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Crystallization Behavior of the System Poly(L-lactic Acid) and Pentaerythrityl Tetrabromide

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ABSTRACT

Differential scanning calorimetry has been used to study the thermal crystallization of poly(L-lactic acid) (PLLA) and pentaerythrityl tetrabromide mixtures at different compositions. The melting temperature-composition phase diagram of the system reveals that PLLA forms a simple eutectic with pentaerythrityl tetrabromide, with a eutectic composition of 46% (w/w) of PLLA and a eutectic temperature of 422 K. Investigation of the microstructures obtained after removal of the diluent from the eutectic using scanning electron microscopy shows that the simultaneous crystallization of PLLA and the diluent proceeded in such a way that the diluent rods are the leading phases.

INTRODUCTION

The crystallization and melting behavior of various binary systems containing polymer and diluent have been studied with great interest [1-4]. Smith and Pennings [3-5] have shown the morphology resulting from the eutectic crystallization of polyethylene and polypropylene with a number of diluents and the porous microstructure that remains after the removal of the low molecular weight diluent from the solidified eutectics.

Poly(L-lactic acid) (PLLA), being biodegradable, biocompatible, and bioabsorbable, may find use in medical application for sutures and surgical implants where porous materials are extremely important. The general crystallization and melting behavior of PLLA has been studied in detail [6, 7]. The present work is concerned with 1) the thermal crystallization of PLLA and pentaerythrityl tetrabromide mixtures at different compositions using differential scanning calorimetry (DSC), and 2) the investigation of the microstructures obtained after the removal of the diluent from the mixture.

EXPERIMENTAL

PLLA was obtained by cationic ring-opening polymerization of (L-)dilactide (supplied by Boehringer and Sons, Ingelheim, Germany) using stannous octoate as the catalyst. The sample was stored over phosphorus pentoxide. Viscosity-average molecular weight (\bar{M}_v) was determined in chloroform at 25°C with an Ubbelohde viscometer using the relation [8] $[\eta] = 5.45 \times 10^{-4} \bar{M}_v^{0.73}$. The PLLA used had a molecular weight of 1.5×10^5 . The diluent employed was pure pentaerythrityl tetrabromide.

Polymer solutions of different compositions were heated to 20°C above their melting points in sealed aluminum pans, kept for 30 min for homogenizing, quenched quickly to 373 K, crystallized at 373 K for 30 min, and then scanned at a heating rate of 8°/min using a Perkin-Elmer Differential Scanning Calorimeter IB in order to obtain the melting endotherms. The peak temperature was taken as the melting temperature.

Microscopic studies were made using a Zeiss polarizing microscope equipped with a Mettler hot stage FP52. For electron microscopic observations the polymer solutions with pentaerythrityl tetrabromide were prepared in sealed glass tubes at 473 K, and the diluent was removed from the solidified solution by sublimation under high vacuum (10^{-6} mm) at 353 K.

The polymeric microstructure was examined by using a JEOL JSMU3 scanning electron microscope.

RESULTS AND DISCUSSION

The phase diagram of the system PLLA-pentaerythrityl tetrabromide consists of the melting temperatures of various alloys of the system rather than an equilibrium melting point-composition diagram. Figure 1 gives the melting thermograms of PLLA-diluent mixtures recorded at a scan speed of 8°/min. As shown in Fig. 1, the pure components and PLLA solution containing 46% (w/w) of the polymer exhibited one melting endotherm while the thermograms of other composition

