General crystallization behaviour of poly(L-lactic acid) PLLA:
2. Eutectic crystallization of PLLA

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The solidification and melting behaviour of quasi-binary systems formed by poly(L-lactic acid) (PLLA) and respectively the diluents *para*hydroxybenzoic acid (PHBA) and hexamethylbenzene (HMB) have been investigated. For both quasi-binary systems the effect of diluent concentration on the measured melting temperatures was in reasonable agreement with the theoretical values calculated according to the Flory–Huggins theory of melting point depression. The PLLA–PHBA system formed an eutectic composition for 84% w/w of PLLA in the mixture. Its eutectic melting temperature is 437K. For the PLLA–HMB system the eutectic composition was 65% w/w of PLLA in the mixture and the eutectic melting temperaturre of 432K. The morphology of the PLLA–diluent mixtures was strongly dependent on the diluent concentration. Fracture surfaces of the mixtures of PLLA and PHBA exhibited faceted crystals of various shape, formed by the diluent. They could not be removed from the polymer by sublimation, probably because of the intermolecular hydrogen bonds formed by PHBA itself and/or PHBA and the PLLA matrix. Sublimation of diluent from PLLA–HMB quasi-binary system led to a highly porous material of varying morphology.

Keywords Eutectic crystallization; poly(L-lactic acid); parahydroxybenzoic acid; hexamethylbenzene; eutectic composition; temperature and morphology; vapour phase crystallization

INTRODUCTION

In a previous paper in this series[1] it was reported that PLLA crystallizes in the hexagonal crystalline modification with unit cell dimensions of $a=b=5.9$ Å, $\alpha=\beta=90^\circ$ and $\gamma=120^\circ$. The equilibrium melting temperature T_m° of PLLA, as estimated from the dependence of the melting temperature on the crystallization temperature, was 488K. Crystallization from the melt produces the spherulitic structure, while crystallization from solution leads to the folded chain lamellar crystals of 100 Å thickness[1].

This paper deals with a eutectic crystallization of PLLA in the presence of the low-molecular weight, high melting diluents. From three different routes of the eutectic solidification, i.e. isothermal, in a temperature gradient or by quenching, the latter was examined in this study. It is known that the eutectic soldification of polymers may lead to porous materials of some potential practical application[2–5]. Porosity of a surgical implant is for instance an important factor which determines tissue ingrowth[6–8].

As PLLA, due to its biodegradibility and biocompatibility may find a wide medical application, it seemed important to know whether the eutectic solidification may lead to the desired porosity.

It will be reported that the eutectic solidification of PLLA from the melt in presence of *para*hydrobenzoic acid or hexamethylbenzene leads, in certain cases, to porous materials of varying morphology.

EXPERIMENTAL

Materials

The PLLA used in the present study was obtained by fractionation according to a method described previously[9], and has a M_w/M_n ratio in the range 1.6 to 2.0. The viscosity-average molecular weight[10] of the polymer was 5.0×10^5, and its melting peak temperature 451K.

*Para*hydroxybenzoic acid (Aldrich, Europe) was recrystallized twice from a water–ethanol mixture (80/20 v/v), its melting temperature was 489.6K.

Hexamethylbenzene (Aldrich, Europe) was recrystallized from acetone and had a melting temperature of 439.1K.

Eutectic solidification

Solutions of proper amounts of PLLA and a diluent in good, miscible solvents were mixed and the solvents were subsequently evaporated[11]. The resulting solid PLLA–diluent mixture was sealed in glass ampoules under vacuum, after evacuation at 1×10^{-5} Torr. For further homogenization the mixture was kept at a temperature 10°C higher than the melting temperature of the highest melting component for one hour. The samples were then quenched to room temperature.

Characterization of samples

Melting characteristics were obtained with a Perkin Elmer DSC-2 apparatus using 5 mg samples and a scan speed of 10°/min. The apparatus was calibrated according to standard procedures.

A Jeol JSM-35C scanning electron microscope was

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Table 1 Experimental values of T_m, ΔH and V used for calculation of the liquidus curves

Material	T_m (K)	ΔH(kJ mol^{-1})	V (cm^3 mol^{-1})
Para hydroxybenzoic acid	489.6	23.7	94.6
Hexamethylbenzene	439.4	13.0	152.7
Poly(L-lactic acid)	451.0	3.6	55.8

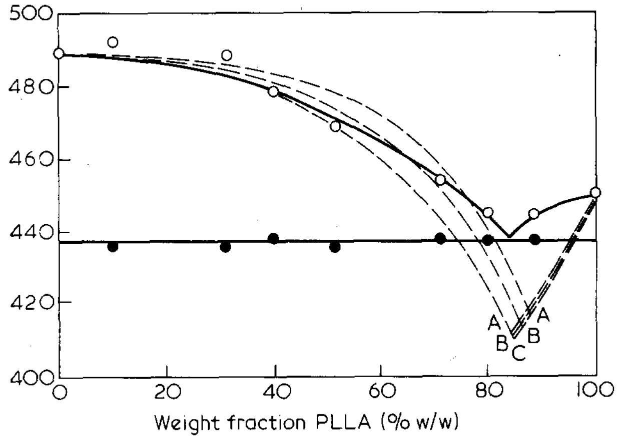


Figure 1 Phase diagram for poly(L-lactic acid)–*para*hydroxybenzoic acid (PLLA–PHBA) system. (——) Experimental values; (— — —) calculated liquidus curves for assumed values of χ the Flory-Huggins interaction parameter, A, 0.4; B, 0.2 and C, 0

used to observe the morphology of the fracture surface of the samples.

