A neutron scattering study of the melting behaviour of polyethylene single crystals

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The changes in chain trajectories occurring during the melting of polyethylene single crystal mats have been studied by using neutron scattering techniques. It is shown that molecules change from a regular superfolded sheet structure into a random coil configuration in a very short time, ≈2–4 s. Further, it is shown that the rate at which this process takes place is substantially independent of molecular weight.

(Keywords: neutron scattering; polyethylene; melting)

INTRODUCTION

There is an enormous body of literature concerning the mechanisms by which an isotropic melt of polymer molecules is converted into a crystalline solid. Changes in overall molecular trajectories from random coil to chain folded lamellae have been documented and rates of motion calculated. The area remains one of very significant activity. By contrast, however, very little consideration has been given to the inverse process, i.e. the melting of a crystalline polymeric solid. In this paper we begin to consider this issue. Clearly, many changes may occur on melting and many questions need to be answered, e.g. do chains detach themselves individually from crystal surfaces and diffuse into the random melt or is melting more like a cooperative bulk process? In the present study we are concerned with the question of how the molecules change their trajectories from oriented chain folded sheets to isotropic random coils in the melt. For this purpose we have used a neutron scattering technique to follow the change in molecular trajectory during melting of solution crystallized single mats.

We shall show that during melting the initially oriented, compact, folded molecules expand rapidly to form large isotropic, random coils typical of the melt. Further, we shall show that this process occurs in a remarkably short time (typically 1–2 s) and the rate is insensitive to molecular weight.

At this stage we merely report these novel results and refrain from placing any interpretation on them, except to draw some analogies with work on the loss of drawability of fibres caused by melting for similar short periods of time. In a subsequent publication we shall address a similar issue, the melting of highly extended polymer chains and show another remarkable result: the chains take an extraordinarily long time to reach a random configuration on melting.

EXPERIMENTAL

Sample preparation

Single crystal mats ≈50 μm thick of mixed hydrogenated (HPE) and deuterated (DPE) polyethylene were prepared from xylene solutions by using the procedures described previously[1] with a crystallization temperature of 75°C. The samples all contained 2% DPE. The molecular weights of the polymers used are summarized in *Table 1*.

Crystal orientation was monitored using both wide and low angle X-ray diffraction. The mats all showed long periods of 12 ± 1 nm.

Melting

The mats were melted by dipping the thin, $1 \times 2\ \text{cm}^2$, sheets into silicon oil at 145°C for the required time before plunging them into iced water to quench in the melt structure. This procedure was performed manually: for short melting times ($\leqslant 10$ s) the samples were held in tweezers, for longer times they were held in nylon mesh baskets to prevent deformation. The melting time quoted is the time for which samples were immersed in hot oil. It typically took 0.25 s to transfer the samples from the oil to the cold water. The samples were dried and washed in acetone to remove any remaining oil and water.

Neutron scattering experiments and data analysis

Small angle neutron scattering (SANS) measurements were performed by using the D11 and D17 instruments at Institute Lavé-Langevin, Grenoble. The data were corrected in the usual way[1–3]. Before melting there was significant anisotropy in the mats[2,3]. In all melted sheets we failed to detect any anisotropic scattering (either from the neutron scattering or from our X-ray measurements).

For the isotropic samples we measured the radius of gyration, r_g, using Zimm plots[2–4]. For anisotropic

Table 1 Polymer molecular weights

	DPE		HPE	
Sample	M_w	M_n	M_w	M_n
1	95000	48000	68000	15000
2	189000	79000	216000	110000
3	390000	205000	386000	158000

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Table 2 Neutron scattering data

	Sample 1		Sample 2		Sample 3	
Time at 145°C (s)	r_g (r_{xy}, r_z) (nm)	$I(0)$	r_g (r_{xy}, r_z) (nm)	$I(0)$	r_g (r_{xy}, r_z) (nm)	I(0)
0	7.2 (4.6, 3.2)		8.0 (5.1, 3.4)		9.8 (6.6, 3.1)	
1	12.0	2.2	15.0	4.8	15.0	9.5
2	16.0	2.4	19.5	5.0	19.0	9.8
4	15.0	2.6	21.0	5.2	31.0	10.2
8	15.5	2.5	20.5	4.9	32.0	11.1
16	15.5	2.8	21.0	5.4	31.0	10.7
30					33.0	11.0
Melt crystallized	15.5	2.5	21.0	5.1	32.0	10.8

NB The factor by which the forward scattering intensity values should be multiplied to obtain molecular weights is estimated to be 32 000

scattering we used the analysis worked out previously[4] to determine r_{xy} and r_z, the sizes of the molecule in the plane of the sheets and normal to the sheets. Then r_g is given by $r_g^2 = r_z^2 + 2r_{xy}^2$.

RESULTS

Table 2 shows the radii of gyration of the samples as a function of the melting time. We also include the values of r_z and r_{xy} of the mats before melting and the value of r_g of the usual melt crystallized material (after melting at 160°C for at least 5 min). The error in all measurements is estimated to be ± 1 nm. *Table 2* also shows values of the forward scattered intensity, $I(0)$, from which molecular weights can be calculated. The fact that all the measurements of $I(0)$ lie close to each other and are close to the values for the melt crystallized samples gives us confidence in our data analysis and the values of r_g.

Before melting the mats showed oriented wide and low angle X-ray diffraction. After melting for >1 s this orientation disappeared and the long period increased from ≈ 12 nm to ≈ 25 nm and did not change on further melting.

