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ORIGINAL CONTRIBUTION

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Ringed spherulites in ternary polymer blends of poly(ϵ-caprolactone), poly(styrene-*co*-acrylonitrile), and polymethacrylate

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Abstract The relationship between ringed spherulite morphology, crystallization regimes/kinetics, and molecular interactions in miscible ternary blends of poly(ϵ-caprolactone) (PCL), poly(benzyl methacrylate) (PBzMA), and poly(styrene-*co*-acrylonitrile) (SAN) was investigated by using differential scanning calorimetry (DSC), polarized optical microscopy (POM), and wide-angle X-ray diffraction (WAXD). The interactions resulted in the deviation of both experimental and calculated T_gs and formation of the specific morphology of the spherulitic structure. Ring-banded spherulites were observed in the PCL/PBzMA/SAN ternary blends. The width of ring bands changed with the blend ratio and the crystallization temperature. Additionally, both composition and wt% of AN in the SAN copolymer had an apparent effect on the morphology of PCL spherulites. Both the crystallization structure of lamellae and molecular interactions greatly influenced the ring bands of PCL spherulites. Furthermore, by using the Flory–Huggins approximation, the depression of the melting point showed that interactions in the PCL/PBzMA/SAN-17 blend were greater than in the PCL/PBzMA/SAN-25 blend. In the ternary blends, the great molecular interactions between amorphous and crystalline polymer resulted in better homogeneity and a larger band period of the extinction rings in the PCL spherulites.

Keywords Ternary blends · Crystallization · Ring-banded spherulites

Introduction

Compatible polymer blends such as homopolymer/homopolymer [1, 2, 3, 4], homopolymer/copolymer [5, 6, 7, 8, 9, 10, 11, 12], and copolymer/copolymer [13, 14] have been widely studied. In a miscible polymer blend, the thermodynamic basis relies more on exothermic heat of mixing; however, the entropy contribution is quite minor in a high molecular weight polymer blend system. Therefore, it is necessary for the blend system to possess a compatible mixing which can result in a negative value of the change in Gibbs free energy in the process of mixing [15]. Based on thermodynamic considerations, miscibility and phase homogeneity in polymer blends can be enhanced because of chemical interactions, physical van der Waals forces, or hydrogen bonding. In a miscible binary system whose constituents involve at least one copolymer, it has been observed that miscibility occurs within a range of copolymer composition. This phenomenon is attributed to the so-called copolymer effect by some researchers [6].