RESULTS AND DISCUSSION

Calculated and experimental phase diagrams

The liquidus curves of the binary homodisperse polymer–diluent mixtures can be calculated using expressions (1) and (2) derived from the Flory–Huggins theory of the melting point depression[12].

$$\frac{1}{T_{m,1}}-\frac{1}{T^{\circ}_{m,1}}=-\frac{R}{\Delta H_1}[\ln v_1+(1-v_1)+\chi(1-v_1)^2] \quad (1)$$

$$\frac{1}{T_{m,2}}-\frac{1}{T^{\circ}_{m,2}}=-\frac{R}{\Delta H_u}\frac{V_u}{V_1}[-(1-v_2)+\chi(1-v_2)^2] \quad (2)$$

The subscripts 1 and 2 refer to the diluent and the polymer respectively. T°_m and T_m are respectively the melting temperatures of the pure component and the mixture. R, ΔH and v are the gas constant, the molar enthalpy of fusion and the molar volume fraction respectively. V is the specific volume and χ is the Flory–Huggins interaction parameter. The subscript u refers to the polymer structural unit. The experimental values of parameters used for calculation of the liquidus curves for both PLLA diluent systems are given in *Table 1*.

Figures 1 and *2* show the phase diagrams for PLLA–PHBA and PLLA–HMB mixtures respectively. The solid lines represent the experimental values of T_m as obtained from d.s.c. measurements, while the broken lines A, B and C in both figures were drawn for assumed values of χ, equal to 0.4, 0.2 and 0 respectively. The PLLA–PHBA mixtures formed an eutectic composition for 84% w/w of PLLA with the eutectic melting temperature of 473K. The eutectic composition of the PLLA–HMB system was found for 65% w/w of PLLA with the eutectic melting temperature of 432K. It can be concluded from *Figures 1* and *2* that there is a reasonable agreement between the calculated and experimental liquidus curves for both the PLLA–diluent systems. This is especially so if one takes into account that the Flory–Huggins theory of melting point depression applies to the equilibrium state, which is generally not reached in the case of polymeric systems.

It has to be noted here that for some copolyesters and copolyamides the minimum in the dependence of T_m *versus* composition is also observed, although no eutectic crystallization takes place[13,14]. It is related to nonisomorphous cyrstallization of both the components in the copolymer.

As one cannot exclude that there was no chemical reaction between the PLLA and PHBA (the latter polymerizes quite easily), it is not possible to distinguish if the minimum in the T_m/composition curve observed for the PLLA–PHBA system is due exclusively to the eutectic crystallization and/or a partial copolymerization of both the structural units[13,14]. Typical melting endotherms of various PLLA–PHBA and PLLA–HMB mixtures with different PLLA concentrations are shown in *Figures 3* and *4*. All the PLLA–PHBA and PLLA–HMB mixtures exhibit two melting peaks in the thermograms, except for the pure PLLA, PHBA and HMB.

The first peak at the lower temperature side of the endotherms, which is independent of the diluent concentration, is assigned to the eutectic composition. The peak at higher temperatures is due to the dissolution of an excess of either pure polymer or pure diluent in the polymer solution.

The melting peak observed for all the PLLA–HMB compositions at the lowest temperature is caused by the solid–solid transition in hexamethylbenzene[15]. This solid–solid transition which is due to the rotation of the methyl groups in the HMB[15] was also found for polyethylene–hexamethylbenzene mixtures[12].

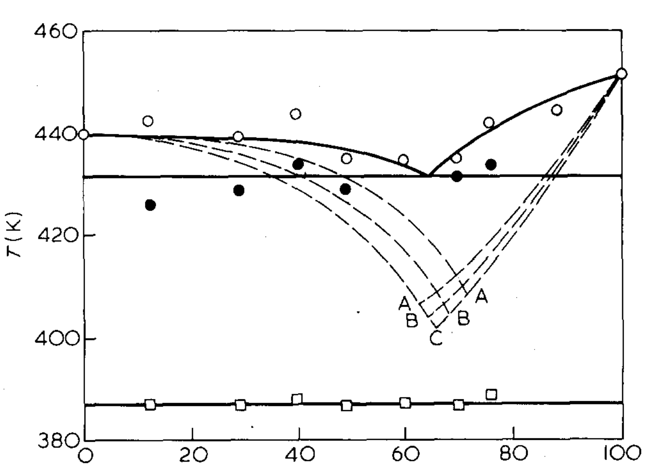


Figure 2 Phase diagram for poly(L-lactic acid)–hexmethylbenzene (PLLA–HMB) system. (——) Experimental values; (— — —) calculated liquidus curves for assumed values of χ, A, 0.4; B, 0.2 and C, 0

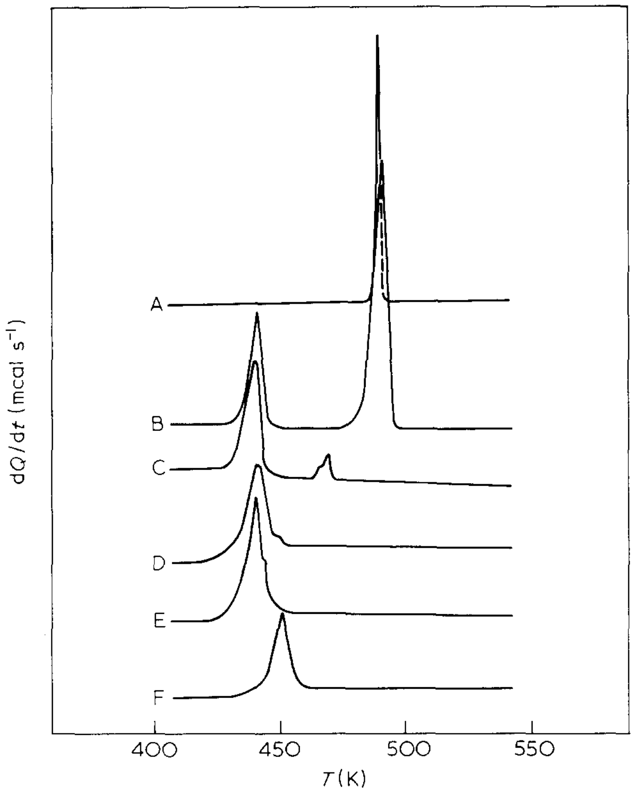


Figure 3 Melting endotherm for different PLLA–PHBA mixtures. PLLA weight fractions in PHBA were (%w/w): A, 0; B, 30; C, 50; D, 80; E, 90; F, 100 respectively

