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Crystallization of sheared polymer melts: poly(ethylene oxide) fractions

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SUMMARY

Crystallization under controlled shear conditions has been optically monitored for a series of sharp molecular weight fractions of poly(ethylene oxide). The minimum shear rate (MSR) necessary to produce oriented crystalline morphologies exhibited a strong molecular weight (M) dependence: MSR = $K/M^{1.47}$. The time necessary for erasure of orientation effects after crystal melting was also determined and found to be proportional to $M^{1.42}$.

INTRODUCTION

Crystallization of the sheared and oriented melt leads to a number of morphologies in the solidified state. These range from spherulites at no or low shear rates, through row-nucleated spherulites and fibrillar structures exhibiting radial epitaxial overgrowth to fibre bundles without radial overgrowth at the highest shear rates (1). This morphological variety is of technical importance because melt-orienting strain fields regularly occur in practically all extruding and industrial moulding operations. Such differences in morphology will substantially influence mechanical and transport properties of the resultant polymer.

Crystallization of polymer melts has been found to be promoted by simple shear flow (2-6). This stands in clear contrast to the behaviour of polymer solutions in which simple shear is ineffective in initiating fibrous crystallization (7). Frank and coworkers (8,9) pointed out that simple shear flow causes an isolated macromolecule to rotate about its centre of gravity which lessens the orienting effect of the flow field. The hydrodynamic origin of the orientation in sheared polymer melts is due to the presence of entanglements acting as temporary crosslinks and causing elastic extension of the chain segments between the entanglement points (5,6). The influence of molecular weight on shear-induced crystallization in broad molecular weight samples has been studied by e g Lagasse and Maxwell (6) and Fritzsche and Price (5). It has been shown that crystallization in higher molecular weight PE and PEO is promoted by shear when the shear rate exceeds a certain critical value and that high molecular weight samples crystallize faster than lower molecular weight polymers. However, in order to obtain a better understanding of shear-induced crystallization in polymer melts, data on sharp molecular weight fractions

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*To whom correspondence should be addressed are needed, especially of higher molecular weight samples. Such data are presented in this paper.

This work seeks to define two related issues in the crystallization of melt-oriented polymers: The shear rate required to produce oriented structures in polymers as a function of molecular weight, and the time necessary for the relaxation of oriented melts prior to solidification.

EXPERIMENTAL

Sharp fractions ($M_w/M_n<1.1$) of molecular weights ranging between 10^3 and 10^6 were obtained from Polymer Laboratories Ltd, U.K.. Films 20-50 μm thick were cast from dilute solution in hot acetone, directly onto the lower glass plate of the shear cell.

The shearing of the samples was conducted in a home-made shear cell apparatus shown schematically in Fig. 1. The shear cell was mounted in a Leitz Ortholux optical microscope to allow observation of the crystallization process under conditions of constant shear.

