from Raman studies parallel the regular sequence lengths. It is this application that we find to be of value here.

EXPERIMENTAL

Samples of highly isotactic polypropylene used in these experiments were supplied by the Hercules Powder Co. For infra-red spectroscopy, samples were prepared in the film form. The procedure used was as follows: the samples, in pellet or thick sheet form, were placed between two pieces of aluminium foil. This sandwich was then transferred to a hot press. (The temperature of the press was adjusted to the desired melt temperature beforehand.) Pressure was applied to give the desired film thickness. The pressure was then released, the foil/polymer sandwich removed and then quenched into refrigerants such as liquid nitrogen. Samples were then allowed to warm to ambient temperature.

Polypropylene infra-red spectra were measured at various temperatures in the melt. A specially constructed hot cell was used in these experiments in a Perkin–Elmer model 580 spectrometer. This instrument incorporates pre- and post-sample chopping and thus, as a consequence, the spectra are not seriously affected by sample emission or non-wavelength-specific absorption.

Infra-red spectroscopy was also used to monitor the kinetics of helix growth in quenched materials. A sample was quenched into the glass phase at 100K, was kept cold and then placed into a precooled infra-red cell described elsewhere[7]. The temperature of the sample holder was then rapidly raised to 255K and held at that temperature for 12 h. During this time, infra-red spectra were repeatedly recorded between 700 and 1050 cm^{-1} as a function of time. The helical content derived from these band characteristics was plotted against time to give *Figure 2.* The instrument used in these experiments was a Unican SP 100 spectrometer.

Helix growth was also monitored in a similar manner during crystallization from the melt (at 400K). The results in this case are plotted in *Figure 2.* As high temperatures are involved, the Perkin–Elmer model 580 was used for these experiments.

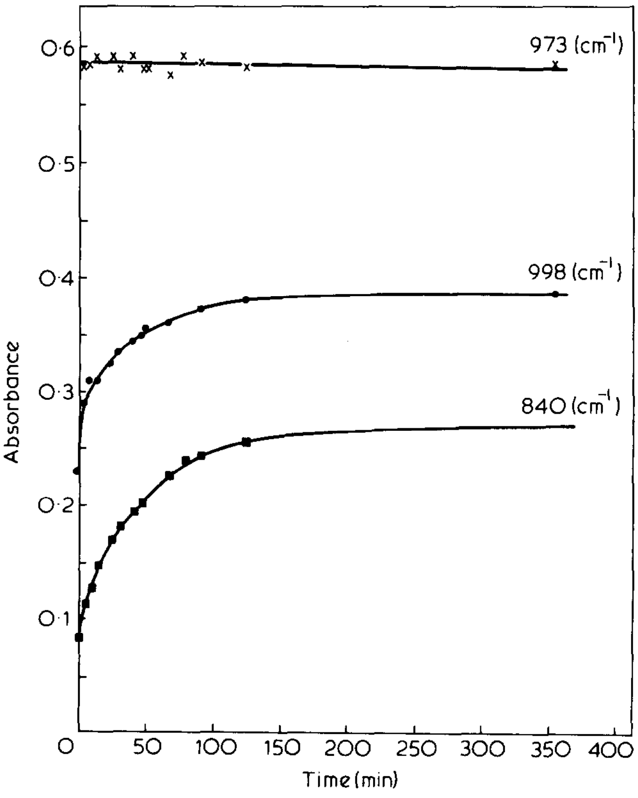

Figure 1 Helix growth in isotactic polypropylene at 255K. Absorbance of 3 infra-red bands as a function of time

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* In the case of a lamellar unit, L is fairly close to the thickness of the crystalline core of the lamellar unit, i.e. it is less than the low-angle X-ray spacing. In melts and other fluid phases L becomes the length (or average length) of the regular sequence—in this case a 3/1 helix. It has been observed in paraffinic liquids, polyethylene and several other systems.

