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ORIGINAL CONTRIBUTION

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Relationships between ringed spherulitic morphology and miscibility in blends of poly(ε-caprolactone) with poly(benzyl methacrylate) versus poly(phenyl methacrylate)

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Abstract Ringed spherulites are an interesting phenomenon that is observed only in very few miscible systems. For the first time, the relationship between the state of chain intermixing and the ring-band pattern was demonstrated. Two previously demonstrated miscible blend systems, poly(ε-caprolactone) (PCL) with poly(benzyl methacrylate) (PBzMA) and PCL with poly(phenyl methacrylate) (PPhMA), were studied in order to understand the mechanism of ring-band formation in the spherulites and the relationships between the ring-band pattern and the state of miscibility. In both miscible PCL/PBzMA and PCL/PPhMA systems, extinction rings were observed within the PCL spherulites. In the PCL/PBzMA blend, the extinction rings are not as distinct (owing to distortion) as those in the PCL/PPhMA blend system. Analysis was performed and discussions were made to reveal relationships between miscibility, interaction strength, and the pattern of the ring bands in the PCL spherulites in polymeric mixtures.

Key words Spherulites · Ring bands Interactions · Miscibility · Poly(ε-caprolactone)

Introduction

Only quite recently (1998) miscibility in a blend of poly(ε-caprolactone) (PCL) with poly(benzyl methacrylate) (PBzMA) was discovered [1]. Following the recent discovery of the miscible PCL/PBzMA system, PCL and poly(phenyl methacrylate) (PPhMA) have been found to exhibit miscibility with each other in the entire composition range [2]. The discovery of the miscible PCL/PBzMA and PCL/PPhMA blend systems is particularly interesting as PCL had not been known to be miscible with any acrylic-type polymers prior to our recent reports on the miscibility of PCL with these two methacrylate polymers. The glass-transition behavior suggests that the intermolecular interactions between the pairs are likely to be non-specific but is sufficient to result in thermodynamic miscibility between the pair. The significant broadening of T_g for PCL/PPhMA of intermediate compositions (e.g., 40/60) suggests that some homomolecular aggregation might exist and that the extent of aggregation changes with composition. The Fourier transform IR spectrum does not indicate any specific interaction between C=O of PPhMA and C=O of PCL or through other pairs of functional groups. Similar behavior has also been found between C=O of PBzMA and C=O of PCL. The lack of a shift of the C=O peak in the amorphous region is the opposite behavior of what was reported for the PVC/PCL system earlier by Coleman and Zarian [3]. The IR spectrum suggests that the interactions leading to the observed miscibility in PCL/PPhMA are mostly nonspecific. Thus, the observed miscibility could be accounted for at most by matched polarity or nonspecific intermolecular interactions. Miscible blends comprising PCL have been extensively studied [4–8], Classically, the miscibility of PCL with poly(vinyl chloride) (PVC) is one of the most well known [5]. In addition, PCL is miscible with some hydroxyl-containing polymers, among which poly(hydroxyl ether of bisphenol-A) (phenoxy) might be one of the most notable. Brode and Koleske [6] have demonstrated miscibility in a PCL/phenoxy blend, with the T_g satisfying the classical Fox equation (dynamic mechanical analysis).

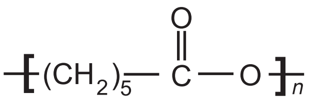
By contrast, miscibility of PCL with other carbonyl- or carbonate-containing polymers has not been common. Earlier, Paul et al. [7] reported miscibility in a blend of PCL with bisphenol-A polycarbonate. The melting point depression of PCL in PCL has also been investigated [8]. Ma et al. [9] have reported that miscibility may also occur in a blend of PCL with an aliphatic-aromatic copolyester, poly(ethylene terephthalate-*co*-caprolactone). PCL is also known to be miscible with poly(styrene-*co*-acrylonitrile) (SAN with AN wt% = 8–28) [10].

Miscible blends comprising PCL and acrylic polymers have not been common. So far, PPhMA and another acrylic polymer, PBzMA, are the only two methacrylate polymers that have been found to form miscible blends with PCL [1, 2]. As a continuing work, it is interesting to investigate crystallization, spherulite geometry/morphology, growth kinetics, interlamellar ring bands, etc., of neat PCL in comparison with PCL in miscible PCL/PPhMA or PCL/PBzMA blend systems. In addition, PCL spherulites in neat PCL are distinctly different from those in miscible PCL/PPhMA or PCL/PBzMA blends. Interlamellar domains are populated with PCL amorphous chains intermingled with miscible but amorphous PBzMA or PPhMA chains. Spherulite patterns are characterized by an interference band with peculiar periodicity. These two miscible polymer mixtures are an ideal model system for studying the mechanism of ring-band formation for two reasons. The state of miscibility in these two blend systems is similar, but the interactions are expected to vary slightly. Secondly, both blends contain PCL as a constituent polymer and both are capable of forming ring bands. Evidence of miscible regions extending from interspherulitc domains into intraspherulites in the interlamellar domains is discussed.

Experimental

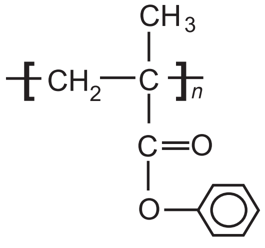
Materials

PCL is a semicrystalline aliphatic polyester derived from ε-caprolactone and was obtained from Polysciences (USA), with an approximate M_w = 35,000–45,000 g/mol and T_g = −70 °C and T_m = 60 °C (supplier's data). PBzMA was purchased from Scientific Polymer Products (USA), with manufacturer's data of M_w = 51,000 g/mol with a polydispersity index (PI) of 2.67 (gel permeation chromatography GPC) and a T_g of 54–60 °C (manufacturer's report). Our in-house laboratory characterization showed M_w = 54,000 (GPC), PI = 2.27, and a T_g (onset) of 57.2 °C for PBzMA. Another methacrylate polymer used was PPhMA, which was supplied by Scientific Polymer Products (USA), with an approximate M_w of 100,000 g/mol (GPC) and a literature-value T_g of 110 °C. The sample materials were free of additives and were used without further purification. The structures of these polymers are shown as follows:

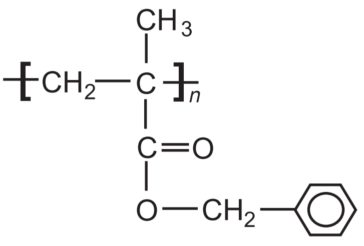


$$-\!\!\left[(CH_2)_5-\overset{\displaystyle O}{\overset{\|}{C}}-O\right]_n$$

PCL



PPhMA



PBzMA

Binary blends of PCL with either of these methacrylate polymers were prepared. It was determined that tetrahydrofuran yielded the best result and was used for preparing samples of both blend systems investigated in this study. The polymers were first weighed and were then dissolved into the solvent with continuous mixing with a magnetic stirrer. Subsequently, the resulting polymer solution was poured into a flat tool-mold kept at 45 °C. The solvent in the cast-film samples was first vaporized under a hood at a controlled temperature, followed by final solvent removal in a vacuum oven for 48 h at 50–60 °C. The casting temperature is expected to influence the blend morphology in many blend systems owing to the kinetic process of solvent evaporation. The blend samples in this study were prepared by solution blending/casting at a temperature of 45 °C, which was found to yield the best result.

