Notes

On the Kinetics of Crystallization of Polymers from Stirred Solutions

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It has been demonstrated[1,2] that the liquid–crystal phase transition in polymer solutions can readily be activated by a hydrodynamic field. In order to achieve a better understanding of the mechanism underlying hydrodynamically induced crystallization, attempts have been made at determining the quantitative rate of crystallization under these conditions.

Crystallization velocity measurements to be reported here were performed dilatometrically on 1% *p*-xylene solutions of a high molecular weight polyethylene sample ($M_w = 720 \times 10^3$) capable of forming fibrillar crystals, and of a low molecular weight sample ($M_w = 9.2 \times 10^3$) which precipitates exclusively as folded-chain lamellar crystals. The dilatometer used consists of a Couette type of glass vessel (capacity 55 ml) attached to a capillary of 0.05 cm inside diameter.

The rotor is supported by tungsten bearings and equipped with a magnet. This arrangement renders it possible to drive the rotor with a revolving magnet from outside the dilatometer. Further experimental details will be described in a subsequent paper.

The results are presented graphically in Figure 1, where the logarithm of the rate of crystallization at 50% of the total transformation is plotted *vs.* the stirrer speed in the number of revolutions per minute (rpm). The rate of crystallization of the high molecular weight sample at 91° remains constant up to a stirrer speed of 270 rpm; in this range of stirrer speeds the polyethylene forms a flaky precipitate distributed uniformly throughout the solution.

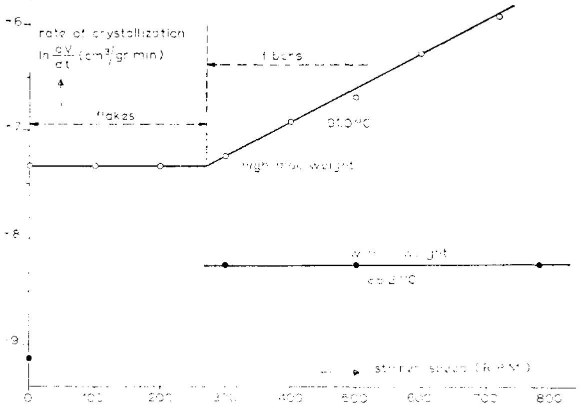

Figure 1. A plot of the logarithm of the rate of crystallization of two polyethylene fractions from 1% *p*-xylene solutions at 50% transformation against the rate of stirring. The upper curve relates to the high molecular weight sample ($M_w = 720 \times 10^3$), the lower curve to the low molecular weight fraction ($M_w = 9.2 \times 10^3$).

At stirrer speeds above 270 rpm, fibrillar crystals develop, which settle on the stirrer at regular intervals. The spacings between these rings on the rotor appear to be twice as large as the dimensions of the annular gap.

The transition from lamellar to fibrillar crystal morphology is accompanied by an increase of the rate of crystallization. The periodic deposition of fibrillar crystals on the rotor was also noted in previous stirred solution crystallization experiments and was then attributed to secondary flow effects known as Taylor vortices.[3] It was further observed that purely laminar shear flow did not induce crystallization at elevated temperatures. From the coincidence of the onset of fibrillar crystallization with the appearance of Taylor vortices it was inferred that the elongational flow is presumably responsible for the formation of bundlelike nuclei and their subsequent development into fibrillar crystals at elevated temperatures ranging from 100 to 112° for the xylene solution of polyethylene.

In the present experiment, carried out at the folded chain crystallization temperature, the stirrer speed marking the transition in morphology as well as in the rate of crystallization also coincides with the critical stirrer speed needed for induction of the ring-shaped Taylor vortices.

The latter speed n_{cr}, expressed in revolutions per minute, may be calculated by means of the equation[3]

$$n_{cr} = \frac{395\eta}{\rho\sqrt{R(\Delta R)^3}}$$

where η represents the viscosity of the polyethylene solution at the crystallization temperature (0.10 P), ρ the density (0.8 g/cm³), R the radius of the rotor (1.75 cm), and ΔR the annular gap (0.25 cm). The critical stirrer speed corresponding to the parameter values given in parentheses amounts to 300 rpm which is in agreement with the experimental figure of 270 rpm. The above evidence seems to justify the conclusion that laminar shear flow is also incapable of inducing fibrillar crystallization at temperatures where normally folded-chain crystals are seen to develop. Also under these conditions Taylor vortices are required for producing bundlelike nuclei capable of rapid longitudinal growth. The backbones thus generated serve as a substrate upon which the remaining polymer molecules crystallize epitaxially. This mode of crystallization is likely to proceed at a higher speed than the process in which relatively few folded-chain type nuclei are formed. The crystallization behavior of the solution of the low molecular weight polyethylene sample turned out to differ substantially from that of the high molecular weight polymer. The fact that in the solution of the low molecular weight polyethylene the first Taylor vortices were observed already at stirrer speeds of 23

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(1) A. J. Pennings, *J. Polym. Sci., Part C*, 16, 1799 (1967).

(2) A. J. Pennings, *Proc. Intern. Conf. Crystal Growth, Boston, 1966*, 389 (1966).

