

Structure of crystalline polymers produced by rapid cooling of their melts:

2. Polyoxymethylene

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An observation of a relationship between melt temperature and lamellar thickness in commercially produced polyoxymethylene following rapid cooling is reported. This is the first evidence of this behaviour in a polymer other than polyethylene and strengthens the view that chains meander through the lamellae in a random fashion, rather than adopting the chain-folded conformation found in solution-grown and slowly-cooled samples.

The crystallization of melts of linear polymers have been analysed theoretically¹ and supported by experimental observations in two cases viz. the formation of crystalline poly(ethylene oxide)² and linear polyethylene³ by slow cooling of their melts. The widely accepted view of the solids so produced is that they consist of sheaves of lamellae similar to those produced by solution crystallization, i.e. the chains fold at the lamellar interfaces with few molecules translating from one lamellar unit to its neighbours.

In two recently published notes^{4,5}, we have shown that in linear polyethylene crystallized under rapid cooling conditions, the lamellar structure so produced has a thickness dependent on the temperature of the melt prior to quenching. We have interpreted these observations as indicating a relationship between the structure of the melt and that of the solid produced from it. Furthermore, we consider it likely that the stacks of lamellae present in the spherulites involve very little chain-folding and that the chains meander throughout the gross structure in a random manner. This conclusion has recently been supported by neutron scattering data^{6,7}.

Although the interpretation described above may be open to discussion, the experimental data have been shown to apply to polyethylene of various origins^{4,5}. It is tempting to propose that our observation linking melt temperature and lamellar thickness is a general one and applies to all crystalline polymers. To date, however, no data have been forthcoming on polymers other than linear polyethylene and long-chain carboxylated paraffins⁵.

In this paper we report the results of attempts to find another polymer which demonstrates the effect described above. If we assume that the conformational structure of the melt varies slightly with change of temperature, then, for our purpose, we require a polymer which is thermally stable over a wide temperature range. We favour the use of small samples as they minimize problems due to the low thermal conductivity and hence variable cooling rates within our samples.

However, the use of small samples in our quenching experiments presents us with a problem in characterizing the lamellar thickness of the samples. The conventional

method of measuring lamellar thickness viz. low-angle X-ray diffraction (LAXD), is unsuitable because our samples are too thin ($<100\ \mu\text{m}$ compared with that of $\sim 3\ \text{mm}$ for LAXD). We therefore have chosen to use low frequency Raman spectroscopy as our diagnostic technique, measuring the frequency of the longitudinal acoustic vibration (*LA* mode) and normally calculating from it the lamellar thickness. This then places a further constraint on our selection of a polymer suitable for our experiments, viz. it must show an *LA* mode easily found within the spectral range of currently available spectrometers, and ideally the correlation between frequency and lamellar thickness should have been previously established. Recently, relevant Raman data has appeared on polyoxymethylene⁸.

Small samples ($\sim 5\ \text{mg}$) of a commercial polyoxymethylene homopolymer were heated in d.s.c. pans in a Perkin-Elmer DSC-2B differential scanning calorimeter to predetermined temperatures, held there for a short period, and then rapidly removed from the instrument and quenched in liquid nitrogen. Raman spectra were measured at room temperature on the polymer samples after their removal from the pans; the results are plotted in *Figure 1*. Similarly, samples which had been quenched using an ice/water mixture were found to have a similar change in their *LA* mode frequencies ($13.0\text{--}16.0\ \text{cm}^{-1}$) over the same range of melt temperature. It is clear that although the cooling rates in the two refrigerants, liquid nitrogen (77K) and ice/water (273K), are inevitably very different, they produce very similar results. These results closely match those reported earlier for polyethylene.

In the case of linear polyethylene, much work has been done elucidating the relationship between the frequency of the *LA* mode and the actual lamellar thickness. Whilst the exact nature of the conversion is still under debate, there is little doubt that a change in lamellar thickness is reflected in a change in the frequency of the *LA* mode.

Unfortunately, when we come to polyoxymethylene, the only work which has been reported so far is that of Rabolt and Fanconi⁸. Their results clearly show that, as for linear polyethylene, a reduction in the LAXD long period is matched by an increase in the *LA* mode frequency. In their paper Rabolt and Fanconi have equated their Raman derived