Apparatus

The T_g and other thermal transitions were measured with a differential scanning calorimeter (DSC) (Perkin-Elmer DSC-7) equipped with an intracooler and a computer for data acquisition/analysis. Unless otherwise specified, all T_g measurements were made at a scan rate of 20 °C/min on second scanning after quenching from above the melting point of PCL (quenched from exactly 140 °C). The T_g values were taken as the onset of the transition (the change of the specific heat) in the DSC thermograms. The measurements of the melting point were performed as follows. The samples were annealed for 7 min at 90 °C and then rapidly quenched down to the T_c in the DSC cell. After isothermal holding for 12 h, the samples were again rescanned in the DSC using a heating rate of 10 °C/min and then the melting point was recorded.

A polarized-light microscope (Nikon Optiphot-2) was used for observation of the spherulites of neat PCL as well as the PCL/

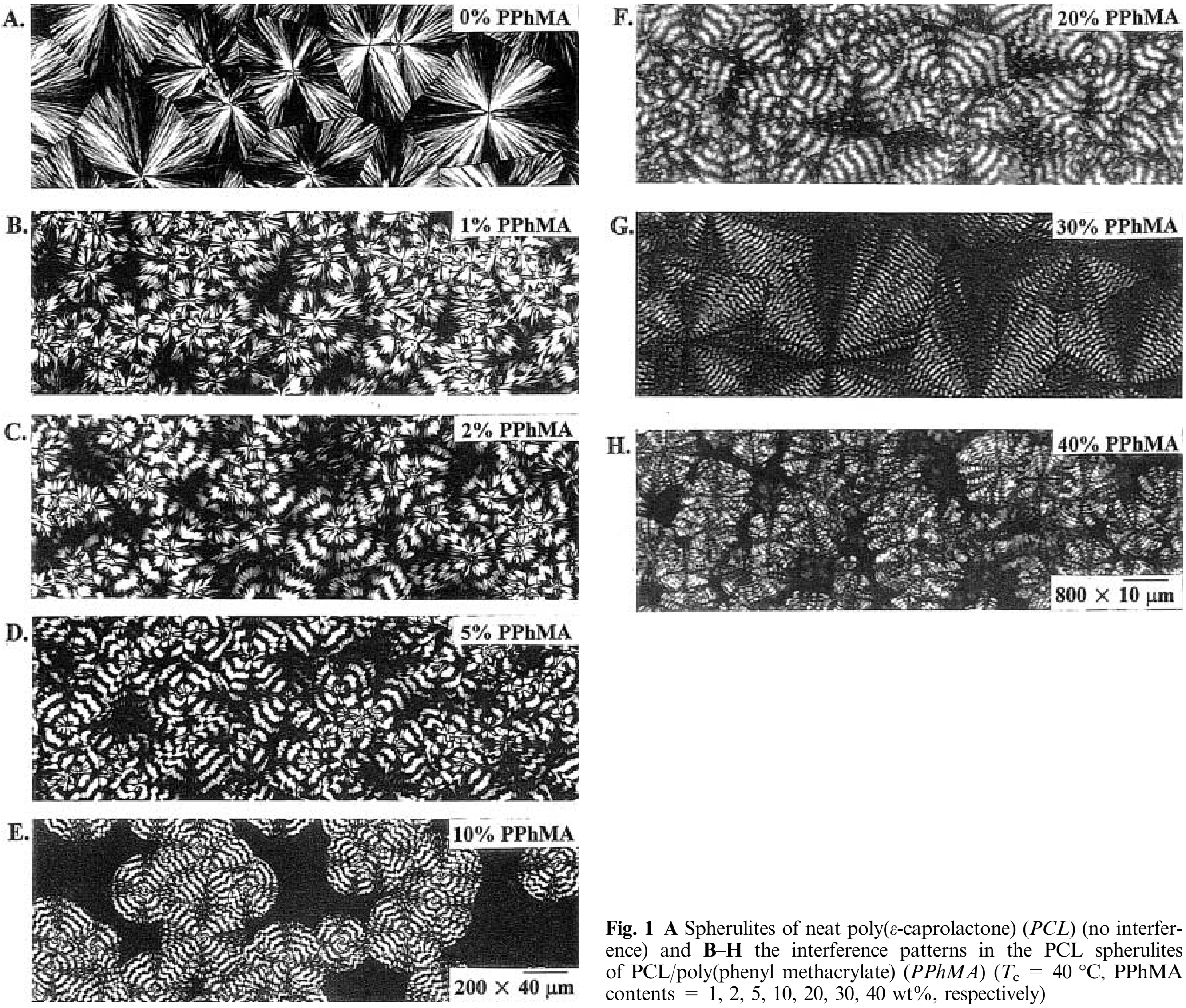


Fig. 1 **A** Spherulites of neat poly(ε-caprolactone) (*PCL*) (no interference) and **B–H** the interference patterns in the PCL spherulites of PCL/poly(phenyl methacrylate) (*PPhMA*) (T_c = 40 °C, PPhMA contents = 1, 2, 5, 10, 20, 30, 40 wt%, respectively)

PPhMA and PCL PBzMA blends. The blend cast films with the free surface (i.e., uncovered) upward were first melted on a hot stage at 90 °C for 5 min and then were rapidly transported to the microscope heating stage (Linkam THMS-600 with TP-92 temperature programmer) maintained at T_c. The purpose was to quickly bring the sample to the intended isothermal temperature.

Results and discussion

Ring bands in spherulites

Extinction rings of regular periodicity may be present in the spherulites of a semicrystalline polymer [11]. A comprehensive literature search revealed that only two semicrystalline polymers are capable of showing such rings in spherulites [12–21]. These two polymers are poly(vinylidene fluoride) (PVF_2) and PCL and the extinction rings are present only in miscible blends involving either of these semicrystalline polymers. The repeating distance (bandwidth) has been reported to change with the amorphous polymer fraction and the temperatures at which the blends are maintained for isothermal crystallization. Some of the most notable examples are PVF_2/poly(methyl methacrylate) (PMMA) [12] and PCL/PVC [13, 14]. PVF_2 is known to be miscible only with PMMA, but many other miscible blends involving PCL as one constituent also show such extinction rings [15–21]. Many have attempted to find a plausible explanation for the mechanisms; however, so far, fully reasonable theories have yet to be proposed. The fact that the ring bands are found in miscible blend systems involving only PCL or PVF_2 is also puzzling. Tanaka et al. [22] have applied a new digital image analysis to clearly illustrate the presence of ring bands in a ternary PCL/poly(vinyl methyl ether)/polystyrene blend, but the mechanism is still yet to be fully understood.