In the compatible semicrystalline/amorphous polymer blend, the addition of an amorphous polymer to a semicrystalline polymer causes an apparent effect on the thermodynamic and kinetic parameters governing crystallization [9, 10, 11, 16, 17, 18, 19]. Some semicrystalline polymer systems are capable of showing the extinction rings of regular periodicity in spherulites under specific conditions [3, 4, 5, 6, 7, 8, 9, 19, 20, 21, 22]. The polymers that exhibit unusual extinction rings are present in these semicrystalline polymers with constituents of several main types, namely, polyethylene (PE) [20], polypropylene (PP) [20], poly(vinylidene difluoride) (PVF_2) [3, 4, 5], and some polyesters or polyamides and their miscible blends [3, 4, 21, 22]. In the polymer blends, some of the most notable examples are poly(trimethylene terephthalate) (PTT) [21], PVF_2/poly(methyl methacrylate) (PMMA) [5], poly(ϵ-caprolactone) (PCL)/PVC [19], PCL/PBzMA [6, 9], PCL/SAN-x [7, 8], and PVF_2/PMMA/PCL [3, 4, 22]. Keith et al. [5, 20] proposed that the basic mechanism leading to the ring pattern should be axial twisting in lamellae under the influence of surface stress and of cooperative arrangement of the twisted crystallites; however, an advanced mechanism leading to the ring-banded spherulite has not been clarified yet. Polymer blends containing a crystallizable component with a lower melting point (e.g., PCL) have attracted much research [9, 10, 11, 16, 17, 19]. The presence of an amorphous component strongly influences the crystallization behavior of PCL; therefore, the morphology of a linear aliphatic polyester and the spherulite structure of PCL depend on the state of chain intermixing of the polymer blend. In a compatible main chain/side chain carbonyl-containing polymer blend, the relationship between miscibility, interaction, and crystallization in both PCL with poly(benzyl methacrylate) (PBzMA) and PCL with poly(phenyl methacrylate) (PPhMA) has been studied in detail by Woo et al. [21]. Thermal properties and morphology of the poly(ϵ-caprolactone) and poly(vinyl methyl ether) blend system depend not only on composition but also on flexure of amorphous segments [17]. The spherulite structure in the compatible mixture has been hindered by the amorphous component, because the amorphous phase was locally depleted of PCL in the growing crystallites. Moreover, the difference between the crystallization temperature (T_c) of PCL, and the glass transition temperature (T_g) of the amorphous phase has also affected the crystallization process. The semicrystalline/amorphous polymer blend not only has a higher T_g than an amorphous phase but also induces a defect of crystallization. In a binary homopolymer/copolymer blend, crystallization in a mixture of PCL and poly(styrene-*co*-acrylonitrile) (SAN) has been investigated as a function of composition [8, 9, 10, 11], wt% of AN content in SAN copolymer [8, 10, 11], and the crystallization temperature [8, 11]. PCL is miscible with SAN within a miscibility window ranging from a copolymer content of 8 to 28 wt% of acrylonitrile in SAN [12]. Within the miscibility window, the growing of spherulites is affected by the interaction strength and the surface free energy for the formation of secondary crystal nuclei. In the crystalline and noncrystalline blends, the depression in spherulitic growth kinetics has been attributed to chain mobility, free energy of nucleation, and competition between the advancing spherulitic front of a crystallizable polymer and diffusion of an amorphous into interlamellar and interfibrillar regions [6, 8, 11]. By analogy, the relationship between spherulite structure and molecular interactions could be an interesting subject in the miscible ternary semicrystalline/compatible blend.

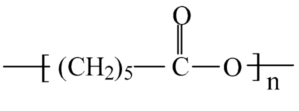
This paper continues from an earlier report [11] on findings of ternary miscibility of the blend system: here we examine and discuss the relationships between the ternary miscibility and effects on ringed spherulites. This work extends the earlier investigation into the crystallization, spherulite structure/morphology, and interlamellar ring bands of PCL in the ternary PCL/PBzMA/SAN-x blends. In this study, the crystallization and melting behavior of these blends were isothermally crystallized at different temperatures. The effects of the AN contents in SAN on crystallization behavior, spherulite structure, and molecular interactions were thoroughly examined.

Experimental

Materials and preparation

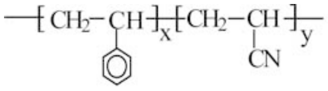
Poly(ϵ-caprolactone) (PCL) was obtained from Aldrich Chemical, Inc. (USA). It has a molecular weight (M_w) of 65,000 g mol^{-1}, $T_g = -70°C$, and $T_m = 60°C$, and was used as received without purification. Poly(benzyl methacrylate) (PBzMA) with manufacturer's data of $M_w = 51{,}000$ g mol^{-1}, polydispersity index (PI) = 2.67 (GPC), and $T_g = 54$–$60°C$ was purchased from Scientific Polymers Product, Inc. (USA). Characterization in our laboratory gave $M_w = 54{,}000$ g mol^{-1} and PI = 2.27 by GPC, and $T_g = 57.2°C$ (onset value, by DSC) for the PBzMA. Poly(styrene-*co*-acrylonitrile)s (SANs) with three compositions of acrylonitrile (AN) contents were used in this study and were prepared in the laboratory by free-radical bulk copolymerization of styrene and acrylonitrile at 60°C using 10^{-3} M azobis(isobutyronitrile) (AIBN) as initiator. Monomeric styrene, acrylonitrile, and AIBN were purified and dried before the synthesis of SAN copolymers. The synthesis and characterization data of the SAN polymers were the same as those listed in earlier reports [6, 11].

