Notes and Communications

*Ringed Spherulites in Poly-*trans*-1,4-isoprene*

DURING measurements on the crystallization of poly-*trans*-1,4-isoprene in which spherulites were observed during growth and melting, it was noticed that under certain conditions ringed spherulites were formed. The process of formation is illustrated in *Figures 1* to *3* (photomicrographs under crossed polarizers). *Figure 1* shows poly-*trans*-1,4-isoprene spherulites of both high and low melting forms after crystallization for 16 h at 50°C; *Figure 2* shows spherulites of the high melting form at 56°C following melting of the low melting form; *Figure 3* shows ringed spherulites formed after further heating to 60°C. Final melting (disappearance of birefringence) occurred at 65–66°C. In order to produce ringed spherulites it was found necessary to use a rapid heating rate of about 10 degC per minute. At a slow heating rate of about 10 degC per hour no rings were observed. Rotating the axes of the polarizers did not alter the position of the rings, indicating that a dark ring was due to the absence of crystalline material rather than to an orientation effect.

It was found that this phenomenon resulted from slight variations in temperature during spherulite growth. Spherulites were normally grown on a microscope hot stage, typically at about 50°C for 24–48 h, but since there was no thermostat the temperature varied some ± 2°C over this period owing to fluctuations in ambient temperature. Spherulites grown in a thermostat at 50°C $\pm$ 0·05°C showed no ring formation.

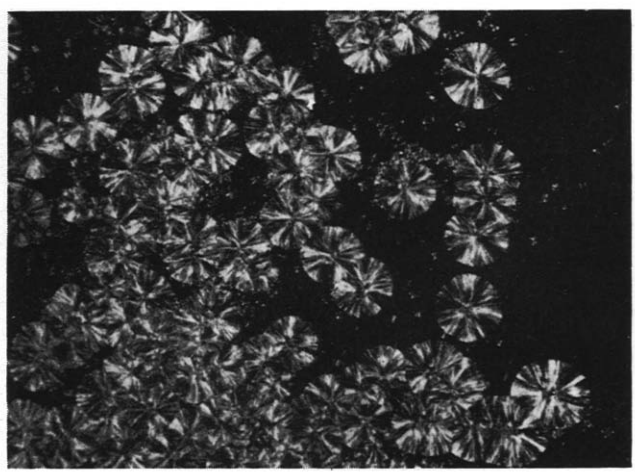

Figure 1—Spherulites of transpolyisoprene crystallized at 50°C for 16 h. The large spherulites (*ca* 130μ) are the high melting form, the small spherulites (*ca* 13μ) are the low melting form

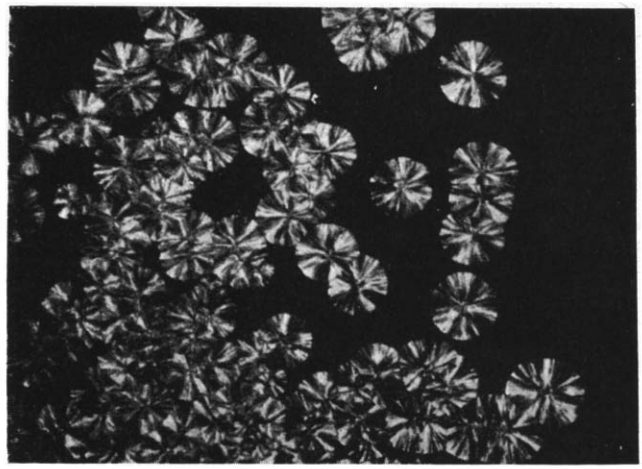

Figure 2—Spherulites of the high melting form of transpolyisoprene at 56°C

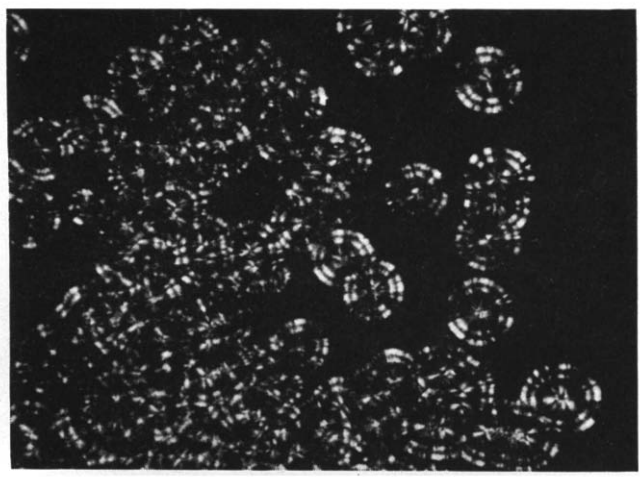

Figure 3—Ringed spherulites of the high melting form of transpolyisoprene at 60°C

It is believed that the small periodic variations in temperature during spherulite growth gave rise to concentric bands of different crystal perfections in the spherulites. Thus, that part of the spherulite formed at higher temperatures would grow more slowly and have a greater perfection (i.e. greater laminar thickness or chain fold length) and a higher melting point than that formed at lower temperatures. As the temperature was raised during subsequent melting observations, the spherulite bands formed at lower temperatures would melt first and give rise to a ringed appearance, the remaining material melting shortly afterwards.

The absence of ringed spherulites at low heating rates is presumably due to an annealing process. At such rates there would be sufficient time for the crystallites to reform, probably by a continuous melting and recrystallization process, to higher melting material. The spherulite would then melt uniformly.

The low melting form was not observed to form ringed spherulites, but this could have been due to the smaller size and general lack of definition of this type of spherulite. There seems no reason why ringed spherulites should not be formed by this mechanism in any crystallizing polymer system.

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