Interference rings (within the PCL spherulites) were observed in both miscible blend systems (PCL/PPhMA and PCL/PBzMA) investigated in this study, but the ring patterns are obviously different between these two systems. Figure 1 shows the spherulites of neat PCL (no interference rings, Fig. 1A) and the interference patterns (roughly concentric) found in PCL spherulites of the PCL/PPhMA blend system (Fig. 7B–H) crystallized at 40 °C. The neat PCL spherulites are apparently free of any interference rings when crystallized at the same temperature. With the introduction of PPhMA to form a miscible PCL/PPhMA blend system, however, ring bands started to appear within the PCL spherulites. At even 1 wt% PPhMA, ring bands were observed in the PCL/PPhMA system; however, at low PPhMA contents (below 5 wt%), the ring bands are slightly distorted. Nevertheless, with increasing amount of the amorphous polymer (PPhMA) in the polymer mixtures, the interference rings persist in the PCL spherulites and, interestingly, the ring pattern becomes more regular (e.g., for blends containing PPhMA >5 wt%). The ring width and separation between successive concentric rings were found to be smaller for increasing PPhMA contents in the mixtures. There have been proposals that the bands are caused by a periodical twisting of the lamellae during crystallization. Owing to miscibility and intimate contact between the two polymer chains, the amorphous component (PPhMA) was easily trapped between the crystalline lamellae of PCL, thus causing twisting of these lamellae. With a greater fraction of amorphous material present in the miscible blend, more amorphous polymer chains would get into the PCL spherulites, leading to more apparent interference in the crystalline lamellae. This may be the reason accounting for the decrease in bandwidth with increasing amount of amorphous polymer.

Similarly, ring patterns in the miscible PCL/PBzMA blend system were examined and compared to those found in the miscible PCL/PPhMA system (Fig. 1). The rings in PCL/PBzMA are less regular in comparison to those in PCL/PPhMA. The interference ring patterns found in the PCL spherulites of the PCL/PBzMA blend system crystallized at 40 °C are shown in Fig. 2. Again, the PCL spherulites in the PCL/PBzMA blends of a series of compositions (containing PBzMA from 1–40 wt%) were examined using a polarized-light optical microscope. Interestingly, the ring band did not appear in the PCL/PBzMA blends until the PBzMA (amorphous diluent) concentration was 5 wt% or greater. This phenomenon is quite different from the PCL/PPhMA system, where the ring bands were observed at compositions as low as 1 wt% PPhMA. Secondly, the ring pattern was found to be distorted for the PCL/PBzMA blends of all compositions investigated (PBzMA = 1–40 wt%), and the extent of distortion did not change with increasing amount of amorphous polymer in the mixtures. Again, this is dramatically different from the trend of the ring pattern observed in the PCL/PPhMA system, whose ring pattern becomes more regular with increasing PPhMA (5 wt% and beyond).

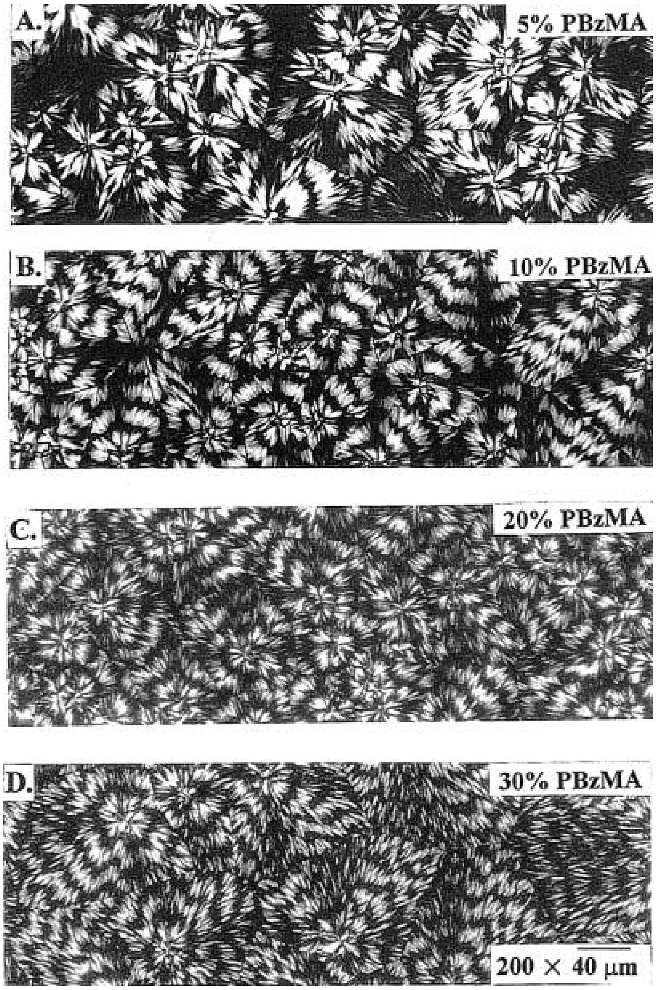


Fig. 2 Interference patterns in the PCL spherulites of PCL/poly(benzyl methacrylate) (*PBzMA*), where the PBzMA contents in the blends are **A** 5, **B** 10, **C** 20, and **D** 30 wt%, respectively (T_c = 40 °C)

As a result of ring distortion, the trends of the variation of the ring width and separation between successive rings were less obvious and more difficult to estimate accurately. Figure 3 shows the composition dependence of the ring-band width (Fig. 3A) and interring distance (Fig. 3B) measured in the PCL spherulites of PCL/PBzMA in comparison to those in the PCL/PPhMA blend system. The figure shows that at increasing concentrations of amorphous polymer in the PCL/polymer blends, the ring-band width and interring distance both decrease steadily. At the same composi-