The structure of the PCL, SAN-x, and PBzMA are given below:

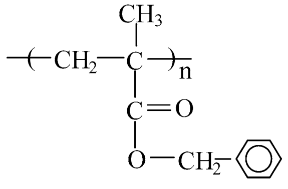


$$-\!\left[(CH_2)_5-\overset{\overset{O}{\|}}{C}-O \right]_n-$$

Poly(ε-caprolactone)



Poly(styrene-co-acrylonitrile)



Poly(benzyl methacrylate)

Blend preparation

Blend samples of ternary polymers were prepared by using solution blending and film casting. We knew from a previous study [11] that the choice of solvents and temperature of casting strongly influence the apparent phase behavior of polymer mixture. Tetrahydrofuran (THF) was found to yield the best result and was used for preparing all samples of blend systems investigated in this study. The film-casting temperature was at 45°C. The temperature of casting might lead to morphology with a homogeneous phase. The polymers were first weighed and dissolved into the THF solvent with continuous stirring. Subsequently, the resulting polymer solution was poured into a flat mold kept at 45°C. The solvent (THF) in solution-blended polymer samples was first vaporized by convection under a hood at the temperature of 45°C, followed by final residual solvent removal in a vacuum oven for 72 h at 120°C.

Apparatus

A polarized-light microscope (Nikon Optiphot-2, POL) was used for observation of morphology/phase structure. The blend cast-films were placed on the microscopic heating stage (Linkam THMS-600 with TP-92 temperature programmer) for observation at temperatures higher than ambient. The blends were first cast as thin films on glass slides and dried properly in a temperature-controlled oven before they were examined using the optical microscope.

The glass transition temperatures and other thermal transitions of ternary blend samples were measured with a differential scanning calorimeter (Perkin–Elmer DSC-7) equipped with a mechanical intracoller and a computer for data acquisition/analysis. Unless otherwise specified, all T_g measurements were performed at a scan rate of 20°C min^{-1} on the second scanning after quenching from above the estimated T_gs. T_g in this study was taken as the onset of the transition in the DSC thermograms.

For wide-angle X-ray diffraction (WAXD) experiments, the same crystallization/annealing conditions as described in the polarized morphology section were carried out on ternary blends that had been thermally treated in the heating stage. It was critical to ensure that the samples for POM and WAXD were treated exactly with the same temperature accuracies and thermal histories for comparisons. A Shimadzu/XRD-6000 with a copper K_α radiation ($\lambda = 0.1542$ nm) was used for the WAXD measurements. The scanning 2θ angle covered a range between 5° and 35° with a step scanning of 0.02°.

Table 1 The glass transition temperature of the PCL/PBzMA/SAN-x ternary blend as a function of composition

Composition	Glass transition temperature (°C)		
	$x = 9$ wt%	17 wt%	25 wt%
I. (X/Y/Y)			
100/0/0	−71.9	−71.9	−71.9
90/5/5	–*	−70.5	−69.5
80/10/10	–*	−65.4	−68.2
70/15/15	–*	−64.1	−64.6
60/20/20	–*	−56.3	−58.5
50/25/25	–*	−48.0	−53.6
40/30/30	–*	−32.6	−25.0
30/35/35	–*	−6.9	5.0
20/40/40	23.6	29.5	30.2
10/45/45	51.8	53.4	51.0
0/50/50	–	82.0	81.0
II. (X/Y/X)			
0/100/0	54.3	54.3	54.3
5/90/5	42.2	45.2	45.7
10/80/10	–	35.8	27.1
15/70/15	25.0	20.6	18.9
20/60/20	–	12.5	10.3
25/50/25	6.3	8.0	5.6
30/40/30	–*	−5.6	0.0
40/20/40	–*	−19.4	−12.9
45/10/45	–*	−26.3	−20.1
50/0/50	–*	−35.0	−34.0
III. (X/X/Y)			
0/0/100	107.7	109.5	105.0
5/5/90	78.6	75.0	82.7
10/10/80	65.9	64.4	63.4
15/15/70	58.2	56.8	54.3
20/20/60	–*	41.1	40.6
25/25/50	–*	30.5	22.5
50/50/0	–*	−43.8	−45.0

*The compositions of the PCL/PBzMA/SAN-9 ternary blends are phase separation as the cast film