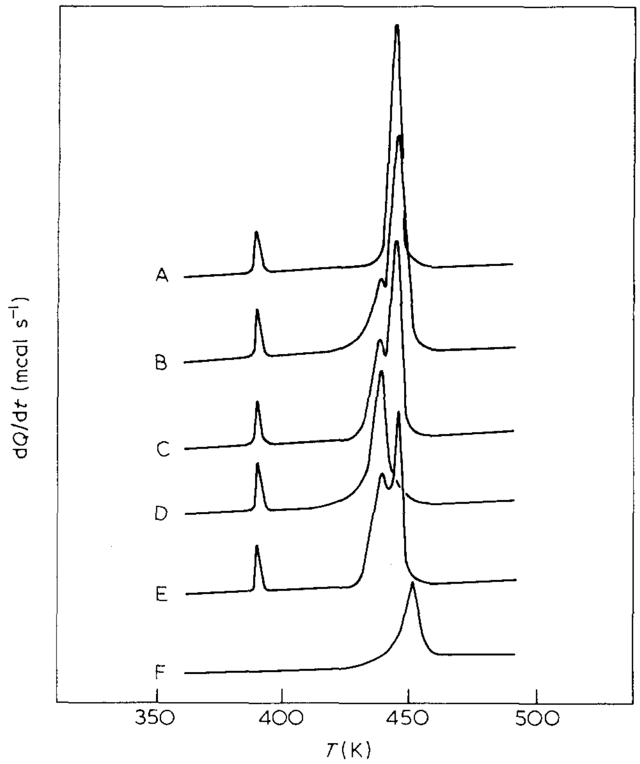


Figure 4 Melting endotherm for different PLLA–HMB mixtures, PLLA weight fractions in HMB were (% w/w): A, 0; B, 10; C, 40; D, 60; E, 80; F, 100 respectively

Morphology

PLLA–PHBA system. Figures 5a and *5b* show the morphology of pure PLLA and pure PHBA respectively, while *Figures 6–11* present the off-eutectic structures of the PLLA–PHBA system, obtained for various diluent concentrations. Pure, as-polymerized PLLA forms typical, folded-chain spherulites with the lamellae running radially to the spherulite centre. Pure PHBA crystallized under vacuum from the melt gives rhombohedral crystals which grow without any preferential orientation. The off-eutectic morphology obtained for the 10 w/w% PLLA and 90 w/w% PHBA cooled from the melt at 320°/min and 10°/min is shown in *Figures 6a* and *6b* respectively. In the latter case, as a result of a lower cooling rate, the size and perfectness of the crystals is significantly improved. A similar type of structure was also found for the off-eutectic composition of PLLA30–PHBA70 and PLLA40–PHBA60 (%w/w), which is shown in *Figures 7* and *8*. It can be concluded from *Figures 6–8* that for polymer concentrations in the range of 10–40 (%w/w) in PHBA, the polymer substrate causes a certain orientation of the diluent crystals grown in the system. It is probably due to the fact that growth of diluent crystals in the mixture is nucleated by the preferential planes of the PLLA crystals. No preferential growth direction was found however for the PLLA–PHBA mixture with concentration of PLLA in the range 50–90 (%w/w), although the shape of the crystals was not drastically changed. It seems that, because of a lower diluent concentration, PHBA can crystallize in any region of the PLLA matrix. *Figure 9* shows the off-eutectic structure of the sample with 50% w/w PLLA in PHBA. The fracture surface exhibits the faceted crystals of PHBA trapped in the polymer matrix.

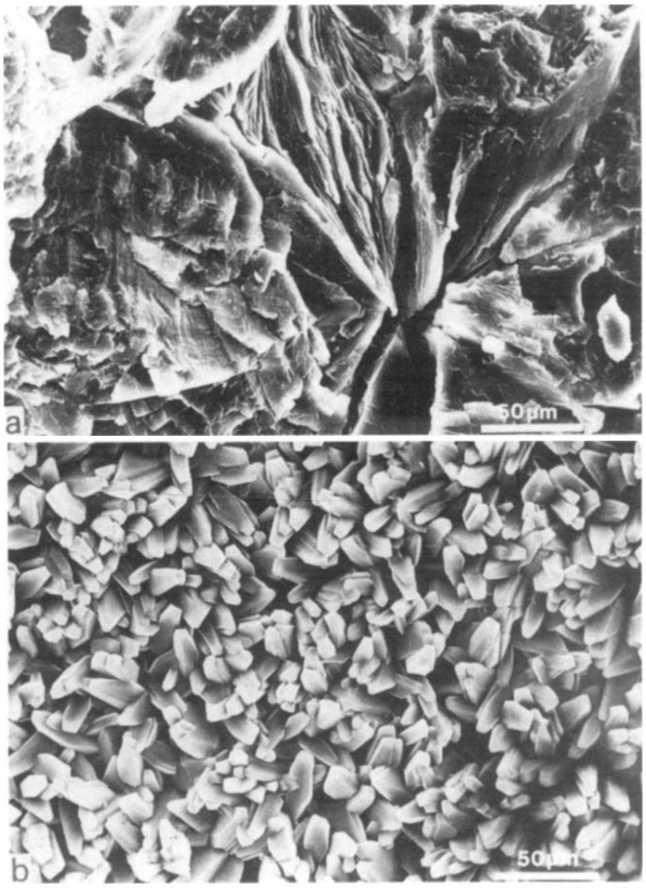


Figure 5 (a) Scanning electron micrograph of the fracture surface of as-polymerized PLLA. (b) Scanning electron micrograph of PHBA crystals grown from the melt under vacuum