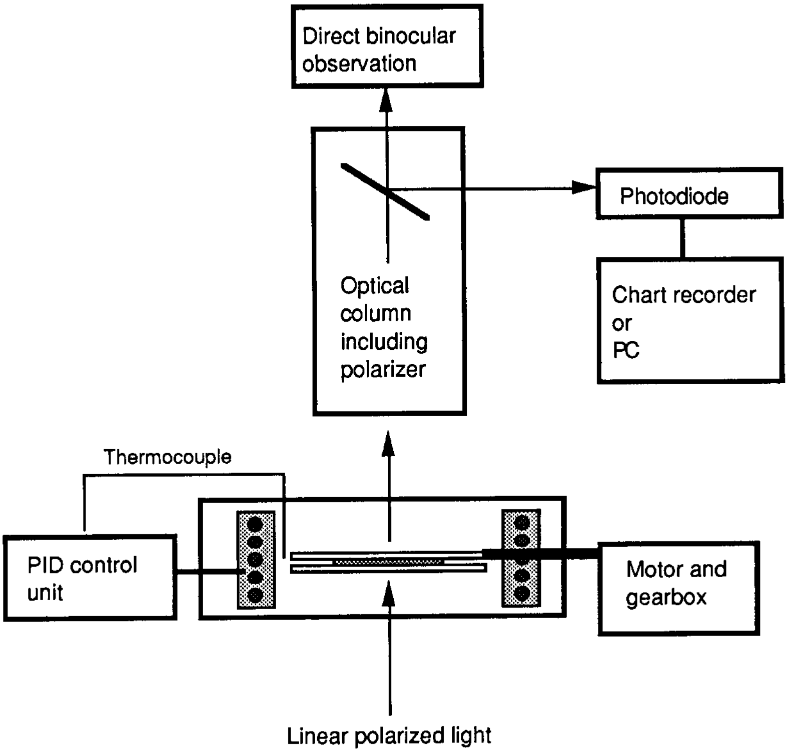

Figure 1. Schematic drawing of the shear apparatus

Polymer samples were held between the glass plates, the bottom one of which was anchored while the top plate was forced to rotate at a fixed speed. The period of rotation was established by adjustment of motor speed and choice of gear from a variable gear box. Shear rates ($d\gamma/dt$) were determined as a function of radial position (r), film thickness (t) and period of rotation (T) according to eq. (1). It was possible to attain shear rates up to 1 000 s^{-1} for samples with a thickness between 20-50 μm.

$$d\gamma/dt = 2\,\pi\, r\,(t\,T)^{-1} \qquad ....(1)$$

Prior to cooling, all samples were sheared for 10 minutes at a temperature well above the melt temperature. Sample cooling was facilitated by an external coil which had N_2 gas (76 K) passing through it. The cooling rate was 14 $K(min)^{-1}$ over the temperature range studied. The motor was halted when crystallization at the outermost portion of the sample was apparent. Further shearing resultet in fracture of the crystallizing film. The remainder of the film was observed to crystallize within 30 s from the time when the motor was stopped.

In the melt relaxation studies, the motor was halted at temperatures above the freezing point and the time to produce an isotropic melt was obtained by measurement of the integrated light intensity. The melt relaxation was also studied by heating solidified, oriented samples above their melting point and recording the time for complete randomization.

RESULTS AND DISCUSSION

Minimum shear rate

Three different zones of crystallization were evident in the solid films. At the lowest shear rates, standard, randomly located spherulites were observed. As the shear rate increased, row-nucleated spherulites became visible. No clear cut change in shear rate distinguished the row-nucleated spherulites from fibrils exhibiting radial epitaxial growth. The latter are in essence the extension of row nucleation to a continuous series of spherulite nucleation sites. Thus, the row-nucleated spherulites and the fibrils with epitaxial overgrowth are both referred to as *structure I*. At the highest shear rates, thickened fiber bundles cover the entire field and none of them exhibit epitaxial growth (denoted *structure II*).

The minimum shear rates (MSR) at which structures I and II occur are plotted vs. molecular weight in Fig. 2. A strong molecular weight dependence is readily apparent, with minimum shear rates approaching zero asymptotically, at the higher molecular weight. From the log-log plot shown in Fig. 2 the following relationship is obtained between MSR and the molecular weight (M):

$$MSR = K_1/M^{1.47} \qquad ... (2)$$

where K_1 is a constant. The coefficient of determination (r^2) was 0.97.