Results and discussion

Thermal transition for the ternary blend

To insure the original thermal properties of the ternary PCL/PBzMA/SAN blend, sample preparation and differential scanning calorimeter (DSC) characterization were performed in a uniform process. To achieve a uniform thermal history, all thermograms shown in the study are the results of second runs after quenching at a temperature just above the glass transition temperature (T_g). Table 1 shows the glass transition temperature of the PCL/PBzMA/SAN-x ternary blend as a function of composition. The serial I, II, and III composition is systematic variation of the three components in the ternary blends. The DSC result revealed that the ternary PCL/PBzMA/SAN-x blend was not totally miscible, whereas the poly(styrene-*co*-acrylonitrile)s with lower wt% of acrylonitrile (AN) content blend samples showed two T_gs corresponding to either a heterogeneous phase or partial miscibility. In the ternary PCL/PBzMA/SAN-9 blend, most of the blend samples were the heterogeneous phase except that the low-PCL composition was homogeneous. In addition, the poly(styrene-*co*-acrylonitrile)s with higher wt% of AN content (e.g., 17 wt% and 25 wt%) showed the homogeneous thermal behavior with a single T_g for the series of ternary PCL/PBzMA/SAN blend systems. In the previous study [11], the trend of variation of phase separation or cloud transition for the miscible ternary PCL/PBzMA/SAN blends also exhibited the window behavior with respect to wt% of AN content in SAN. Apparently, homogeneity behavior for the ternary PCL/PBzMA/SAN-x blends varied due to the different molecular interactions in the same composition. In the ternary PCL/PBzMA/SAN-x blends, the component of PBzMA was almost independent of the compatible behavior in the same composition with different AN contents in SAN-x. This homogeneous phase has been attributed to the mutual repulsion among the constituents of the SAN prevailing over other interactions, and the repulsion of the higher AN content in SAN-x leads to miscibility in the ternary blend.

Figure 1 shows the DSC trace for the ternary PCL/PBzMA/SAN blends, whose samples were obtained by solvent casting. In the ternary blend samples, poly(styrene-*co*-acrylonitrile)s with an AN content of 25 wt% revealed a single T_g and had a homogeneous phase in a wide range of composition. Additionally, the T_g of the ternary blends increased with the addition of an amorphous component (PBzMA and SAN). In the ternary blend samples containing higher PCL contents (>60 wt%), crystallization and melting transition occurring in the formation of the crystalline PCL domain were evident in the DSC thermogram. In the ternary PCL/PBzMA/SAN-25 blend, the melting peak was independent of the blend ratio but the crystallization temperature (T_c) was influenced by the composition of the blend. The experimental method for the polymer blends with PCL as the semicrystalline component has an apparent effect on the melting behavior of crystallization [7, 18, 23]. The DSC thermograms of PCL/chlorinated polyethylene (CPE), PCL/phenoxy, and PCL/poly(styrene-*co*-maleic anhydride) (SMA) blends were prepared by the dissolution/coprecipitation method and those of the PCL/SAN blends prepared by the melting method had shown two melting endotherms in the DSC trace [23]. The double-melting behavior occurred because the formation of thin crystalline lamellae recrystallized and then melted. It was also found that the formation of thin crystalline lamellae was located between thicker ones in forming the spherulites of PCL [18]. Interestingly, the solution-casting blend samples showed the single-melting behavior in the binary PCL/SAN [7] and PCL/PBzMA [9] blends. In the PCL-rich composition (PCL > 90 wt%), there was a close double-melting transition in the DSC thermograms. In the ternary PCL/PBzMA/SAN-25 blends prepared by the solution casting, recrystallization of the original lamellae and melting of the recrystallized PCL influenced the double-melting

