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Growth of n-Paraffin Crystals from Solution and the Effect of Polymers on Them

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SUMMARY

The crystallization of n-paraffins has been investigated. The crystallizations were carried out in dilute solution under carefully defined cooling conditions. In some of the runs small quantities of synthetic polymers which were similar in structure to the n-paraffins were added to the solutions. The studies have shown that the habits of the crystals are very sensitive to the growth conditions, that n-paraffins are potent mutual crystal modifiers, and that the addition of small amounts of polymers can affect the crystal growth considerably.

INTRODUCTION

Many polymers find use as solid materials and consequently there is much interest in their crystallization [1-3]. In many respects n-paraffin mixtures can be considered to be representative of unusually well-defined low-molecular weight polyethylenes. Consequently it is felt that mixtures of n-paraffins with and without small amounts of added polymeric material comprise useful and reproducible model systems for investigation.

EXPERIMENTAL TECHNIQUE

Ideally, pure *n*-paraffins with chain lengths of the order of 10^2 carbon atoms would be preferred for study. Because these materials are difficult to obtain, *n*-paraffin of chain lengths ranging from *n*-C₂₀ to *n*-C₃₆ are presently being employed. The purities of the materials, as determined from gas chromatographic measurements, range from 98 wt% for the lower molecular weight material to 95 wt% for *n*-C₃₆. The impurities consist of other *n*-paraffins.

The polymeric materials were synthesized by the free radical polymerization of ethylene with vinyl acetate. Ditertiary butyl peroxide was used as the initiator. *o*-Xylene was used as the solvent in the initial work. This solvent has a boiling point of 144°C. However, great care had to be taken to make certain that the crystals which were photographed had not been affected by evaporation of this solvent. Accordingly, in later work a petroleum naphtha that boiled at 200°C was used as the solvent.

It was also found early in the studies that the cooling rate greatly affected the sizes and, in some circumstances, the shapes of the crystals. Accordingly, the conditions under which the crystals were grown were carefully standardized. Except where stated otherwise, the crystals were grown in stoppered flasks in a cold room using a controlled cooling rate of 0.6°C/hr. The photomicrographs were obtained by gently transferring a few drops of solution from each flask onto a microscope slide and photographing *in situ* inside the cold room. Because the crystals were often extremely thin and have a refractive index close to that of the solvent, they are difficult to distinguish using ordinary illumination. All the photographs shown were taken using phase-contrast transmitted-light illumination, and all have the same magnification.

RESULTS

Morphology

Figure 1 shows the effects which can arise when solvent is allowed to evaporate. A 4-wt% solution of *n*-tetracosane in *o*-xylene was allowed to cool until crystals appeared, whereupon a few drops of the solution were transferred from the crystallizing solution to the microscope slide. The first photograph shown was taken immediately after transfer. After about 1 min the crystals shown in the second photomicrograph appeared where

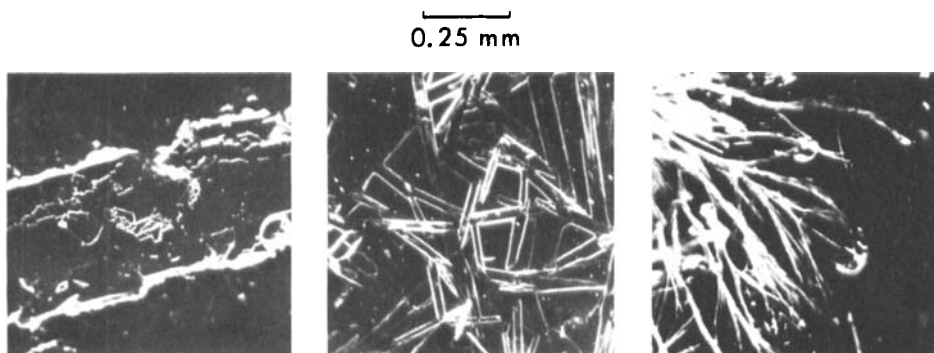


Fig. 1. $n\text{-C}_{24}\text{H}_{50}$ crystallized from *o*-xylene.

the solution had previously been clear. When more of the solvent had evaporated the crystals shown in the final photograph appeared. It is apparent from Fig. 1 that in order to make meaningful comparisons of crystal photomicrographs, the growth conditions must be very carefully defined.