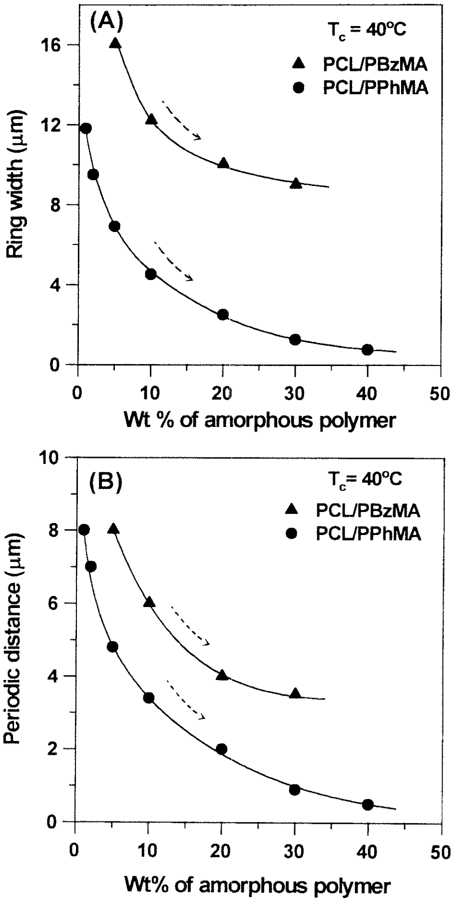


Fig. 3 A Composition dependence of the ring-band width and **B** interring distance measured in the PCL spherulites of PCL/PBzMA in comparison to those in the PCL/PPhMA blend system (T_c = 40 °C)

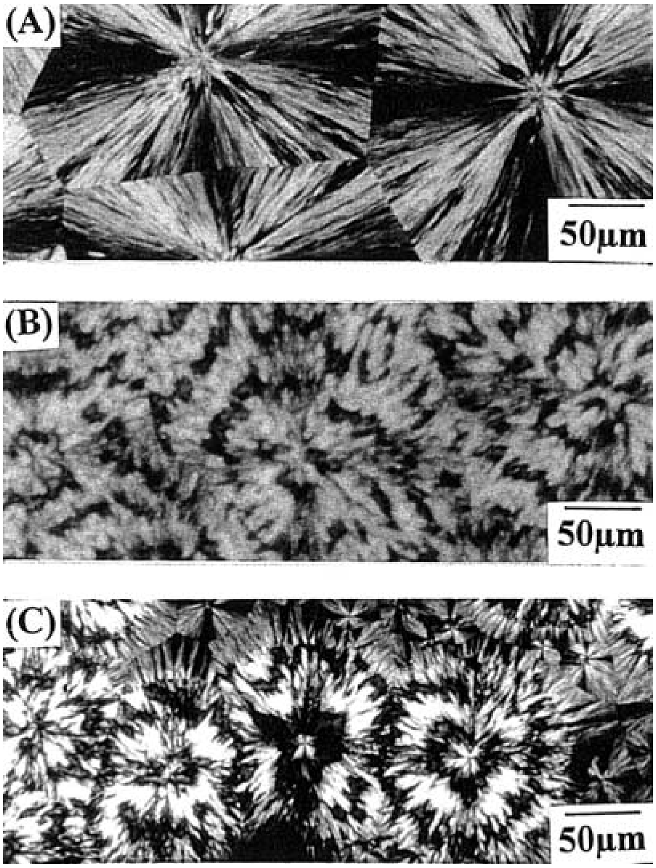


Fig. 4 Spherulites in neat PCL at **A** 45 °C, **B** 50 °C, 24 h, and **C** 55 °C, 96 h

tions, the ring-band width and the interring separation in the PCL/PPhMA blend are significantly smaller than in the PCL/PBzMA blend. In addition, the minimum concentration of the amorphous polymer in the PCL/polymer mixtures required for inducing ring bands is apparently different for different blend systems. The minimum concentration is 1 wt% (PPhMA) in the PCL/PPhMA, but it is significantly higher (5 wt% PBzMA) for the PCL/PBzMA system.

Ring bands in neat PCL

To understand the mechanism, the spherulites of neat PCL was carefully examined. Ring bands were not observed in neat PCL spherulites when crystallized at 45 °C. A comparison of spherulites in neat PCL when crystallized at different temperatures is shown in Fig. 4A. No ring bands were found in PCL when crystallized at 45 °C regardless of time duration. Crystallization at 45 °C was fast; however, to ensure that the morphology (absence of ring bands) remained the same regardless of time, the crystallization at 45 °C was maintained for a minimum of 12 h. However, for crystallization at higher temperatures, rings were found in the PCL spherulites. Figure 4B and C show that crystallization at 50 or 55 °C may result in a pattern of distorted ring bands. Crystallization at 50 or 55 °C was extremely slow; thus, isothermal crystallization for 1 day or 3 days was imposed, respectively, on the samples. Apparently, ring bands in neat PCL were possible only at higher temperatures (50 °C or above), but not at 45 °C or lower. This could be regarded as an indication of a small amount of low-molecular-weight PCL that melted as amorphous chains and acted as a self-diluent (plasticizer) interacting with the PCL spherulites to cause interference rings. At 45 °C, no low-molecular-weight PCL species melted; thus, no ring patterns were present in the spherulites even upon extended annealing.

Partial miscibility

Partial miscibility may also induce a slight extension of the ring bands; however, the ring pattern is distorted or diminishes at the range of compositions within which phase separation takes place. In this study, binary mixtures of PCL and poly(ethylene oxide) (PEO) were found to be partially miscible, with phase separation occurring in most mixtures of intermediate compositions. The PCL/PEO samples of several representative compositions were all crystallized at 45 °C. Figure 5 shows ring bands in PCL/PEO (90/10) mixtures, and the absence of ring bands in PCL/PEO (70/30) and (50/50) mixtures (Fig. 5B, C). For the samples of PCL blended with a small amount of PEO (less than 10 wt%), the PCL/PEO mixtures exhibited ringed spherulites when crystallized at 45 °C. At most intermediate PCL/PEO compositions (e.g., 80 > PCL > 20 wt%), no ring bands were observed in the PCL spherulites. Note that in addition to the absence of ring bands, the spherulites were also smeared by the presence of phase-separated domains and possibly by overlapping of PEO and PCL spherulites.