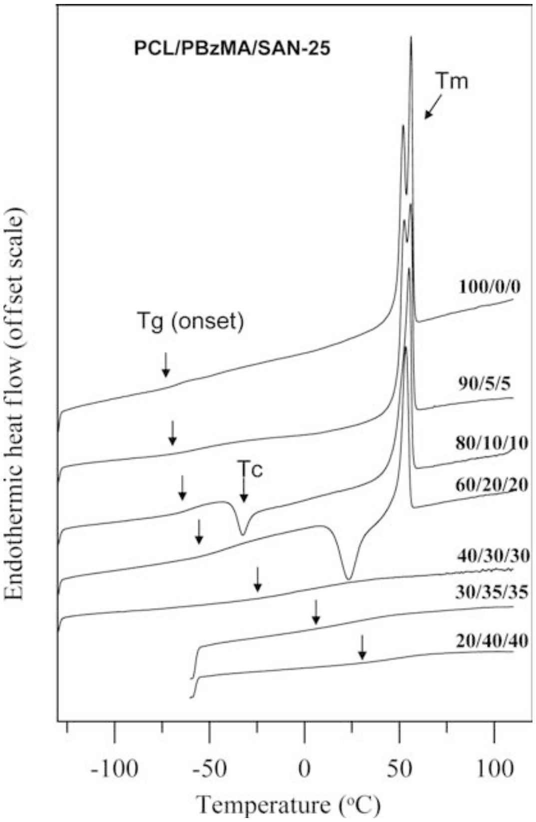


Fig. 1 DSC thermograms of the PCL/PBzMA/SAN-25 ternary blends heated at 20°C min^{-1}

behavior. In the DSC thermograms, the ternary blends with PCL/PBzMA/SAN-25 = 80/10/10 and 60/20/20 compositions showed an exothermic peak of crystallization of PCL in the DSC trace at a scan rate of 20°C min^{-1}. The crystallization temperature (T_c) was dependent on the composition of the blend in the scanning process. The T_c increased with the greater fraction of amorphous materials present in the miscible blend because more amorphous polymer chains would get into the crystalline lamellae and hinder the mobility of crystallizable molecular PCL. On the other hand, when the content of an amorphous component (PBzMA and SAN) with a high T_g increased, the crystallizable component (PCL) needed a higher temperature to overcome the energy barrier and to reorganize the regular molecular arrangement in the blend samples. In the ternary blend samples containing higher PCL contents, crystallization and melting transitions in the crystalline PCL domain were evident. All the thermograms clearly show that there is only one T_g for each composition, and the only T_g exists in the composition. The DSC thermal evidence has clearly shown that this is a miscible ternary blend sample.

Figure 2 shows the thermal transition temperatures for the ternary PCL/PBzMA/SAN-17 blends within a wide range of composition (the relative PBzMA/SAN-17 contents were kept constant at 1/1). Similarly, the compatible ternary PCL/PBzMA/SAN-17 blends had the same thermal transition like that in the blend with an AN content of 25 wt% in the SAN copolymer. The dilution effect and the stereo-hindered effect affected the crystallization behavior of the lower AN content in SAN in the ternary blends. Based on the thermodynamics theory of the glass transition temperature, Fox et al. [15] derived relationships to predict the T_g composition dependent on binary mixtures of miscible polymers. By means of mathematics and assumptions, the glass transition temperature can be derived for a miscible binary blend. If $\Delta C_p T_g = \text{constant}$, the Fox equation becomes

$$\frac{1}{T_g} = \frac{\omega_1}{T_{g1}} + \frac{\omega_2}{T_{g2}} \tag{1}$$

where T_g represents the glass transition temperature of the miscible blend. ω_1, ω_2, T_{g1}, and T_{g2} represent the weight fraction and the glass transition temperature, respectively, of an individual component for components 1 and 2. In the ternary component (PCL/PBzMA/SAN-17) blend, a generalized relationship may be proposed for the T_g composition relationship:

$$\frac{1}{T_g} = \frac{\omega_{(\mathrm{PBzMA+SAN-17})}}{T_{g,(\mathrm{PBzMA+SAN-17})}} + \frac{\omega_{\mathrm{PCL}}}{T_{g,\mathrm{PCL}}} \tag{2}$$

where $\omega_{(\mathrm{PBzMA+SAN\text{-}17})}$ and $T_{g,(\mathrm{PBzMA+SAN\text{-}17})}$ represent the weight fraction and the glass transition temperature, respectively, of a miscible binary blend in which relative PBzMA/SAN-17 contents are kept constant at 1/1. The calculated result (Fig. 2) showed that the Fox equation apparently deviated significantly from the ternary T_g data for most of the ternary blend composition. The deviation between the experimental and calculated T_g values for the miscible ternary blend may be attributed to the copolymer effect, whose mutual repulsion prevails over other interactions and whose repulsion in the copolymer leads to miscibility in the homopolymer/copolymer pair [6].