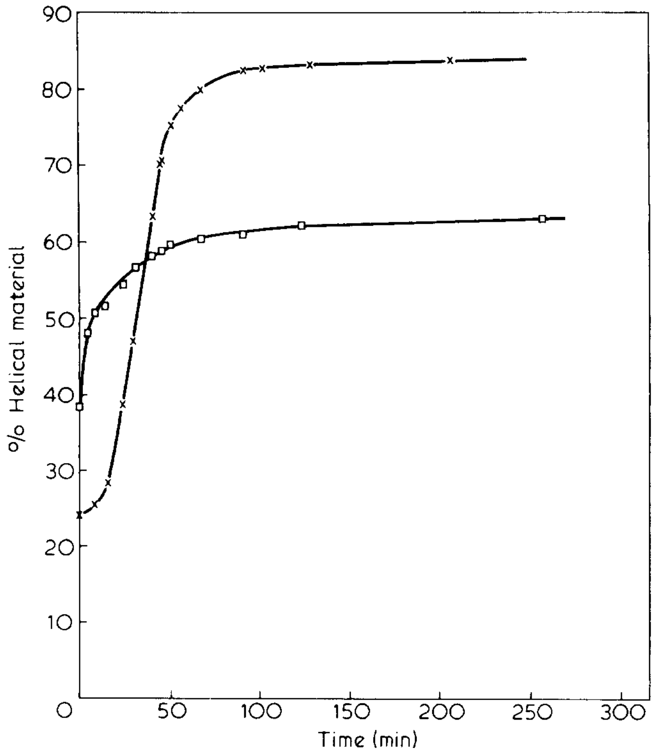

Figure 2 Helix growth in isotactic polypropylene as a function of time. □, Growth from the glass phase at 255K; x, growth from the melt at 400K

Raman spectroscopy was used to determine the *LA* modes of some of the samples. Typical spectra showing the *LA* mode are given in *Figure 5*. The average length of regular chain segment was determined using the formula described earlier, and the results are shown in *Table 2*. A modified Coderg T800 instrument, fitted with Ortec Brookdeal 5Cl photon counting electronics, was used for measurements.

Crystallization was also monitored by obtaining X-ray diffraction photographs from a paracrystalline sample annealed successively for 1 min at increasing temperatures. (Typical results are shown in *Figure 3*.) A Nickel-filtered CuKα radiation was used in all cases. Where appropriate, microdensitometer traces were recorded from the photographs using a Joyce–Loebl instrument.

Glassy specimens of polypropylene were warmed to room temperature, stored and then heated to elevated temperatures (up to 410K) for short periods ($\sim$1 min) before cooling and examination by X-ray methods.

In *Table 1*, we present the densities of isotactic polypropylene samples which were quenched, stored at room temperature, and then annealled at the temperature indicated for 1 min. The density was measured using a standard density gradient column, using a water–ethanol system. Crystallinity was calculated using the following formula:

$$\text{Crystallinity} = \frac{V_{am} - V_{pr}}{V_{am} - V_{cr}}$$

where V_{am} = specific volume of the amorphous polymer; V_{pr} = specific volume of the specimen; and V_{cr} = specific volume of the crystalline polymer (l kg^{-1}). Values of V_{am} and V_{cr} were taken to be 1.173 and 1.072, respectively[26,28]

The crystallinity of the specimen increases as the annealling temperature is increased. This is in agreement with the X-ray and Raman spectroscopic data.