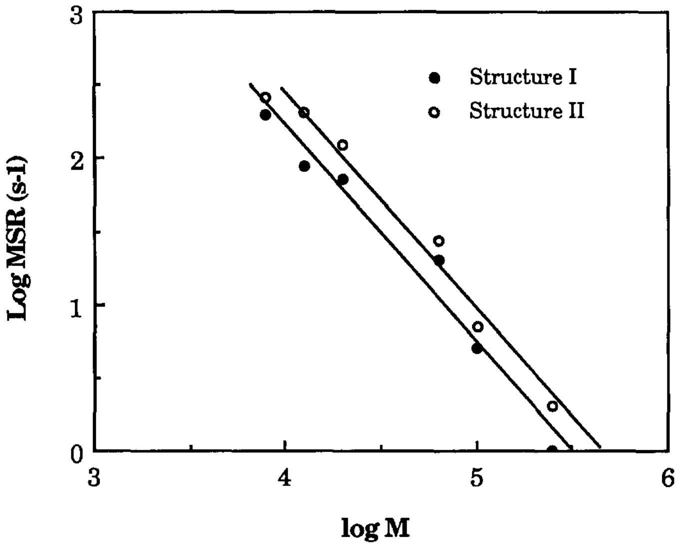

Figure 2. The logarithm of the minimum shear rate (MSR) required for the formation of structures I(●) and II (○) vs. the logarithm of the molecular weight (M).

Melt relaxation

A remarkable feature of oriented polymer crystal structures is their ability to regenerate themselves after melting. Although complete loss of crystal register occurs at the time of melting, orientational randomization of molten polymer chains is not instantaneous. If the melt is recrystallized soon enough, oriented structures will reappear. The minimum time necessary after melting of oriented crystal structures before subsequent recrystallization does not again yield oriented structures, serves as a mean-field relaxation time (τ) for the process. Fig. 3 indicates the time range within which such mean-field relaxation times fall as a function of molecular weight (M). A least squares fit of the data presented in Fig. 3 yields:

$$\tau = K_2 M^{1.42} \qquad \text{....(3)}$$

where K_2 is a constant.

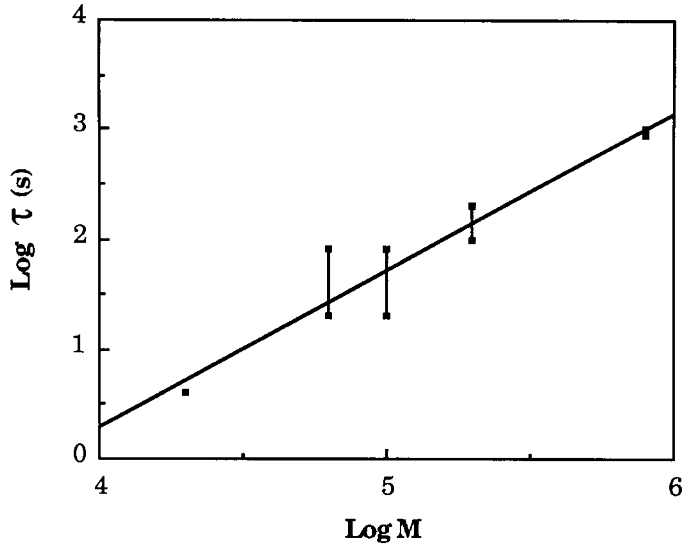

Figure 3. The logarithm of the relaxation time for recoiling in the melt vs. the logarithm of the molecular weight.

The longest relaxation time (τ) for the recovery of the macromolecules to their statistical random coil conformation is strongly dependent on the molecular weight. For polymer solutions τ is proportional to $M^{1.5\text{-}2}$ (8) whereas for polymer melts above the critical molecular weight for entanglement coupling (M_c) it is proportional to $M^{3.4}$ (10). The critical molecular weight is for PEO equal to 4 400 (11), so that all data displayed in Fig. 3 are of a molecular weight greater than M_c. However, the relaxation time measured is proportional to $M^{1.4}$ which is two orders of magnitude lower than the reported data. One possible explanation is that only the high molecular weight tail (only a few percent of the sample) participate in the relaxation. The molecular weight of this part for the different samples is not known .

CONCLUSIONS

The minimum shear rate (MSR) necessary for establishing oriented structures in melt-crystallized polymers has been considered as a function of molecular weight (M) for poly(ethylene oxide) fractions. It is shown that MSR is inversely proportional to $M^{1.47}$.

The time necessary after melting of oriented structures before their reappearance is precluded was also considered. The time needed was observed to increase rapidly with molecular weight, and appeared to be proportional to $M^{1.42}$, which is a weaker molecular weight dependence than predicted by theory.

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