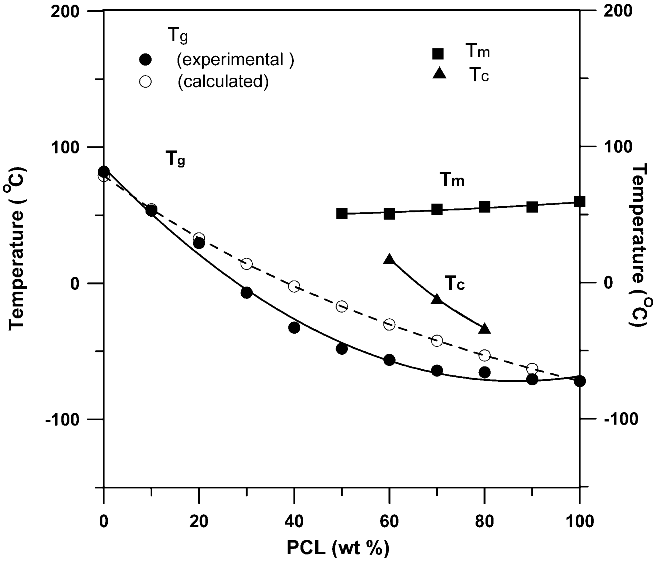


Fig. 2 The thermal transition temperature of the PCL/PBzMA/SAN-17 ternary blends heated at 20°C min^{-1}

Ring-banded spherulite structure

The isothermal crystallization process of the PCL/PBzMA/SAN ternary blend was investigated by using a hot stage equipped with a polarized optical microscope. The blend cast-films were placed on the microscopic heating stage and were melted, and then the crystallization of PCL in the blend samples disappeared at 80°C. The crystallization behavior of the clear PCL/PBzMA/SAN-x ternary blend was used for observation at the temperatures higher than ambient. In the PCL/PBzMA/SAN-x ternary blends, the ring bands of interference patterns were observed at the temperatures of crystallization when the copolymer contents in SAN was 17 and 25 wt% of AN. Figure 3 shows the spherulite structure of PCL/PBzMA/SAN-17 ternary blends crystallized at 45°C for 8 h. In the polarized micrographs, the bright ring band represents the crystallization of PCL spherulites, and the dark ring band represent the rich amorphous (PBzMA and SAN) phase in the ternary blends. An interference band characterizes spherulite patterns