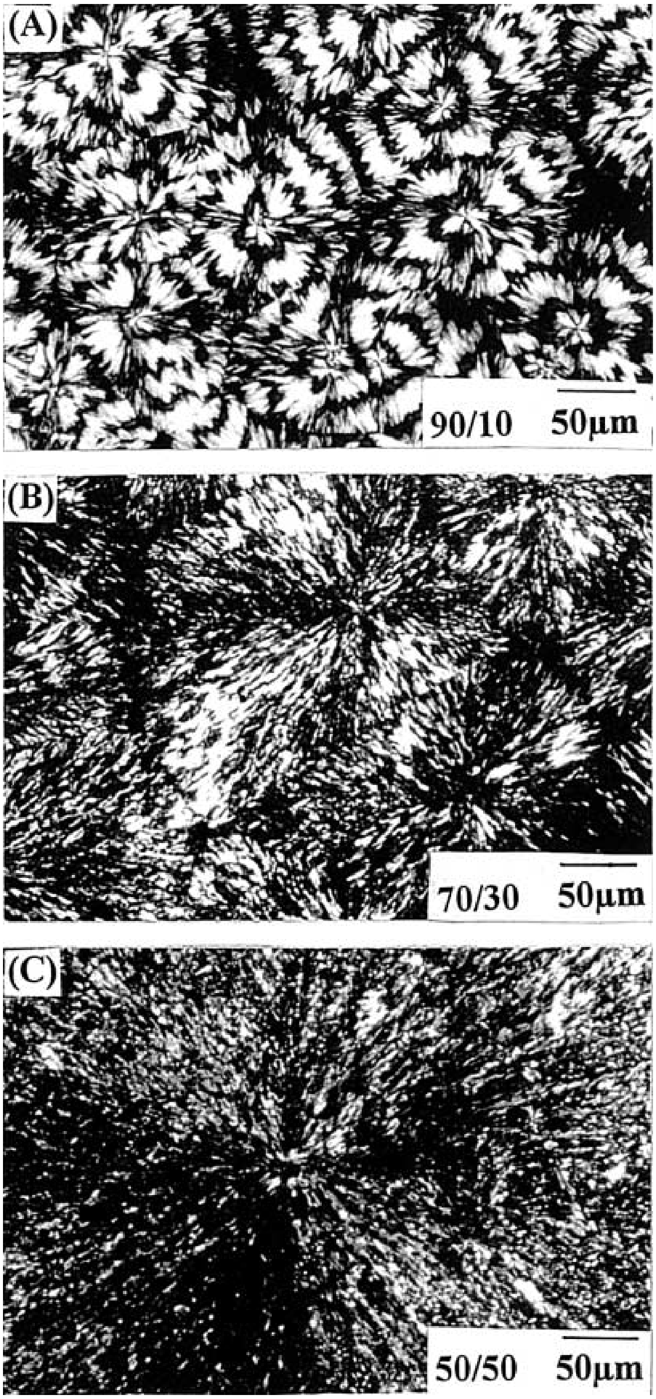


Fig. 5 Ring bands in **A** PCL/poly(ethylene oxide) (*PEO*) (90/10) **B** PCL/PEO (70/30) and **C** PCL/PEO (50/50) mixtures. **B** and **C** show no ring bands

Comparison of intermolecular interaction

The miscibility in both blend systems has been proven and the T_g-composition relationship for both blend systems has been found to deviate significantly from the Fox equation [1, 2]. The T_g-composition relationships are similar. Other thermal transitions were also compared. Negative deviation from linearity (suppression of crystallization) is usually observed for miscible blends owing to the disruption of the crystallizing polymer chains by the interacting amorphous polymer chains. For example, the crystallization of crystallizing PCL in miscible blends of PCL/PVC can be significantly disturbed (depressed), presumably by favorable molecular/segmental polar interactions [24]. A comparison of the heats of fusion (ΔH_f) as functions of the weight percent of amorphous polymers in the PCL/PBzMA and PCL/PPhMA blend samples is shown in Fig. 6. For uniform thermal treatment, all measurements were obtained from

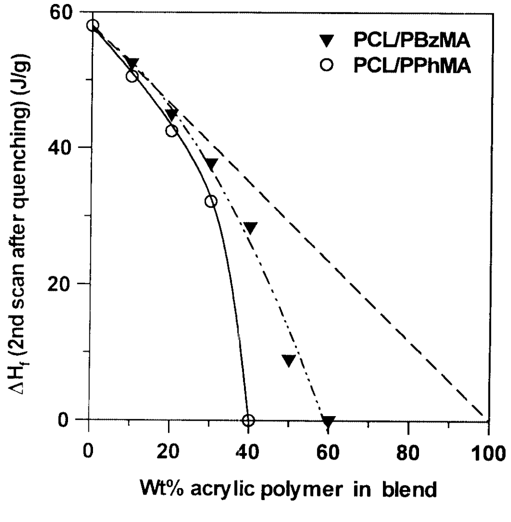


Fig. 6 Comparison of the depression effects on the heat of fusion (ΔH_f) plotted as functions of weight percent of the amorphous polymer in PCL/PBzMA and PCL/PPhMA samples

second DSC scans after quenching from melting. A negative deviation from linearity in the T_g-composition relationships is seen in both blend systems; however, the figure shows that crystallization suppression is more significant in the PCL/PPhMA than in PCL/PPzMA blend system. The dependence of the enthalpy of the transitions on blend composition can give some clues regarding intermolecular interactions. For noncompatible (immiscible) blend components, the measured heat of melting for the blend is usually linear with respect to composition, suggesting two separated, noninteracting domains (PCL versus amorphous acrylic polymer) in the blends containing two segregated phases.

Although the miscibility for both blend systems has been reported, the interaction between the binary polymers has yet to be investigated. The interaction strength is commonly estimated from the Flory–Huggins equation for the melting point depression, which can be expressed as follows [25]:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\left(\frac{RV_1}{\Delta H_f V_2}\right)\left[\frac{\ln(1-\phi_2)}{n_1} + \left(\frac{1}{n_2} - \frac{1}{n_1}\right)\phi_2 + \chi_{12}\phi_2^2\right] , \quad (1)$$

where T_m is the equilibrium melting point of the mixture, T_m^0 is the equilibrium melting point of the neat crystalline polymer, V_1 and V_2 are the molar volumes of the repeating unit of the crystalline and amorphous polymers, ΔH_f is the heat of fusion of the fully crystalline polymer (PCL), n_1 and n_2 are the degrees of polymerization of the two components, χ_{12} is the interaction parameter, and ϕ_2 is the volume fraction of the amorphous polymer. By ignoring the entropic term, the equation can be simplified to

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_1}{\Delta H_f V_2}\chi_{12}\phi_2^2 , \quad (2)$$

where the interaction parameter, χ_{12}, can be related to B by

$$\chi_{12} = \frac{BV_2}{RT_m} . \quad (3)$$

Alternatively, for a self-consistency check, Eq. (2) may be reexpressed as follows:

$$\left(\frac{1}{T_m} - \frac{1}{T_m^0}\right) \Big/ \phi_2 = -\frac{BV_1}{\Delta H_f}\left(\frac{\phi_2}{T_m}\right) . \quad (4)$$

Note that Eqs. (2) and (4) should, in principle, yield the same value if measurements on the equilibrium T_m for each composition were accurate; however, the extrapolation (Hoffman–Weeks plot) easily led to a certain degree of uncertainty. As a result, the data error and scattering for blend compositions may lead to a different result depending on which expression is used. Thus, plotting according to these two equations is a good way to check consistency. The interaction parameter and the interaction energy density for the miscible PCL/PPhMA and PCL/PBzMA blend systems were estimated using these two different forms (Eqs. 2, 4).