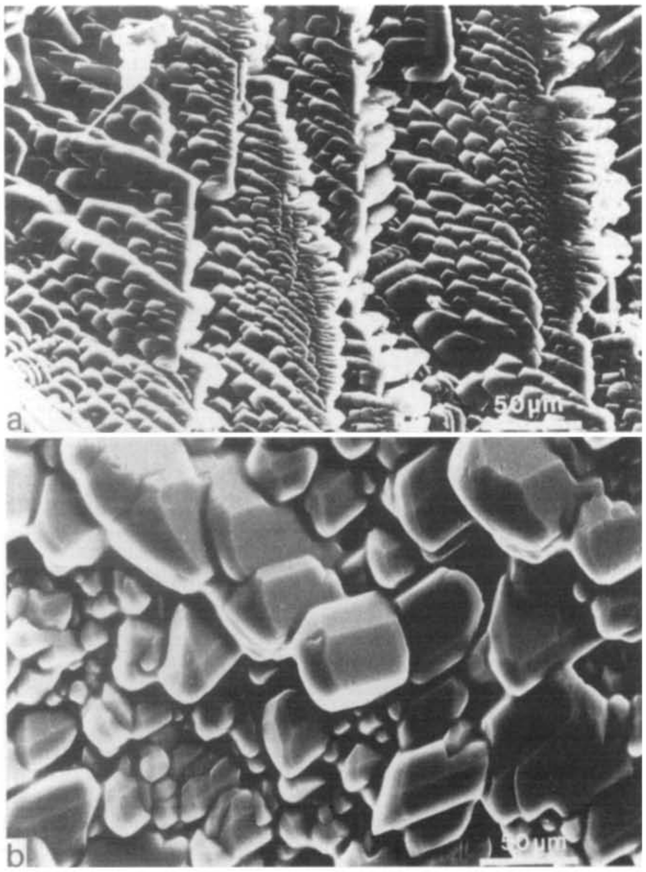


Figure 6 (a) Scanning electron micrograph of faceted structure that was left after solidification of the off-eutectic mixture PLLA 10—PHBA 90 (%w/w). Cooling rate 320°C/min. (b) Scanning electron micrograph of faceted structure formed on solidification of the off-eutectic mixture of PLLA 10—PHBA 90 (%w/w). Cooling rate 10°C/min

Figures 10 and *11* show the fracture surface of the sample which contained 80% w/w PLLA in PHBA. This concentration was close to the eutectic composition. The morphology shown in *Figure 10* was produced on fast cooling at 320°/min, while the morphology shown in *Figure 11* was obtained for a cooling rate of 10°/min. Fast cooling of the PLLA80–PHBA20 (%w/w) mixture leads to the glassy, structureless polymer matrix in which spherical areas are frequently observed. In these areas the diluent concentration is much higher than in the other parts of the sample, and because of that the PHBA crystals growing in these areas are much smaller than those formed outside of the spheres, where the undisturbed growth leads to larger and more perfect crystals. Slow cooling of this mixture (*Figure 11*) results in the spherulitic structure of PLLA, while the diluent rejected from the polymer by the crystal growth front crystallizes in the interspherulitic regions. In both the cases the dimensions of the diluent crystals decrease on increasing of the cooling rate.

All the micrographs shown in *Figures 6–11* do not exhibit the typical eutectic holes but only the teeth-like or rhombohedral faceted structures of *para*hydroxybenzoic acid growing out of PLLA–PHBA solution, which takes place in the vapour phase. For a low diluent concentration this vapour-phase crystallization favours the formation of the large, perfect crystals of PHBA that

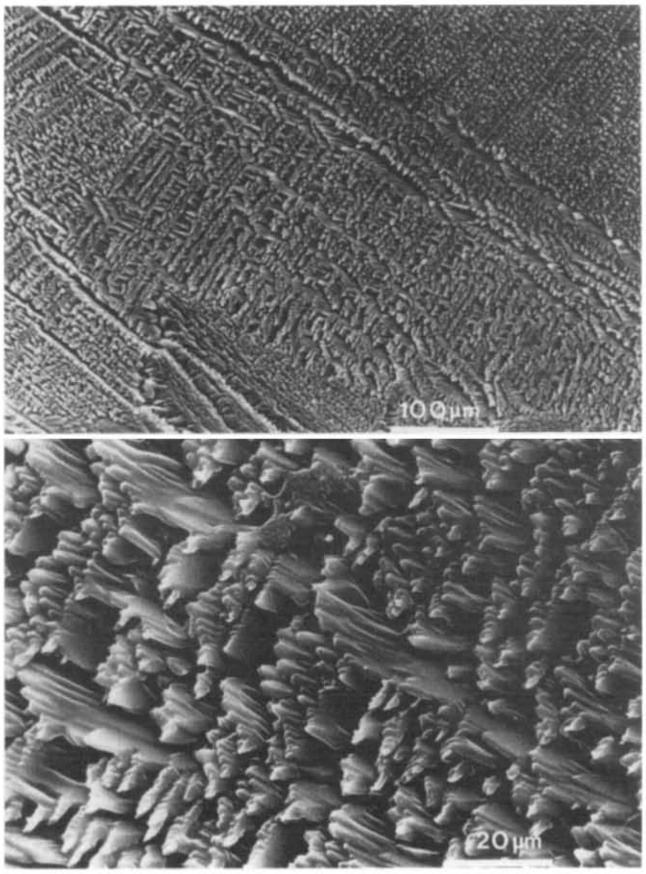


Figure 7 Scanning electron micrograph of faceted structure formed on solidification of the off-eutectic mixture of PLLA 30—PHBA 70 (%w/w)