DISCUSSION

As mentioned in the Introduction, helix content is monitored in the partly crystalline polypropylene by the method proposed by Zerbi *et al.*[22]. Although the onset of helices in the solid does not indicate crystal formation, we deduce the 'progress of the crystallization process' by monitoring the proportion of the polymer present in extended helical sequences. To do this log $d(H_\infty - H_t)/dt$ was plotted against $\log(H_\infty - H_t)$ where H_∞ is the intensity of the helical band extrapolated to fully crystallized sample and H_t is that intensity at time 't'. The plot is shown in *Figure 4* for the crystallization of a glass sample

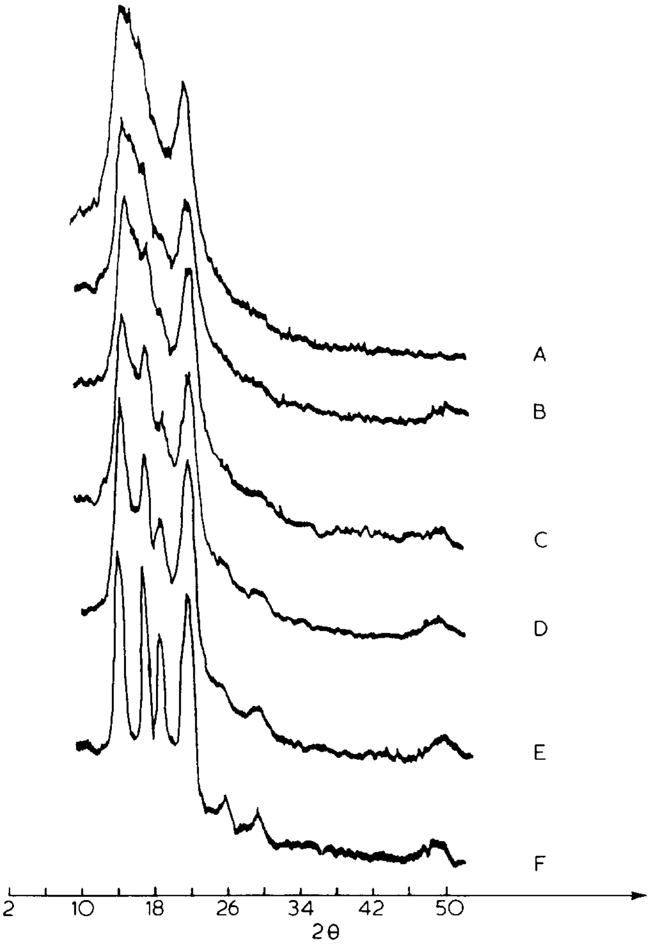

Figure 3 X-ray diffractograms of a paracrystalline sample kept at room temperature and successively annealed for 1 min at different temperatures. A, 318K; B, 343K; C, 353K; D, 363K; E, 373K; F, 410K. Trace F is obtained from a sample isothermally crystallized

Table 1 Densities of isotactic polypropylene samples melt quenched and annealled at temperature *T* for 1 min

T (K)	Density (g cm^{-3})	Crystallinity (%)
298	0.8841	41.49
323	0.8884	46.90
343	0.8937	53.52
353	0.8983	59.19
373	0.9048	67.11