The equilibrium T_m of the neat PCL and PCL in the mixtures (blends) was first obtained from extrapolation of Hoffman–Weeks plots. The plots are numerous and, for simplicity, they are not shown here. From the plots, the values of the equilibrium T_m were obtained. The equilibrium melting temperature data were then used to estimate the interaction between PCL and the amorphous diluent polymers (PBzMA or PPhMA). Figure 7 shows a plot of the left-hand side of Eq. (2) versus ϕ_2^2, yielding a fairly consistent straight line for both PCL/PBzMA and PCL/PPhMA. The following constants were used [26]: ΔH_f = 3690 cal mol^{-1}, ρ_{PCL} = 1.143 g cm^{-3}, ρ_{PPhMA} = 1.21 g cm^{-3}, ρ_{PBzMA} = 1.179 g cm^{-3}, V_{PCL} = 105 cm^3 mol^{-1}, V_{PPhMA} = 131.3 cm^3 mol^{-1}, V_{PBzMA} = 149.3 cm^3 mol^{-1}. From the slope, the interaction parameter was obtained for PCL/PPhMA: $\chi_{PCL\text{-}PPhMA} = -0.40$ (or $B_{PCL\text{-}PPhMA} = -1.997$ cal cm^{-3}) at 60 °C. For PCL/PBzMA, the value of the parameter was found to be lower: $\chi_{PCL\text{-}PBzMA} = -0.22$ (or $B_{PCL\text{-}PBzMA} = -0.96$ cal cm^{-3}) at 60 °C. It would be instructive to compare these values for the miscible PCL/PBzMA and PCL/PPhMA systems to other classical miscible blend systems involving PCL. For example, the interaction parameters for other miscible PCL-blend systems (e.g., PCL/PVC [27] and PCL/SAN [28]) are $\chi_{PCL\text{-}PVC} = -0.32$ and $\chi_{PCL\text{-}SAN} = -0.34$, respectively. In addition, PCL is also known to be miscible with a few chlorinated methacrylic polymers, such as PCL/poly(chlorinated methyl methacrylate) (PCMMA) and PCL/poly(chlorinated ethyl methacrylate) (PCE-

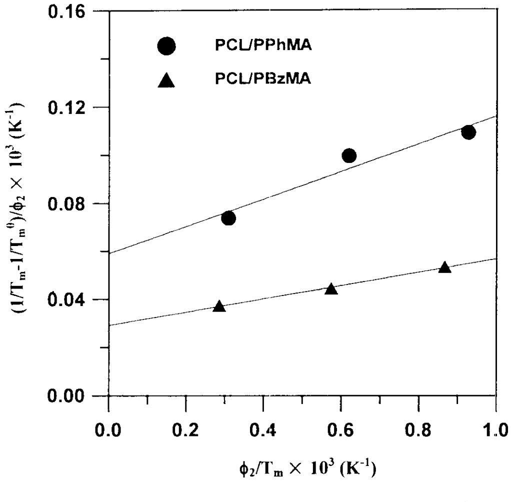


Fig. 7 Plot of the left-hand side of Eq. (2) versus ϕ_2^2, for PCL/PBzMA and PCL/PPhMA

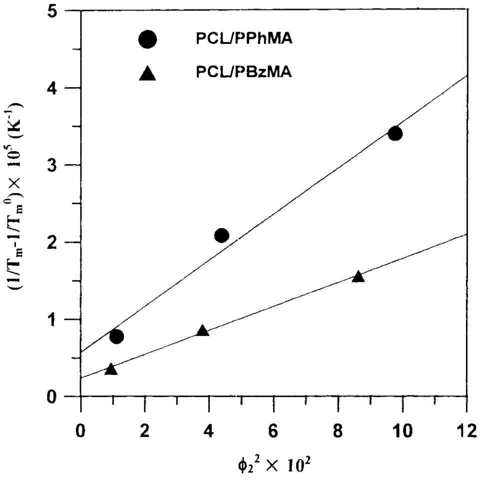


Fig. 8 Alternative plot (left-hand side of Eq. 4 versus ϕ_2/T_m) for estimating the interaction parameter for the PCL/PBzMA and PCL/PPhMA systems

Table 1 Interaction parameters for miscible poly (ε-caprolactone) (*PCL*)/poly(phenyl methacrylate) (*PPhMA*) and PCL/poly(benzyl methacrylate) (*PBzMA*) systems. χ and B are related by $\chi_{12} = (BV_2/RT_m)$

Equation used for estimation	PCL/PPhMA		PCL/PBzMA	
	B (cal cm^{-3})	χ_{12}	B (cal cm^{-3})	χ_{12}
Equation (2)	−3.487 (60 °C)	−0.697	−1.812 (60 °C)	−0.412
Equation (4)	−1.997	−0.399 (60 °C)	−0.961	−0.218 (60 °C)

MA) [4]. The reported interaction parameters are $\chi_{\text{PCL-PCMMA}} = -0.82$ and $\chi_{\text{PCL-PCEMA}} = -0.76$.

For consistency checks, Fig. 8 shows a plot of the left-hand side of Eq. (4) versus ϕ_2/T_m, yielding a fairly consistent straight line for both PCL/PBzMA and PCL/PPhMA. Again, the slope yielded the values of the interaction parameter. The values obtained from such plots were found to be different. In principle, these two different plotting methods should yield the same results. The difference suggests that data scattering owing to experimental error is present. To obtain a reasonable estimate, an average of the values from these two different plotting methods was used. As a summary, the interaction parameters for PCL/PPhMA and PCL/PBzMA resulting from both plotting methods are listed and compared in Table 1. The table shows that for miscible PCL/PBzMA and PCL/PPhMA blends, the interaction strength for the latter system is more significant.

In addition, the phase diagrams for these two miscible blends are different. For the miscible PCL/PPhMA of any composition, no lower critical solubility temperature (LCST) was found up to degradation. For the miscible PCL/PBzMA, however, the LCST curve is located at 230–245 °C for all compositions [1, 2]. Presumably, the fact that no LCST phenomenon was observed in the PCL/PPhMA system does not ensure the absence of phase separation at elevated temperatures; however, the LCST might be located at higher temperatures beyond experimental verification. The temperature location of the LCST can usually be taken as an indication of the extent of interaction strength in maintaining the phase stability. For example, in the miscible PBzMA/SAN (with 3.5–24.4 wt% AN) [29], the blends at the center of the window exhibit a much higher LCST than those at the margins of the miscibility window. A comparison of the LCST indicated that the PCL/PPhMA system tended to exhibit a better phase stability and greater interactions than PCL/PBzMA. This is in good qualitative agreement with the observation of the interaction parameter determined using the melting point depression technique.