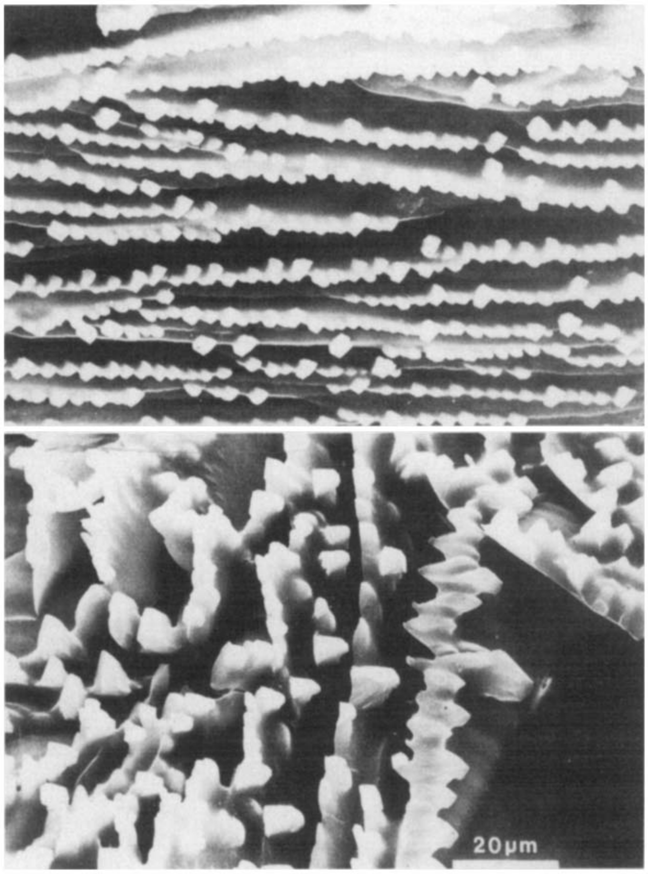


Figure 8 Scanning electron micrograph of the structure formed on solidification of the off-eutectic mixture PLLA 40—PHBA 60 (%w/w)

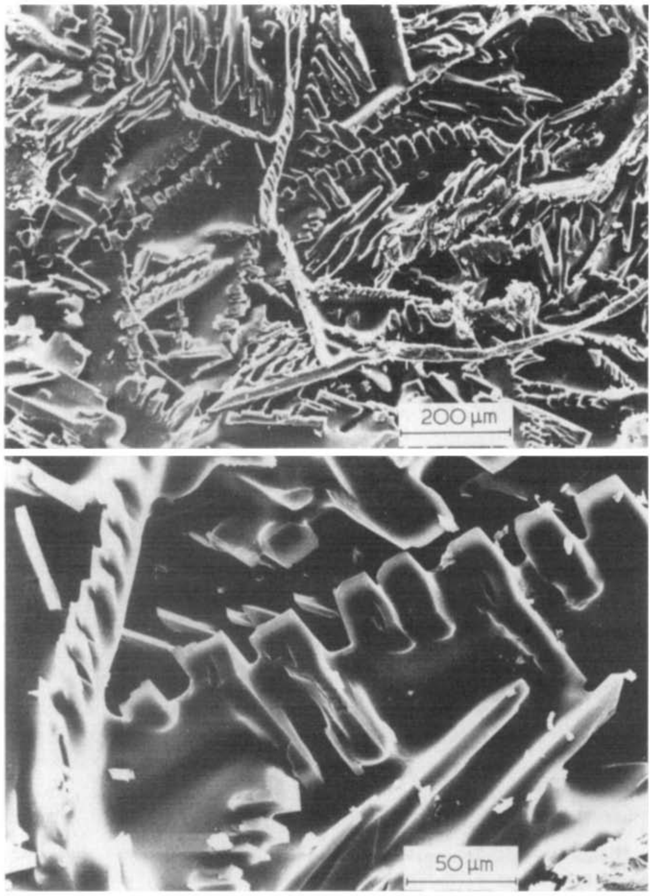


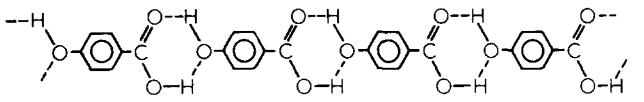
Figure 9 Scanning electron micrograph of the structure formed on solidification of the off-eutectic mixture of PLLA50–PHBA 50 (% w/w)

grow independently of each other at various sites on the PLLA matrix.

It seems however that for a high diluent concentration the PHBA crystals are nucleated on the preferential planes of PLLA crystals which may lead to their oriented overgrowth.

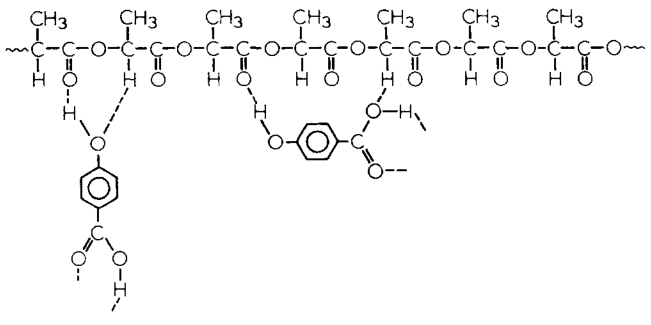
This vapour-phase crystallization of PHBA can be enhanced by formation of the hydrogen bonds between the PHBA structural units:

PHBA-PHBA



as well as between the PHBA structural units and the PLLA matrix:

PHBA-PLLA



The latter was probably the reason why it was not possible to remove the *para*hydroxybenzoic acid from the PLLA samples by sublimation, even after prolonged evacuation at elevated temperatures.

The unique morphology formed in the PLLA–PHBA mixtures over a wide range of concentrations was different from that reported for other polymer–diluent eutectic systems[2,3,12]. Thus it seemed important to know if this morphology is due to the specific chemical nature of the polymer or to the chemical character of the diluent. To