(3) A. J. Pennings, J. M. A. A. van der Mark, and H. C. Booij, *Kolloid-Z.*, in press.

rpm must be ascribed to the low viscosity of the solution (0.0077 P). The rate of crystallization of this polymer at 88.2° did not vary within a wide range of stirrer speeds, but the unstirred solution was found to crystallize at a considerably slower rate. In the course of this experiment it was noticed that comparatively small crystals were formed which sedimented on the bottom of the dilatometer. The slow crystallization of this unstirred solution may therefore be due to the accumulation of growing crystals and the consequent reduction of the growth face area available to the dissolved molecules in the remaining part of the system.

This interpretation is substantiated by the observation that at 50% transformation the high molecular weight polyethylene sample crystallized about 15 times more slowly in a wide-gap dilatometer where the flakes were seen to deposit than in the narrow-gap dilatometer where they remained uniformly distributed throughout the solution.

Finally, some remarks should be made regarding the experimental observation that laminar shear flow and the Taylor vortices in the low molecular weight polyethylene solutions apparently have no effect on the folded chain crystallization. One might have anticipated an increase in rate of crystallization with stirrer speed in view of the possibility that the shear stresses might cause fracturing of the platelet-like single crystals[4] and generate screw dislocations.[5] Although it remains to be ascertained by morphological observations whether or not these growth accelerating processes take place under the present conditions of flow, the information on the growth rate at least suggests that they do not vary within the range of stirrer speeds employed.

Apparently the rate of folded chain crystallization is controlled by the interfacial process and not influenced by the transport of polymer molecules to the growth faces; this would be in line with the predictions based on the kinetic theories of polymer crystallization.[6]

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Initiation Process in the Oxidation of Polypropylene[1]

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Accelerated tests are used for the prediction of the useful lifetime of polymers. Acceleration is most frequently obtained by elevation of temperature.

For polypropylene the time is measured to the occurrence of mechanical failure, or the time to the onset of oxygen absorption (induction period). Results obtained at high temperatures (110–150°) are extrapolated to the temperature of interest by an Arrhenius plot. However, this method leads to errors, especially when extrapolations are extended to temperatures below 70°.[2]

The length of the induction period depends on the initiation process. In order to get more information about this process, a study of what happens during the induction period was undertaken. The present paper describes the use of a color reaction in detecting early signs of oxidative degradation in thin films of polypropylene.

Experimental Section

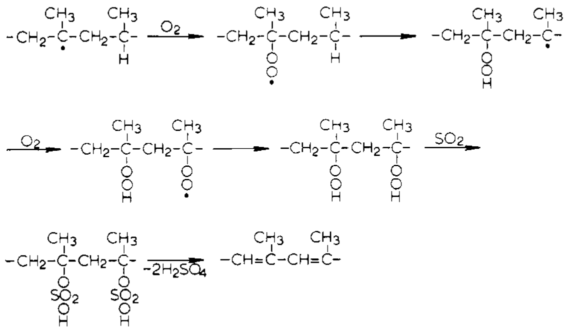
A clear, blown film of polypropylene, $[\eta] = 2.60$, decalin, 135°), thickness 0.05 mm, was used for most experiments. The residue after ashing was 0.025%. The film contained 15 ppm Ti, >25 ppm Al, 8.5 ppm Fe, 0.09 ppm B, 6 ppm Si, 2 ppm Mg, 0.03 ppm Mn, 0.08 ppm Pb, 0.09 ppm Cr, 0.5 ppm Mo, 0.2 ppm Ni, 1 ppm Zn, >25 ppm Na, 0.4 ppm Cu, 3.5 ppm Ca, 0.08 ppm Sn. Traces of K and Cl were also present. Other polypropylene types showed similar behavior. Stabilizers were extracted successively with *n*-hexane at about 20° and a boiling mixture of methanol and ethyl acetate (1:1). The residue of phenolic stabilizer was less than 1 ppm as determined by glpc analysis. The oxidation was followed by measuring the absorption of oxygen.

Laser microprobe analysis was carried out with a LMA-1 instrument (Carl Zeiss, Jena).[3] An ARL-EMX instrument (Metal Research Institute TNO, Delft) was used for electron microprobe analysis. Both sides of the polypropylene film were covered with a layer of aluminum about 500 Å thick. Particles suitable for analysis could be located using a microscope. However, the particles which are embedded in a nonconductive polymer film started to move during the analysis, probably owing to a buildup of static charge. Therefore electron and X-ray pictures could not be taken. However, point analyses at short time intervals showed the presence of iron. Chlorine and oxygen were not present.

Color Reaction. Oxidized polypropylene film turned brown on treatment with sulfur dioxide at room temperature. Heating at 100° intensified the coloration.

Sulfur dioxide transformed hydroperoxides, which are the first products of oxidation, into alkyl sulfates.[4] Decomposition of these alkyl sulfates led to conjugated systems of double bonds, as shown in Scheme I.

Scheme I



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[1] Presented at the IUPAC Symposium on Macromolecular Chemistry, Budapest, August 25–30, 1969.

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