DISCUSSION

Figure 1 shows a plot of radius of gyration against time in the melt for all three samples. It appears from *Figure 1* that all the samples increase their radius of gyration at the same rate, but the final radius of gyration increases with molecular weight. All the samples show an increase in r_g of ≈ 5 nm s^{-1}. Thus the time taken for the molecules to reach their final 'equilibrium' size depends linearly on the final radius of gyration, i.e. it scales as $M^{0.5}$, where M is molecular weight.

Figure 2 shows a computer generated sketch illustrating typical trajectories of a molecule ($M = 390\,000$) before and after melting. Before melting the molecule is arranged in super folded sheets[2,3]. The sketch was generated by using a molecule with 200 crystalline stems each of length 12 nm with a probability of adjacent re-entry of 0.75. After melting the molecule adopts a random coil configuration. The sketch was generated by the projection of a 3D random walk of 10 000 steps of length 0.3 nm (for ease of plotting this is represented by drawing straight

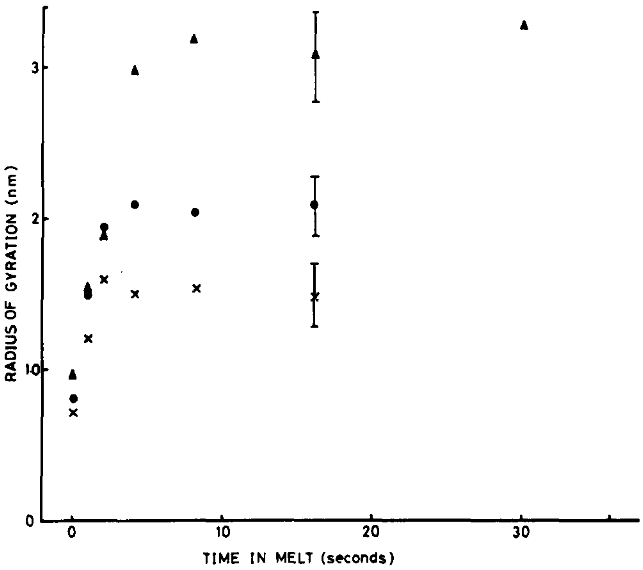

Figure 1 Increase of radius of gyration with time in melt during melting at 145°C: ×, $M_w = 95\,000$; ●, $M_w = 189\,000$; ▲, $M_w = 390\,000$

Figure 2 Typical molecular trajectories before and after melting a polymer of molecular weight 390 000. ----, Final radius of gyration, diameter 64 nm

lines between every 25th position along the chain). The dashed circle represents the radius of gyration averaged over a large number of chains (NB for the particular chain sketched it would be much smaller).

We find it difficult to conceive how the molecule can make such a dramatic change in its overall shape in such a short interval. In particular we note that, according to the super-folding model, before melting the molecule is in a compact form and it interacts with only a few (≈ 4) other similar molecules. After melting the molecule adopts a random coil nature so that it occupies a large volume and shares this volume with many other molecules; from density considerations we deduce that in this state the molecule interacts with at least 80 others. A similar conclusion has been reached from a totally different experiment. Bastiaansen *et al.*[5] have shown that if a solution cast film of ultra-high molecular weight polyethylene (UHMWPE) is uniaxially drawn at ≈ 120°C the maximum achievable draw ratio is ≈ 100 (with corresponding excellent mechanical properties). However, if the same sheet is melted for a few seconds at 145°C before drawing then this high drawability is lost and the material behaves exactly as a melt crystallized sample.

Thus it appears that heating a solution crystallized polyethylene sample to 145°C (i.e. only ≈ 10°C above its melting point) for just a few seconds is sufficient for the polymer to reach an 'equilibrium' melt configuration, with little or no dependence on molecular weight.

The most commonly quoted mechanism for motion of polymer molecules is reptation. This refers to motions within a tube surrounding the randomly coiled molecule whose dimensions are determined by the interactions of the molecule with its neighbours. This model is perhaps not strictly applicable in this case as the molecule must move 'sideways' as well as along its length to achieve the changes illustrated in *Figure 2*. Nevertheless, it is worthwhile to calculate the time one might expect a molecule to take to move through a distance of its radius of gyration (the reptation time) and compare this with the time taken for the molecules to reach their 'equilibrium' radii of gyration on melting. We give some values for the reptation time in *Table 3* using the diffusion rate data of Reference 6. These reptation times are much longer than the timescale on which the UHMWPE lost its drawability in the experiments of Bastiaansen *et al.*[5], and at the highest molecular weight we have used (390 000) the process of randomization occurs faster than would be predicted by the reptation model. Further, we note that reptation time scales as r_g^2/D, which itself scales as M^3 while the time for the molecules to reach their 'equilibrium' size scales as $M^{0.5}$. Accordingly, we do not believe it is appropriate to use the reptation model in this case.

Table 3 Reptation times (R_g^2/D) from Reference 6

Molecular weight	Reptation time (s)
95 000	0.15
189 000	1.13
390 000	11.1
1 000 000	132
4 000 000	8400

We prefer to imagine that the molecule in the crystal is rather like a coiled spring constrained from expanding by the lattice forces. Once these constraints are removed by melting, the molecule springs out, driven by the need to increase its entropy. This must be a cooperative process involving many molecules so that after melting each molecule interacts with many others. We anticipate that only after this initial, sudden, process does reptation become important as molecules move along their length to achieve some 'equilibrium' degree of entanglement.

CONCLUSIONS

We have shown that on melting single crystal mats the molecules very rapidly change their trajectories from superfolded sheets to random coils. This process occurs very quickly, with radii of gyration increasing at $\approx 5\ \mathrm{nm\ s^{-1}}$ independent of molecular weight.

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