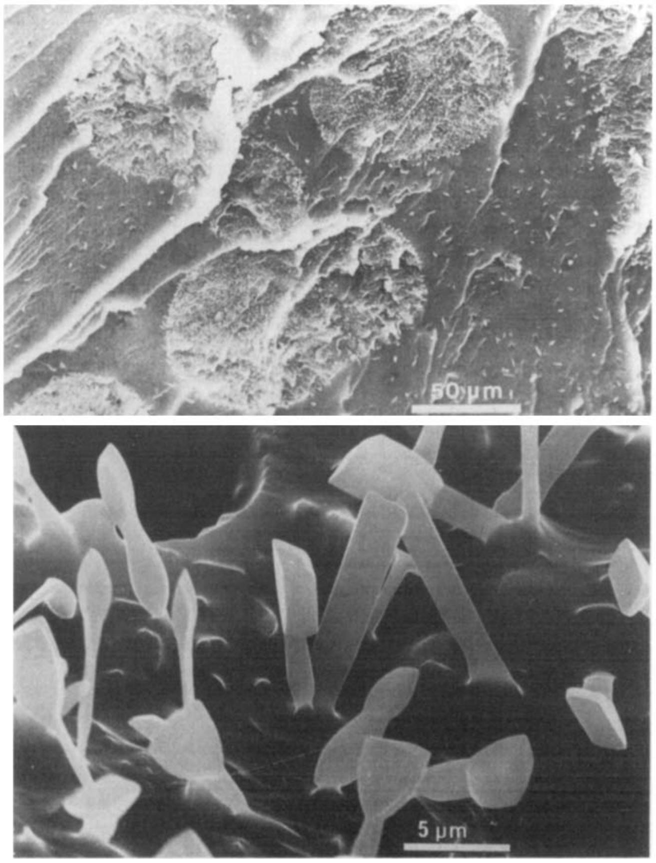


Figure 10 Scanning electron micrograph of the structure formed on solidification of a PLLA 80–PHBA 20 (%w/w) mixture, whose composition is close to the eutectic one. Cooling rate 320°C/min

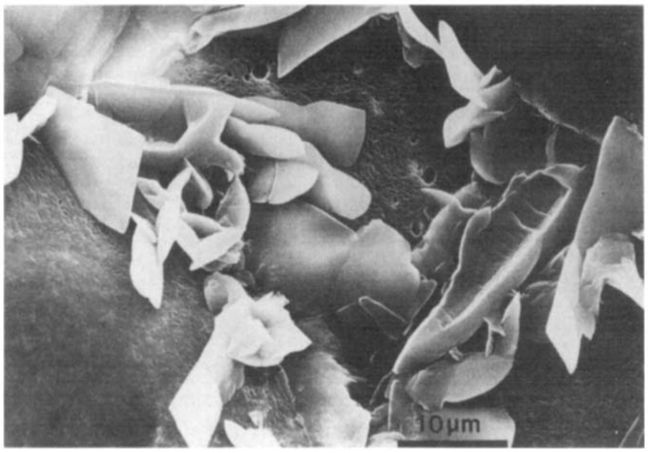


Figure 11 Scanning electron micrograph of the structure formed on solidification of a PLLA 80–PHBA 20 (%w/w) mixture, whose composition is close to the eutectic composition. Cooling rate 10°C/min

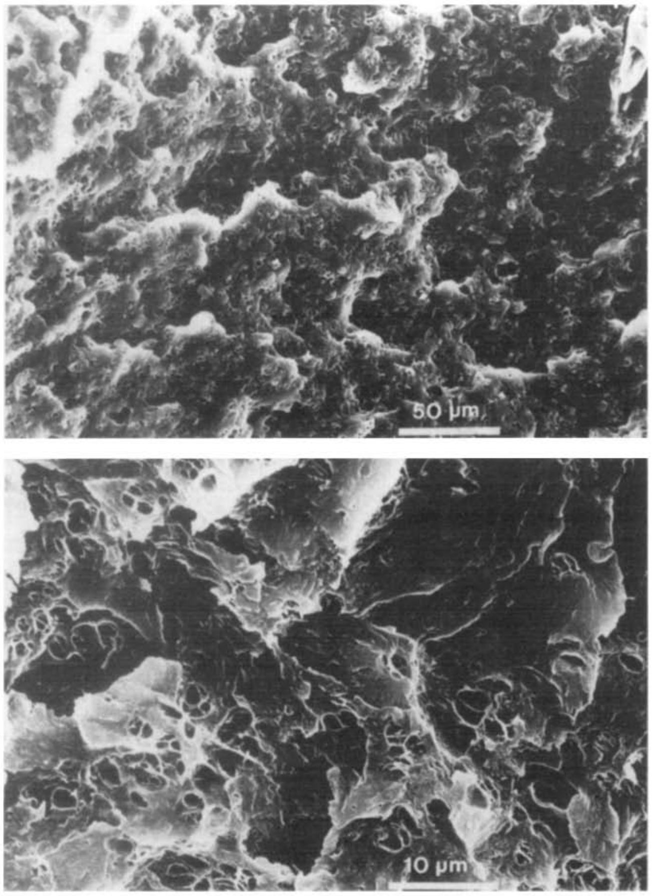


Figure 12 Scanning electron micrograph of the porous structure formed on solidification of the PLLA 90–HMB (%w/w) mixture, left after sublimation of the diluent

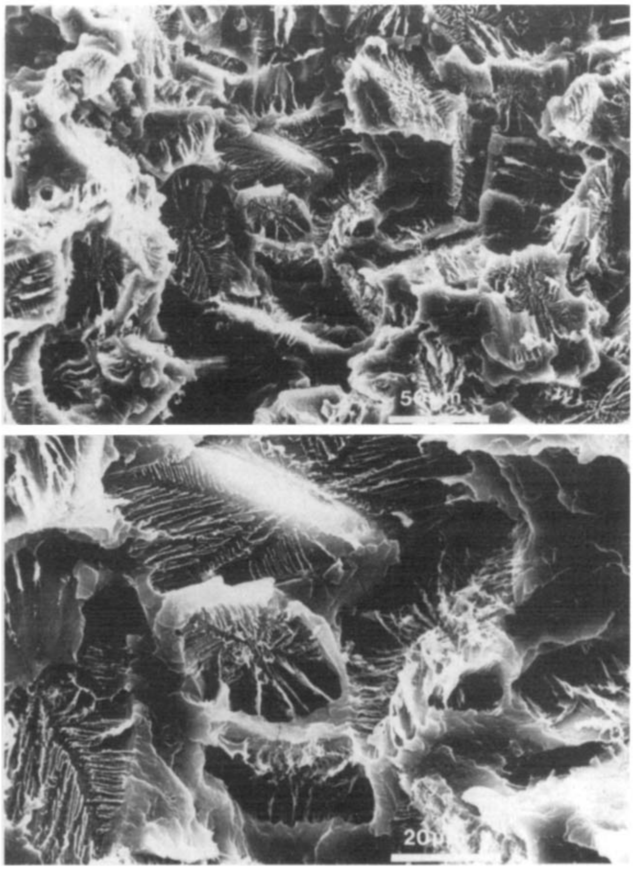


Figure 13 Scanning electron micrograph of the polymeric structure formed on solidification of the off-eutectic mixture PLLA 80–HMB 20 (%w/w)