Figure 2a shows typical crystals obtained when the *n*-paraffins were crystallized individually from their 4 wt% solutions in the naphtha. It would be expected that similar photomicrographs would be obtained with each of the *n*-paraffins. This proved to be the case with the lower molecular weight material, i.e., $n\text{-C}_{20}$, $n\text{-C}_{22}$, and $n\text{-C}_{24}$. In each case thin lath-shaped

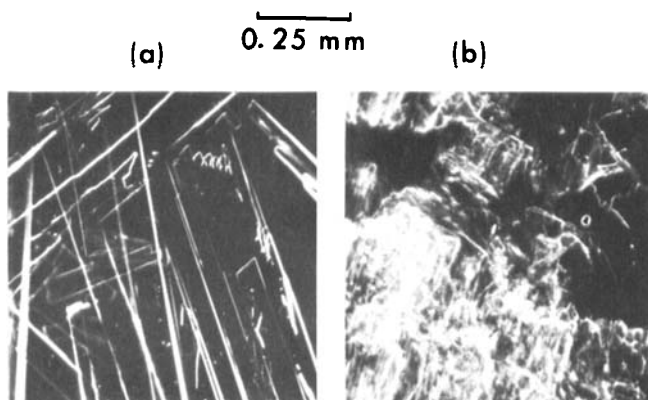


Fig. 2. Typical crystals of individual *n*-paraffins. (a) Low MW, higher purity. (b) Higher MW, lower purity.

crystals were obtained. At higher molecular weights, however, the crystals obtained were very irregular in shape (Fig. 2b). It is believed that these less regular crystals are caused by the greater amounts of impurity present in these systems. As mentioned earlier, these impurities consisted of other n-paraffins. The crystals produced depend upon the growth conditions as well as on composition, thus any generalization that mixtures of n-paraffins necessarily give poorly-defined crystals is not correct.

The effect of changing the n-paraffin composition on the habits of the crystals was investigated by crystallizing mixtures of n-paraffins. The total n-paraffin concentration was maintained at 4 wt%. When C₂₂ was doped with 10 wt% of C₂₀, or vice versa, very irregular crystals were obtained, giving an appearance similar to that shown in Fig. 1b. With the 50/50 blend, however, spherulites formed as shown in Fig. 3. Spherulitic growths were also obtained with a 75/25 blend of C₂₀ and C₂₂. However, the range of composition and

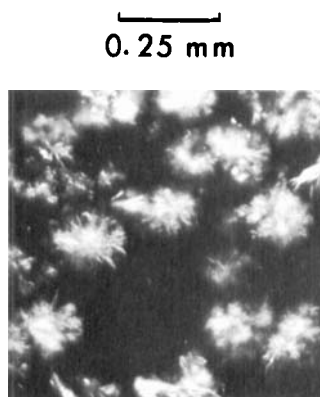


Fig. 3. Spherulitic growths obtained by crystallizing a 50/50 mixture of n-C₂₀ and n-C₂₂.

the conditions under which these sorts of crystals are produced has not yet been evaluated. Detailed discussions of spherulitic growth in polymers have been given by a number of workers, e.g., Keller [4], Keith and Padden [5], and Price [6].

When the n-paraffin crystals were grown in the presence of polymer, marked changes in morphology resulted. Figure 4a shows the effect of 0.1 wt% of polymer on the single n-paraffins. As can be seen, the crystals obtained were much smaller and less well-defined than in the presence of polymer (cf. Fig. 2a). These crystals were much easier to photograph than

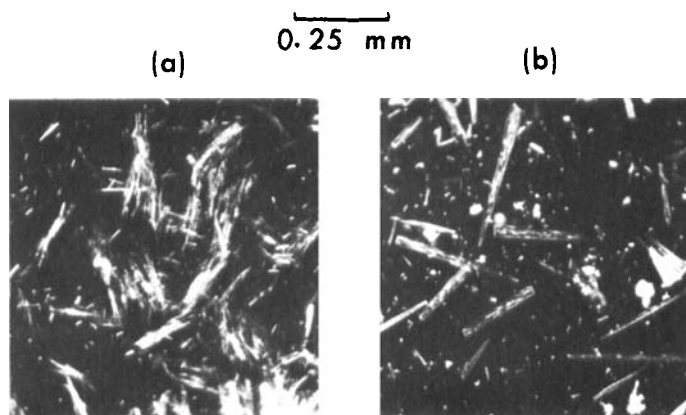


Fig. 4. Typical crystals grown in the presence of polymer. (a) Single *n*-paraffin. (b) 50/50 mixture of *n*-C₂₀ and *n*-C₂₂.

the blades which had been obtained earlier, indicating that they were much thicker. When the effect of 0.1 wt% of polymer on the 50/50 blend was tested, the crystal modification was also profound. A typical photomicrograph is shown in Fig. 4b. Instead of the spherulites a variety of more massive shapes, the most common of which could be described as a distorted tetrahedral pyramid, were obtained.

Nucleation and Growth

Since the morphological studies showed that the *n*-paraffins were acting at mutual growth inhibitors and also that polymer could interfere with the growth of either single or of mixed *n*-paraffins, some semiquantitative rate measurements on the crystallization have been carried out. The apparatus used was similar to that employed for cryoscopic molecular weight determinations. During the determinations the solutions were stirred continuously and the temperatures were measured using a Beckman differential thermometer. This thermometer was calibrated at each temperature setting against a conventional thermometer so that the correct solution temperatures, as well as the cooling rates, were known. Particular care was taken to ensure that the cooling bath temperature was kept constant throughout each series of runs.