Discussion on miscibility and ring pattern

All these facts indicate that the extent of chain intermixing in PCL/PBzMA is less than that in PCL/PPhMA, although both systems are classified as being "miscible" according to miscibility criteria. The ring bands are caused by a periodical twisting of the lamellae during crystallization. During crystallization, the amorphous component remains between the crystalline lamellae, thus causing twisting of these lamellae. If there is more amorphous material present, the crystalline lamellae twist more. This is the reason for the decrease in the interference bandwidth within the PCL spherulites in proportion to the increasing amount of amorphous polymer in PCL/PBzMA and PCL/PPhMA. The extent of chain intermixing is associated with the intimacy of the contacts between the two polymer chains. The interaction between PCL and PBzMA is less than that between PCL and PPhMA. Greater interaction strength means less segregation and more interchain mixing, thus leading to the amorphous polymer being more easily trapped between the crystalline lamellae during spherulite growth, causing more significant twisting/interference. This may be the reason for the fact that the rings of the spherulites in the PCL/PPhMA system are more distinct than in the PCL/PBzMA blends. In addition, more intimate contacts between chains also result in the appearance of a twisting band in the PCL spherulites at lower concentrations of the amorphous polymer (PPhMA).

It must be noted here that neat PCL might develop ring patterns when crystallized at 50 °C for long time (24 h); however, no rings were found if the samples were crystallized at 35, 40, or 45 °C. The reasons why rings occurred in PCL only at 50 °C, but not at lower temperatures about to be investigated. At 50 °C (near

T_m), some lower-molecular-weight PCL species melted and existed as amorphous chains during the growth of higher-molecular-weight PCL lamellae crystals. Thus, the low-molecular-weight PCL moieties can be viewed as a miscible "diluent" and as self-compatibilizing the amorphous region of PCL, leading to a ringed structure similar to that seen in the miscible PCL/PPhMA and PCL/PBzMA systems. The effect of low-molecular-weight PCL moieties on ring formation is similar to that of miscible PPhMA and PBzMA in PCL.

To summarize the comparison, the extinction rings in the PCL/PBzMA blend are not as distinct (owing to distortion) as those in the PCL/PPhMA blend system. In addition, the ring bands in the PCL/PBzMA system are less regular (more distorted) than those in PCL/PPhMA. The bands in the PCL/PBzMA system were found to be distorted into zig-zag rings, which occurred for all blend compositions (5–40 wt% PBzMA). The extent of ring distortion did not seem to change with blend composition. For the PCL/PPhMA system, the ring pattern was initially disordered only at low contents of PPhMA in the blends, but became more regular with increasing PPhMA content (5 wt% and beyond). Furthermore, the minimum contents of the amorphous diluent polymer in the blend required to induce ring bands in PCL/PBZMA were found to be higher. The rings are probably induced by periodic insertion of amorphous polymer chains within the PCL spherulites. This indicates that the phase behavior can strongly influence the pattern of the ring bands in the PCL spherulites in miscible PCL blends.

Reversibility of interference rings

As discussed earlier, the miscible PCL/PBzMA blend becomes phase-separated at elevated temperatures and exhibits a LCST at 220–240 °C, while the PCL/PPhMA system remains homogeneous and does not show a phase transition up to above 330–350 °C (degradation). For most miscible polymer blends, phase separation at the LCST, once taking place, is kinetically hindered from returning to homogeneity even upon cooling slowly; however, it has been reported that the LCST phase separation in the PCL/PBzMA blend is reversible to the original homogeneity by cooling slowly from above the LCST to ambient temperature [30]. That is, the temperature-induced phase separation can be fully restored to homogeneity similar to that of the originally unheated (as-cast) miscible PCL/PBzMA sample. By comparison, the PCL/PPhMA system does not phase-separate upon heating; thus, its reversibility of phase separation to homogeneity upon cooling cannot be discussed here. It was of interest to investigate whether or not the ring bands were a reversible phenomenon after cooling from phase separation at above the LCST.

As the miscible PCL/PPhMA system did not show a LCST transition within the experimentally accessible temperature range, this study focused on the miscible PCL/PBzMA system. Two sets of PCL/PBzMA samples (compositions in each set: 90/10, 80/20, and 70/30) were prepared and they were labeled as (1) slowly cooled/crystallized and (2) quenched and crystallized. One set (set 1) of the PCL/PBzMA blends were heated to 240 °C for 30 min to develop the maximum phase-separated domains, then slowly cooled from 240 °C at 2 °C/min to ambient temperature. The other set (set 2) of samples were heated to above the LCST (above 240 °C) to induce full phase separation and then directly quenched into liquid N_2, and then they were exposed to ambient temperature for crystallization. Set 1 samples returned

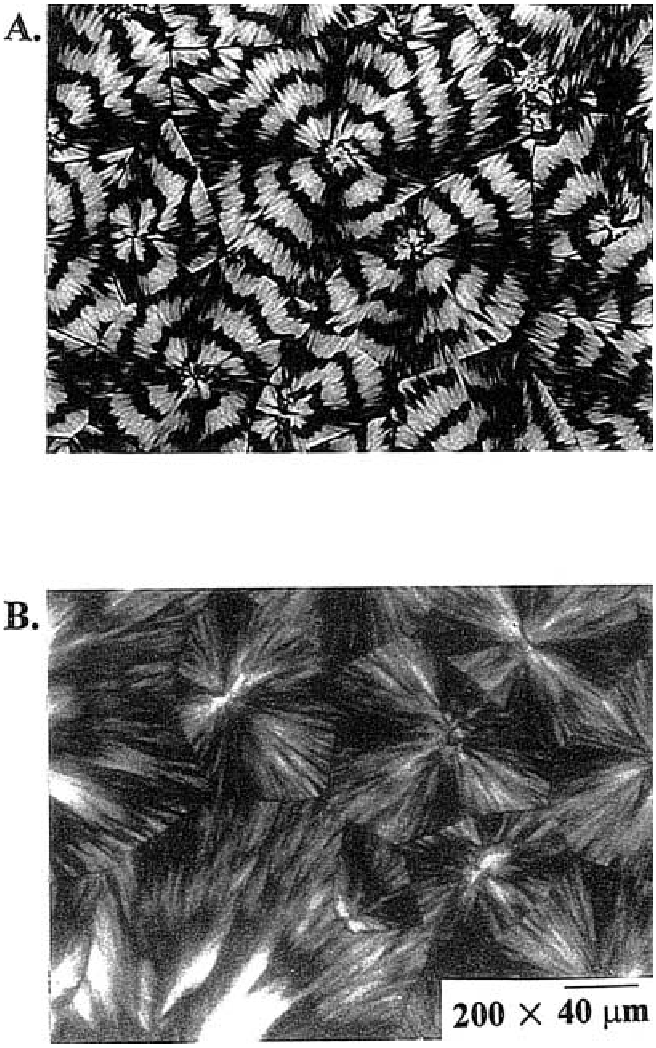


Fig. 9 Reversibility of the ring bands in the PCL/PBzMA blend (90/10): **A** slowly cooled, then crystallized samples (retaining miscibility state in amorphous region); **B** quenched, then crystallized samples (locked into a phase-separated state)