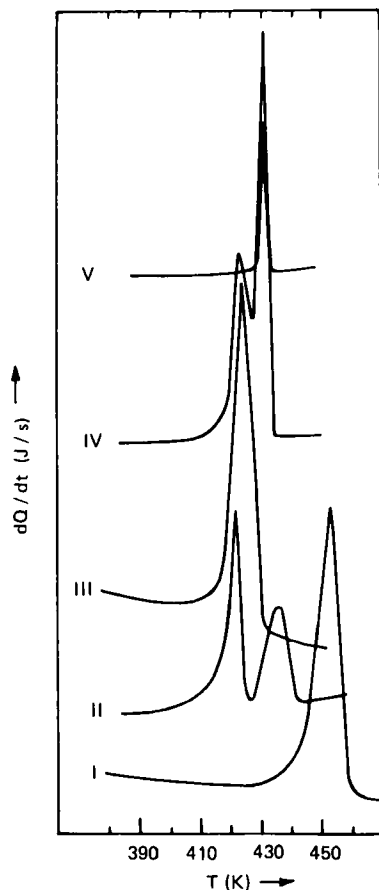


FIG. 1. DSC melting thermograms of various mixtures of PLLA and pentaerythrityl tetrabromide at various PLLA weight fractions: I, 1.0; II, 0.627; III, 0.46; IV, 0.206, V, 0.0.

showed two peaks. Figure 2 presents the melting temperature-composition diagram for PLLA and the diluent, and from this diagram it is clear that we are dealing with a simple eutectic polymer-diluent system with a eutectic composition of 46% (w/w) of PLLA and a eutectic temperature of 422 K.

The eutectic solidification under isothermal conditions was characterized by purely spherulitic growth with a growth rate of ~ 100 mm/hr. This is illustrated by the optical photomicrograph of Fig. 3 which was taken from an eutectic film crystallized at 397 K from the melt. Direct microscopic experiments revealed that the simultaneous crystal-

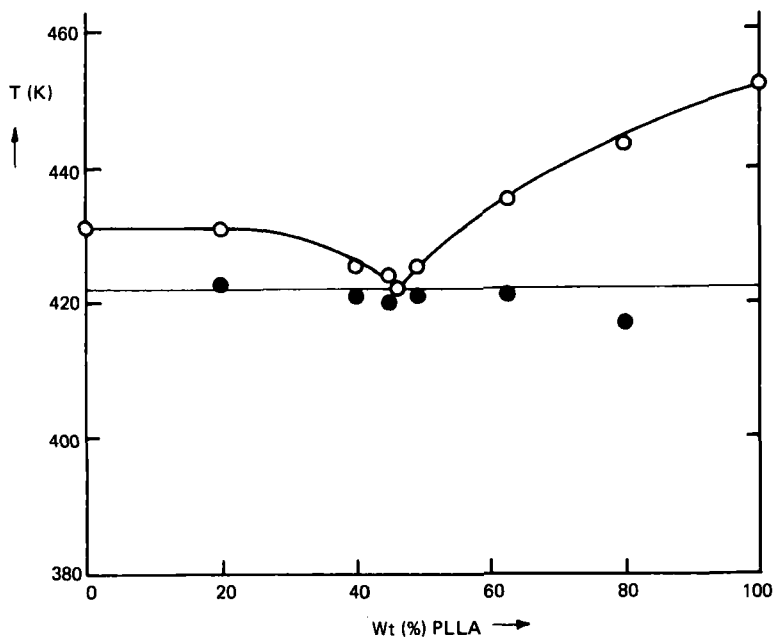


FIG. 2. Melting (peak) temperature-composition diagram of PLLA and tetracythryl tetrabromide. (●) Eutectic temperature. (○) Melting points of individual components in the mixture.

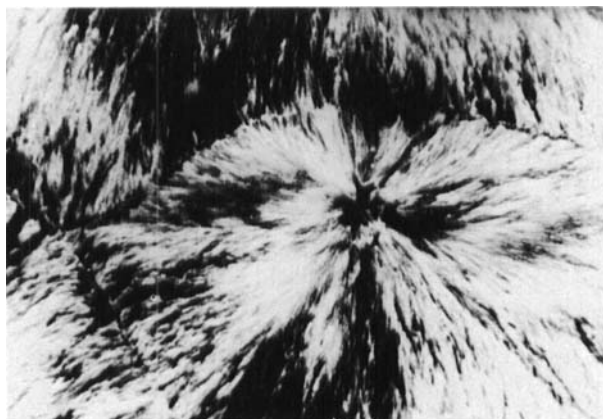


FIG. 3. Optical photomicrograph of the sphere-like eutectic microstructure produced by crystallizing at 397 K.