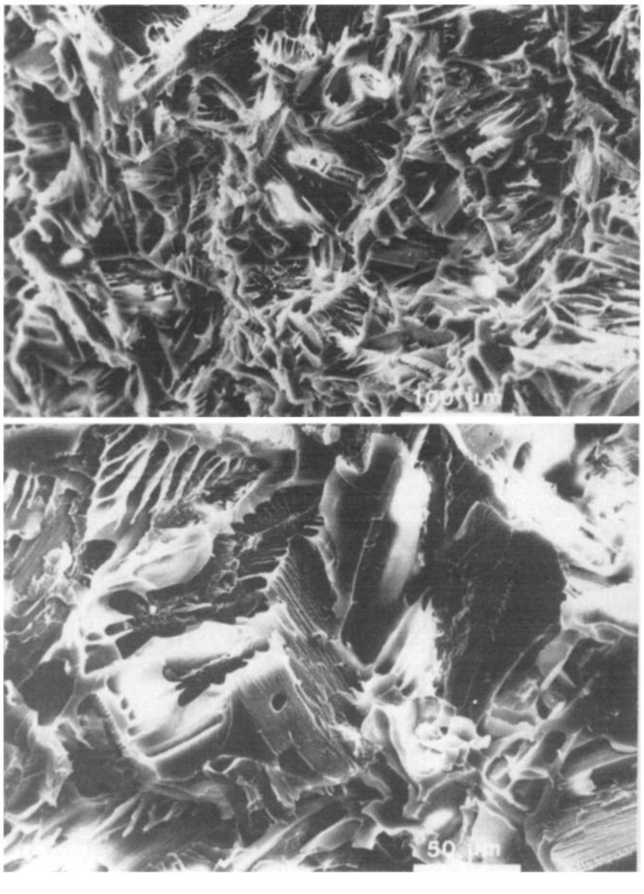


Figure 14 Scanning electron micrograph of the polymeric structure formed on solidification of the PLLA 60–HMB 40 (%w/w) mixture, which is close to the eutectic composition

answer this question the crystallization of PLLA was performed in presence of hexamethylbenzene, which was known to form the eutectic structures with polyethylene[12]. The eutectic morphology of the PLLA–HMB system is presented in *Figures 12–17*. *Figure 12* shows an electron micrograph of the off-eutectic composition of 90% PLLA in HMB with the eutectic pores uniformly distributed in the polymer matrix. The sample was very elastic and could be fractured only after freezing in liquid nitrogen, while the other PLLA–HMB mixtures fractured easily at room temperature.

The micrograph of the off-eutectic composition of 80% PLLA in HMB shown in *Figure 13* exhibits the rectangular centres in which the needle-like HMB crystals are formed, without preferential growth direction. The morphology formed in the mixture of 60% PLLA in HMB which is close to the eutectic composition is shown in *Figures 14* and *15*. Large rod-like pores are regularly spread over the whole sample. Inside these pores the rows of a fibrillar or ribbon-like polymeric structure can be observed. Also in this case no preferential orientation of the fibrils was found which appeared at different locations.

Figures 16 and *17* present the morphology of the off-eutectic composition of 30% and 10% PLLA in HMB respectively. Cellular PLLA exhibits rectangular and quadratic holes formed by sublimation of HMB crystals of the same morphology. Growth of these crystals is arrested upon increasing the PLLA concentration in the intercrystalline regions. The fracture surface of these

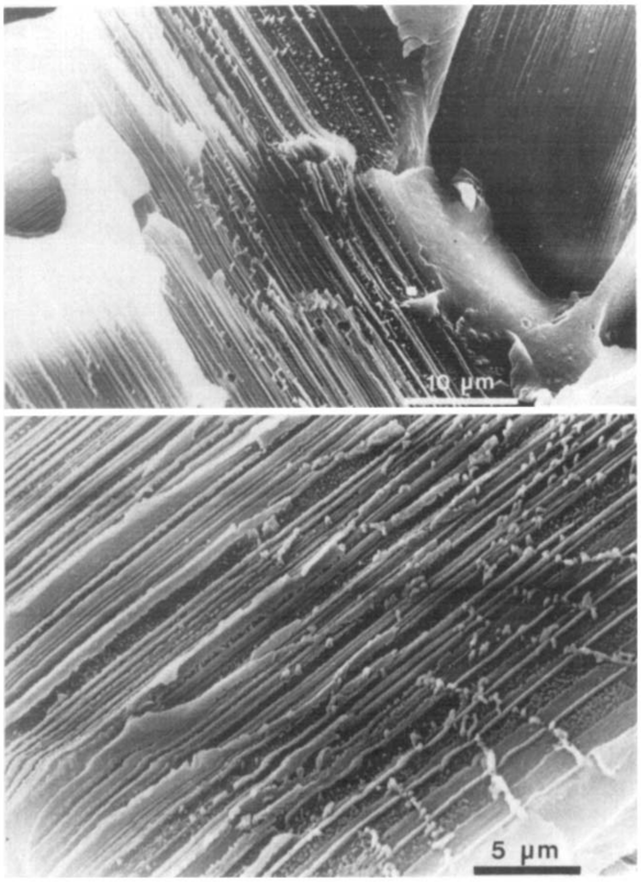


Figure 15 Scanning electron micrograph of the polymeric structure presented in *Figure 14* taken at higher magnification. Notice the fibrillar structure in the pores of the material