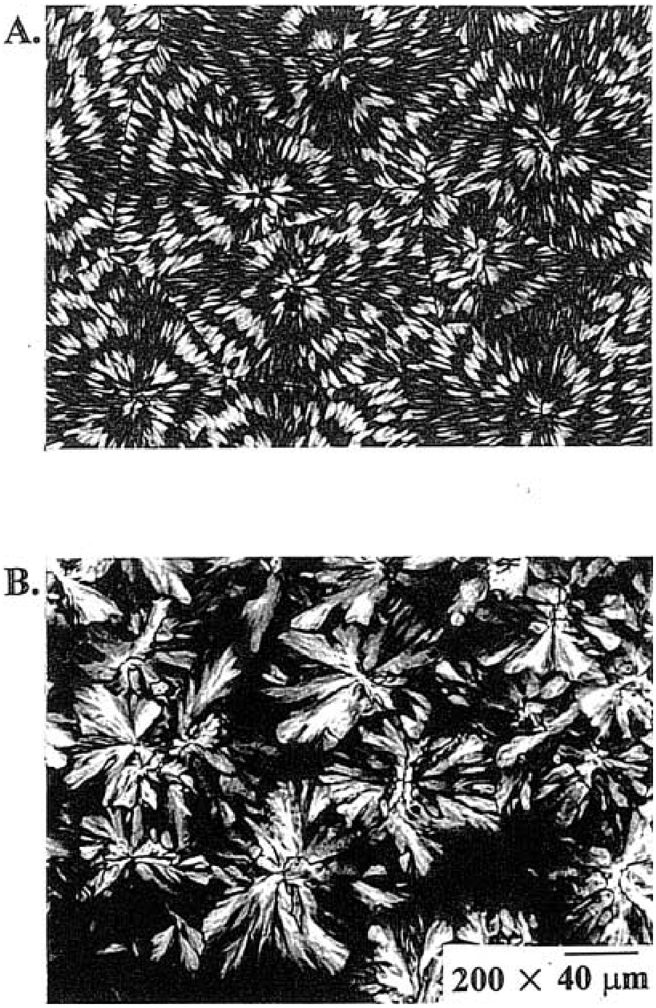


Fig. 10 Reversibility of the ring bands in PCL spherulites in the PCL/PBzMA blend (70/30): **A** slowly cooled from above the lower critical solubility temperatures (LCST) returning to phase homogeneity and subsequent ring bands; **B** quenched from above the LCST showing the absence of ring bands owing to a phase-separated state

to a homogeneous amorphous phase (except for the PCL spherulites), while set 2 samples were apparently frozen (preserved) in a phase-separated morphology. The PCL spherulites in the blend samples were observed using the polarized-light optical microscope.

Optical micrographs of the PCL spherulites in the PCL/PBzMA blend (90/10) are shown in Fig. 9. Figure 9A demonstrates that the ring bands reappeared after slow cooling from phase-separation above the LCST to ambient temperature. Apparently, slow cooling from the LCST restored the polymer melt to a homogeneous mixture. The growth fronts of PCL were probably interwined with PBzMA chains; thus, crystallization of PCL from this homogeneous mixture led to ring-laced spherulites. On the other hand, for the quenched/crystallized PCL/PBzMA sample (quenched from above the LCST), Fig. 9B shows that ring bands are mostly absent from the PCL spherulites if crystallization occurred in the phase-separated PCL/PBzMA blend. In the quenched blend, the morphology was frozen in a phase-separated state by quick cooling from above the LCST. The PCL crystallization took place in the segregated PCL domain of the quenched–cooled PCL/PBzMA blend; thus, the PCL spherulites which developed assumed the characteristic pattern of regular spherulites of neat PCL (i.e., no interference rings).

Similarly, other compositions of the PCL/PBzMA blend were investigated. Ringed PCL spherulites in the PCL/PBzMA blend (70/30) are shown in Fig. 10. Figure 10A demonstrates again the reversibility of the ring bands in the set 1 sample, while ring bands are not seen (Fig. 10B) in the quenched and phase-separated PCL/PBzMA blend (set 2). The sets of samples for the two other compositions (80/20 and 60/40) also exhibited similar behavior. For brevity, they are not all shown. In summary, not only the phase homogeneity in the amorphous phase is reversible, but also the ring bands in the spherulites are reversible in the PCL/PBzMA blend after a heating/cooling cycle between ambient homogeneity and the LCST phase separation.

Conclusion

Two miscible blend systems comprising PCL were studied in order to understand the mechanism of ring-band formation in the spherulites and the relationships between the ring-band pattern and the state of miscibility. The melting point depression technique was used for measuring the interaction parameters for PCL/PBzMA and PCL/PPhMA systems. χ for the PCL/PPhMA system assumes a larger negative value than χ for the PCL/PBzMA system, which indicates that PCL interacts more intensely (more intimately) with PPhMA than with PBzMA. Other thermal evidence (glass transition, crystallization suppression) suggested that the interaction strength is greater and that the state of intermixing is more intimate in PCL/PPhMA than in PCL/PBzMA. The evidence suggested that the state of mixing in PCL/PPhMA is better that in PCL/PBzMA and that the scale of segregation is less in PCL/PPhMA.

For the first time, interesting relationships between the state of chain intermixing and the ring-band pattern were demonstrated. In both miscible PCL/PBzMA and PCL/PPhMA blends, extinction rings were observed within the PCL spherulites. Furthermore, the width and the periodic distance of the ring decrease with increasing amorphous components (PPhMA and PBzMA) in PCL/acrylic polymer blends. In other words, the extinction rings are more populated with increasing amorphous component in the PCL/acrylic polymer blends. This fact suggests that at higher volume fractions of the amorphous polymer, a greater fraction of the amorphous polymer can be trapped between the spherulites to form interference rings. The rings also became increasingly irregular if the blends were crystallized at higher temperatures, where the PCL spherulites were larger and the growth rate was higher.

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