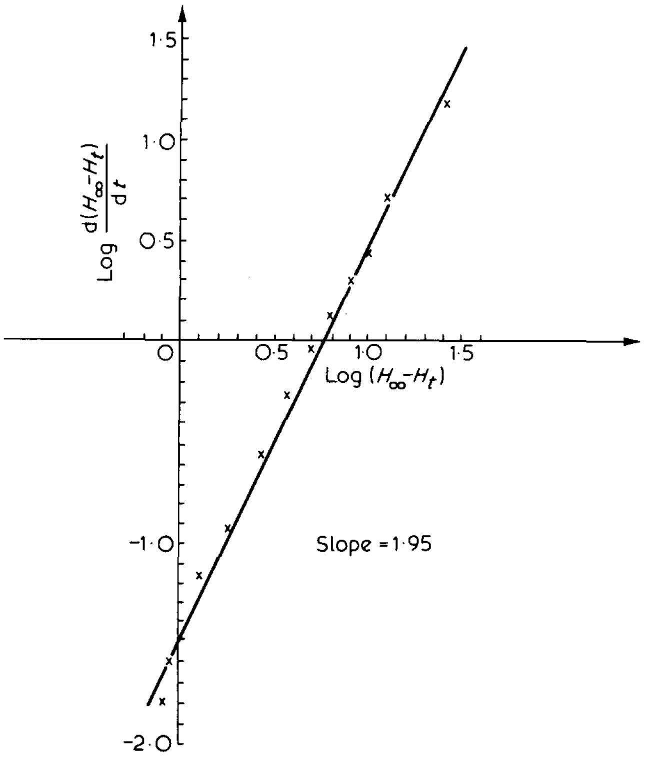

Figure 4 Determination of the kinetics of helix growth from the glass phase at 255K by a differentiation technique in isotactic polypropylene H_∞ = intensity of helical band (998 cm^{-1}) extrapolated to the fully crystallized state. H_t = Intensity at time 't'

at 255K and it is clear that this is a second order process. For comparison, the equivalent experiment was carried out for crystallization from a melt and this appears to behave as a zero order process at least during part of the reaction.

The kinetics for the two processes are quite different. However, two different phenomena are operating simultaneously in the case of crystallization from the melt, i.e. growth of helices themselves and the crystallization into the monoclinic (α) form. There is no simple way of differentiating between the two phenomena. The S-shaped curve in *Figure 2* is typical of many crystallization processes, in that it shows a nucleation process followed by rapid growth, which in this case is linear with time (a zero order process), and a subsequent second order process which tends to complete the crystallization reaction.

The X-ray and Raman results of *Figures 3* and *5* show that, as expected, raising the temperature of the glass to temperatures well in excess of T_a results in increasing degrees of crystallization[†]. What is surprising is that the glassy material after storage at room temperature appears to contain helical sequences of quite considerable length and that the Raman results show an increase in length of approximately 40% during the processes involved here (*Table 2*). Holding the specimen at room temperature may well cause some slight crystallization but it will be observed from *Figure 3* that this does not involve much crystalline perfection. The sample heated to 373K for 1 min has partly crystallized, as expected.

The processes involved in these experiments are kinetically stopped since the samples were kept at higher temperatures for a short time and quenched rapidly. The samples were not kept at high temperatures long enough for the equilibrium to be achieved. During a relatively rapid crystallization process, we do not believe gross molecular movement occurs.

Figure 6 shows the infra-red spectrum of the glass made, kept and studied at low temperatures. There is considerable order in the glass phase (the 'helix band' at 998 cm^{-1} is prominent). In this respect, the spectrum of the glass differs markedly from that of the melt (in the melt, the 'helix band' at 998 cm^{-1} is almost non-existent). This contention is supported by the Raman spectrometric evidence. In *Figure 5* the *LA* mode can be clearly distinguished in the room temperature spectrum of the quenched sample. The glass phase, however, is X-ray disordered, as can be observed from the diffractogram of the quenched sample (*Figure 3*)