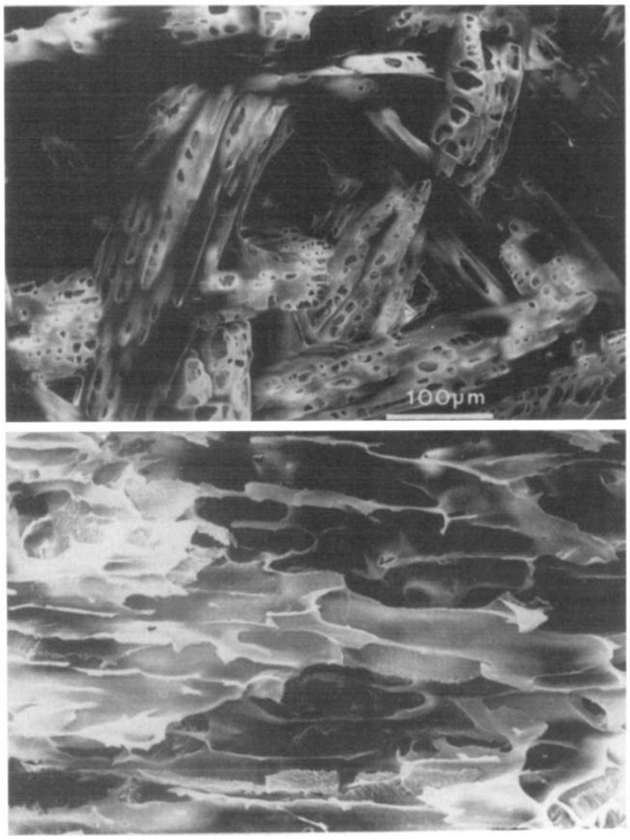


Figure 16 Scanning electron micrograph of the polymeric structure formed on solidification of the off-eutectic mixture of PLLA 30–HMB 70 (% w/w)

materials also reveals the large rod-like holes originating from primary crystals. As can be concluded from a comparison of *Figures 16* and *17*, which illustrate the difference in the pore sizes due to the difference in HMB concentration, the number of nucleation centres existing in the sample with a high concentration of HMB is so large that the optimum growth of HMB crystals cannot take place. The morphology of the PLLA–HMB system presented here, which is formed as a result of the eutectic solidification, is more or less similar to that reported for the polyethylene–HMB system[12]. Thus it can be concluded that the unique morphology found for the PLLA–PHBA system is due to the chemical nature of the specific diluent.

CONCLUSIONS

(1) Liquidus curves found for PLLA–PHBA and PLLA–HMB systems are in reasonable agreement with prediction of the Flory–Huggins theory of the melting point depression of polymers in the presence of low-molecular weight additives.

(2) PLLA–PHBA and PLLA–HMB systems form the eutectic composition for the concentration of PLLA in the mixture of 84 and 65% (w/w) respectively.

(3) The eutectic melting temperature is 437K for the PLLA–PHBA system and 432K for the PLLA–HMB system, as compared with 451K found for pure PLLA.

(4) It is hard to distinguish if the minimum in the melting temperature/composition curve observed for the PLLA–PHBA system is exclusively due to the eutectic

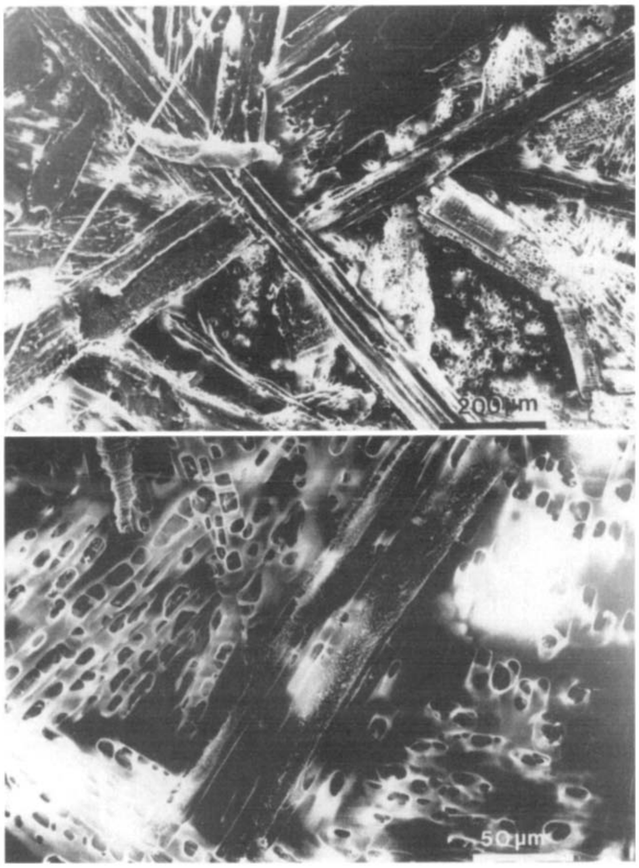


Figure 17 Scanning electron micrograph of the polymeric structure formed on solidification of the off-eutectic mixture of PLLA 10–HMB 90 (%w/w)

crystallization and/or partial copolymerization between these two components. Also the latter process may result in an eutectic point on the melting temperature *versus* composition dependence.

(5) Unique morphology formed in the PLLA–PHBA mixtures over a wide range of diluent concentrations is due to faceted growth of PHBA crystals which takes place in the vapour phase.

(6) This growth may be enhanced by formation of the intramolecular hydrogen bonds in PHBA.

(7) Formation of the hydrogen bonds between the PHBA and the PLLA matrix may be the reason that the PHBA cannot be removed from the polymer by sublimation. Formation of these bonds along a preferential plane of the PLLA crystal, may result in the orientation of the diluent crystals formed in the mixtures with a low polymer concentration. For a high polymer concentration the diluent crystals grow randomly in any place of the polymer substrate.

(8) PLLA–HMB system forms a eutectic morphology similar to that observed for polyethylene–HMB mixtures.

(9) Preparation of the polymer–diluent mixtures by simultaneous dissolution of both the components in good solvents followed by solvent evaporation, results in a more homogenous eutectic structure.

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