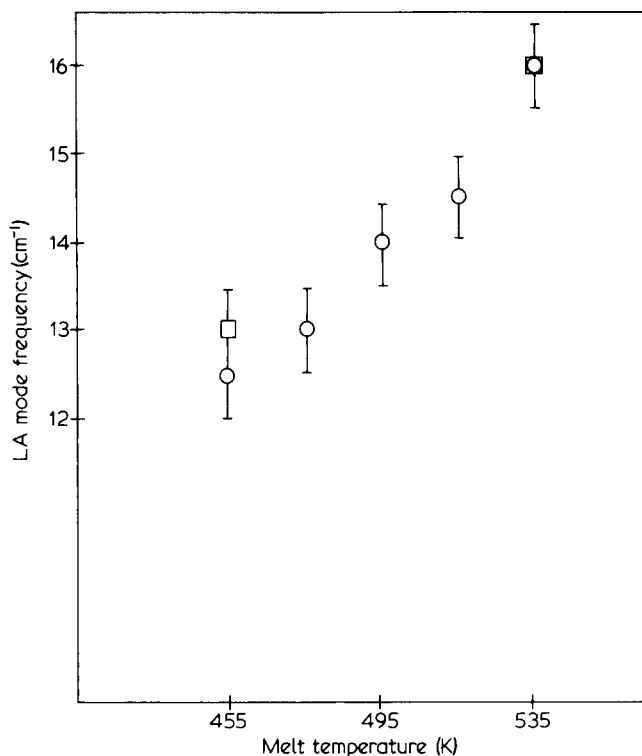


Figure 1 Plot of LA mode frequency as a function of melt temperature. □, cooled to 273K; ○, cooled to 77K

lamellar thicknesses and the LAXD long spacings. Strictly, this is not permissible because the Raman experiment 'measures' the thickness of the lamellar cores with some contribution from the disordered phase. The subject is a matter for debate⁹ and therefore we will avoid converting LA mode frequencies to lamellar thicknesses in this paper.

As was stated in our earlier work on polyethylene, these results do not in themselves prove any connection between the structure of the melt and the solid produced from it, as other factors, such as degradation and nucleation density, could be the reason for the observations.

Another possible explanation is that although the crystalline core thickness observed by Raman spectroscopy does indeed increase with decreasing melt temperature, the overall lamellar thickness does not. This would require a compensating decrease in the amorphous thickness of the amorphous region, so that the overall effect would be a change in the proportion of the two phases as a function of melt temperature. This hypothesis can be shown not to be true for polyoxymethylene as was the case for linear polyethylene⁴. A measure of the crystallinity obtained by high angle diffraction is given by the expression:

$$\text{crystallinity} = \frac{l_c}{2l_f + l_c}$$

where l_f = half the thickness of the disordered phase between the lamellar cores of thickness l_c . Hence $2l_f + l_c$ = the long spacing. If the latter were to remain constant then the observed crystallinity should be proportional to l_c . The X-ray crystallinities of three of the samples of polyoxymethylene quenched into liquid nitrogen were obtained by standard procedures¹⁰. The results are shown in Table 1, together with the corresponding values of the LA modes obtained by Raman spectroscopy. It can be seen

Table 1 High angle X-ray crystallinities of polyoxymethylene samples quenched from different temperatures

| Melt temperature (K) | LA mode (cm ⁻¹) | $l_c/2l_f + l_c$ |
|----------------------|-----------------------------|------------------|
| 455 | 12.5 ± 0.5 | 0.64 ± 0.1 |
| 495 | 14.0 ± 0.5 | 0.68 ± 0.1 |
| 535 | 16.0 ± 0.5 | 0.65 ± 0.1 |

Table 2 The effect of heat treatment on the nucleation density and LA mode in film samples of polyoxymethylene

| Melt temperature of film sample (K) | LA mode (cm ⁻¹) | Number and size of spherulites |
|-------------------------------------|-----------------------------|--------------------------------|
| 458 | 14 ± 0.5 | Large number, small |
| 523 | 16 ± 0.5 | Small number, large |
| Remelted at 458 | 14 ± 0.5 | Large number, small |

that there is no correlation between the two sets of results. This is taken to indicate that the 'quenching effect' is not caused by a change in the ratio between the crystalline and amorphous contents.

The effect of the temperature variation of nucleation density and its relationship to the lamellar thickness was also investigated. The heating of polymer melts leads to a loss of nucleation sites. Consequently, the spherulites observed microscopically are fewer in number and larger in size. This behaviour was confirmed in polyoxymethylene and furthermore, the number of spherulites remained depleted when thin film samples were remelted and quenched from a lower melt temperature. The LA mode value however, appears to be independent of nucleation density because after remelting and quenching from a lower temperature it reverted to a low value indicating an increase in the lamellar thickness without a change in the size of the spherulites. Table 2 gives details of these experiments.

Contrary to crystallization theories (1), contribution to the degree of supercooling from the nucleation density appears not to govern the observed lamellar thickness under cooling conditions. However, when rapidly cooled, the melt temperature prior to cooling appears to dictate the eventual structure produced. The use of a slower cooling rate of 320 K min⁻¹, produced in the calorimeter, was found to give a smaller change in the LA mode frequency (11.5–13.0 cm⁻¹). A similar reduction of the change in the LA mode following the same cooling treatment has previously been found in polyethylene⁴.

We therefore conclude that our earlier observations on the quenching behaviour of linear polyethylene may be extended to other polymers. We concluded that our observations on polyethylene indicated that a chain folded lamellar structure for rapidly crystallized material was unlikely and it is presumed that this also applies to polyoxymethylene.

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