The effect of 0.1 wt% of polymer on the cooling curves of the 4 wt% solutions of the two single *n*-paraffins *n*-C₂₀ and C₂₂ is shown in Fig. 5. The upper pair of cooling curves shows the data for *n*-C₂₂ and the lower

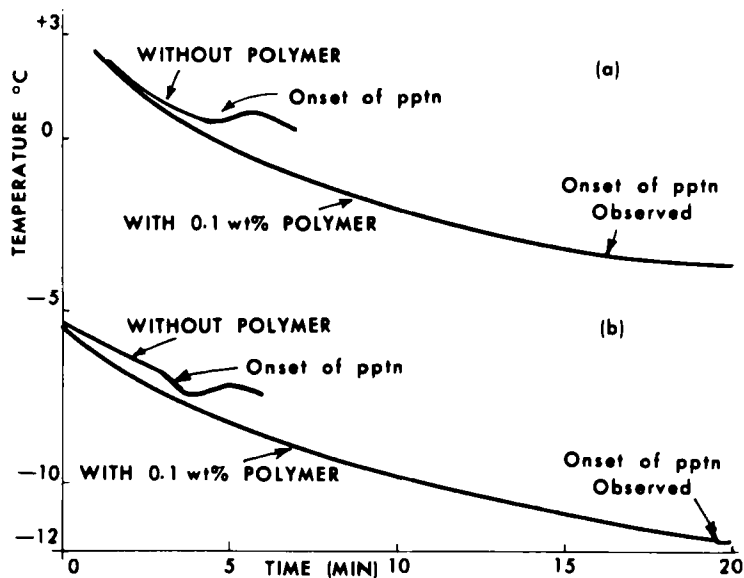


Fig. 5. Polymer affects the cooling curves of stirred single *n*-paraffin solutions. (a) 4 wt% $n\text{-C}_{22}$. (b) 4 wt% $n\text{-C}_{20}$.

pair of curves the data for $n\text{-C}_{20}$. In both solutions the visually-observed onset of precipitation was lowered by 3 to 4°C due to the presence of the polymer. Also, although the cooling curves for the solutions without polymer showed the expected sharp changes in slope at the onset of crystallization, no discontinuities were shown by the polymer-containing solutions until the 3 to 4°C of supercooling had been attained.

Figure 6 shows the effect of the polymer on the 50/50 blend of $\text{C}_{20}/\text{C}_{22}$ at a concentration of 4 wt%. Curve A shows the plot obtained in the absence of any polymer, and Curve B shows the corresponding results in the presence of 0.1 wt% of polymer. As can be seen, there was relatively little difference in the two curves though the polymer appears to have retarded the onset of crystallization somewhat. This small effect contrasted markedly with the large effect which the same concentration of polymer had on the separate 4 wt% solutions of $n\text{-C}_{20}$ and $n\text{-C}_{22}$.

CONCLUSIONS

The studies have indicated that high molecular weight *n*-paraffins and

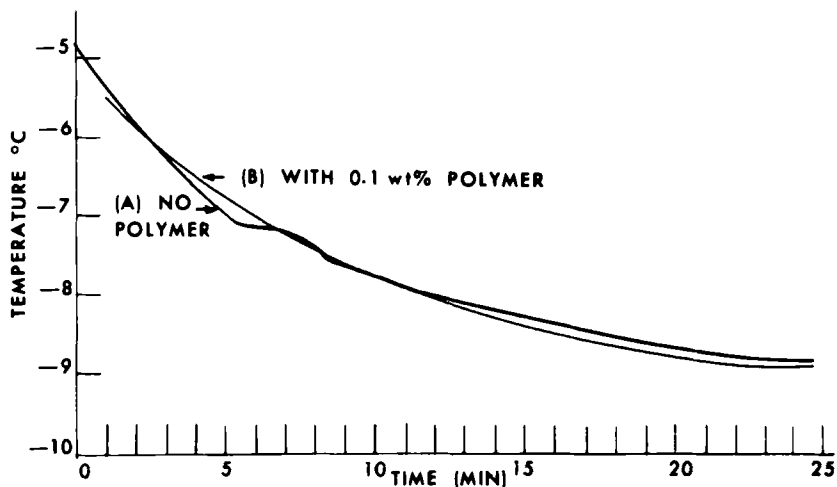


Fig. 6. Polymer has a relatively small effect on the cooling curve for a stirred mixture of 2 wt% n-C₂₀ plus 2 wt% n-C₂₂.

their mixtures are useful systems for obtaining information about polymer crystallizations. *n*-Paraffins are potent mutual crystal modifiers. Thus spherulites were produced when n-C₂₂ was doped with n-C₂₀. The addition of small amounts of polymers to these systems can affect the crystal growth considerably.

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