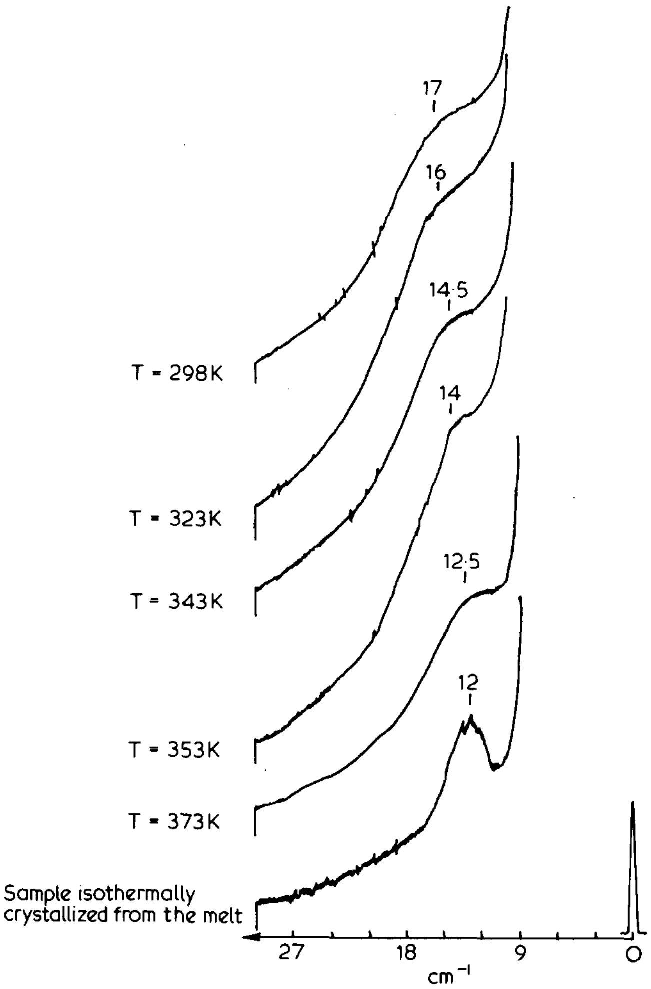

Figure 5 Low frequency Raman spectra of melt quenched isotactic polypropylene samples annealled at temperature *T* for 1 min

Table 2 Average length of regular chain segments as determined from *LA* mode measurements for isotactic polypropylene samples melt quenched and annealled at temperature *T* for 1 min

T (K)	*L* (Å)
298	93
323	101
343	112
353	116
373	130

[†] Crystallization here is used rigorously, not as above when describing processes measured by infra-red methods.

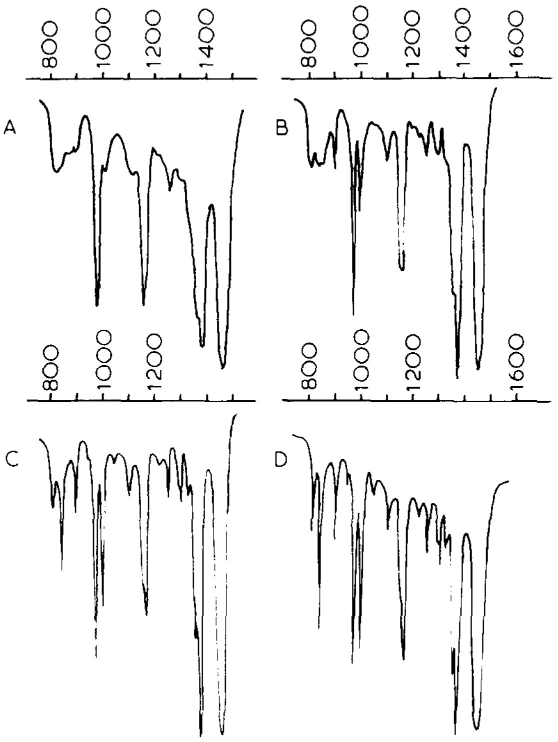

Figure 6 Infra-red spectra of isotactic polypropylene. (A) Molten (448K); (B) quenched from the melt (448K) into acetone at 193K; (C) sample b held at 255K for 12 h; (D) sample c held at 373K for 10 min

CONCLUSIONS

To account for our observations, we suggest that the glass contains rods of ordered helical molecules, which are not coherent, i.e. they are not packed into developed three dimensional crystalline micelles. The rods and the disordered material are randomly distributed in the glass. Warming the material to temperatures close to T_g (255K) permits a relatively slow build-up of moderately extended helices. Further warming encourages these to extend further and the X-ray crystallinity to develop by annealling.

During annealling, for the rods to assemble into ordered crystallites, their main relative movements will probably be along their length. The free energy change for this latter process should be small. This results in increasing crystallinity apparent in X-ray diffraction, while there is little change in that derived from vibrational methods. The crystallites may or may not at inception be recognizably lamellar in nature but they will eventually become so and hence take part in eventual spherullite formation.

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