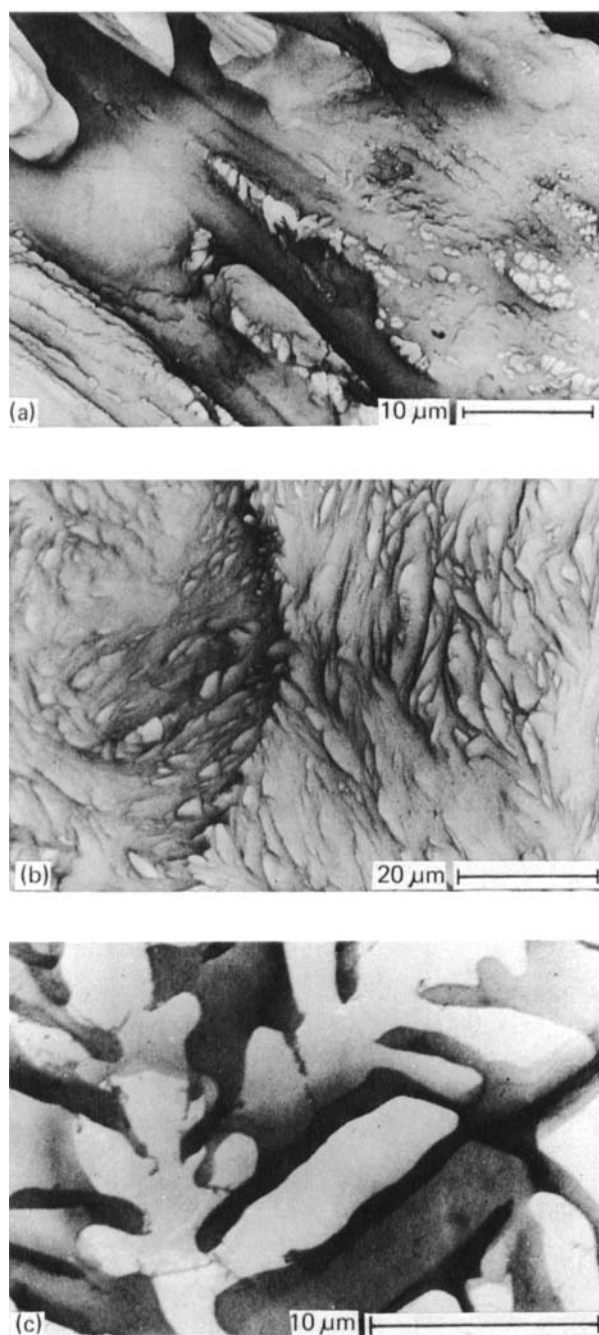


FIG. 4. Porous polymeric structure remaining after sublimation of the diluent from a eutectic solution which was solidified (a) by quenching the melt in cold water, (b) by fast cooling ($40^{\circ}/\text{min}$) of the melt to 410 K, and (c) by slow cooling ($15^{\circ}/\text{h}$) of the melt from 415 K.

lization of the polymer and the diluent proceeded in such a way that the diluent rods were the leading phases.

This is further confirmed in the scanning electron micrographs presented in Fig. 4. Figure 4 shows the PLLA microstructures (in the growth direction) left behind after sublimation of the solvent under reduced pressure from eutectic solution which was solidified (a) by quenching the melt in cold water (Fig. 4a), (b) by fast cooling ($40^{\circ}/\text{min}$) from the melt to 410 K (Fig. 4b), and (c) by slow cooling ($15^{\circ}/\text{h}$) from the melt to 415 K (Fig. 4c). These reveal long canals with a tendency to line up in the growth direction which originated from the diluent rodlike crystals.

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