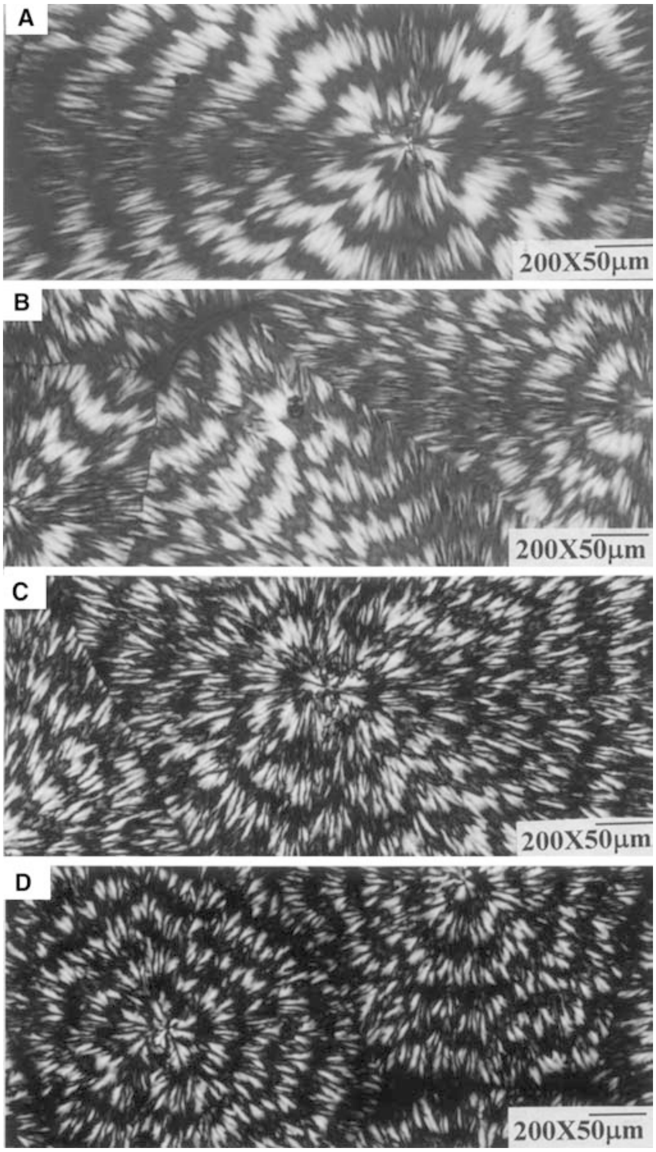


Fig. 3 Ring patterns of the PCL/PBzMA/SAN-17 ternary blends whose contents of PCL (wt%) are from *top* to *bottom* 90, 80, 70, and 60 ($T_c = 45°C$)

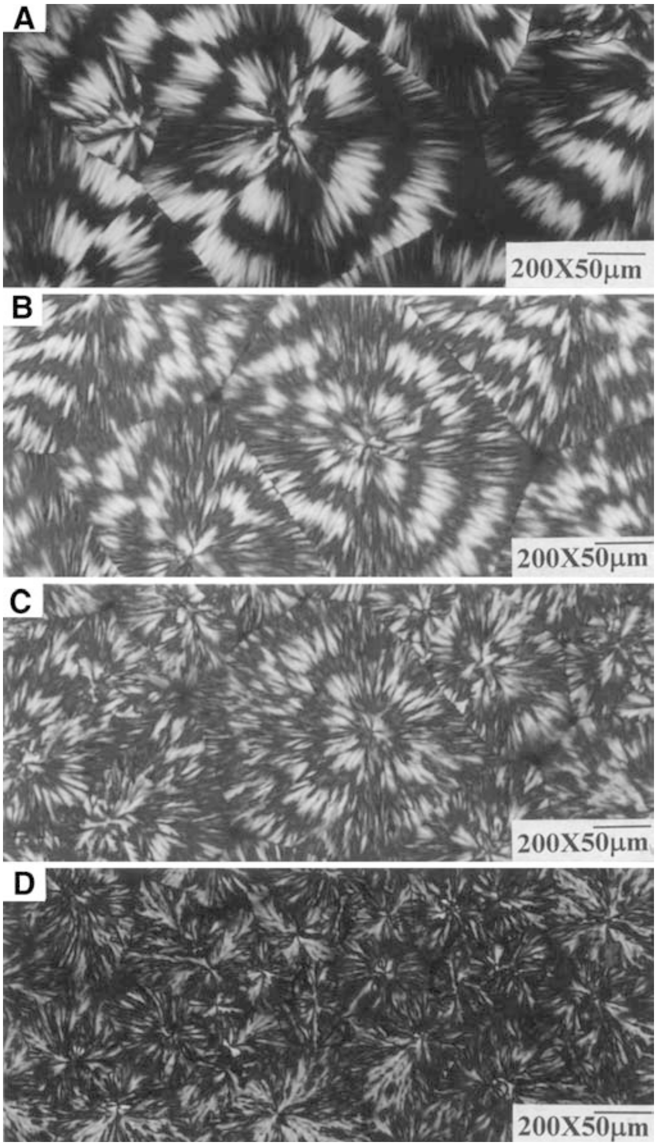


Fig. 4 Ring patterns of the PCL/PBzMA/SAN-25 ternary blends in which the contents of PCL (wt%) are from *top* to *bottom* 90, 80, 70, and 60 ($T_c = 45°C$)

with peculiar periodicity. The spherulite in the pure PCL had a Maltese cross appearance [9, 19], but the ring-banded spherulite structure could be observed in the blends with PCL contents of 60–90 wt%. Apparently, the spherulite of PCL has a distinct pattern of extinction rings instead of the Maltese cross in the ternary blends. In the blend with the PCL component, the extinction ring is ascribed to the twist of the lamella structure of PCL [5, 20].

At a temperature of isothermal crystallization, it was found that the more amorphous contents the blend contained, the smaller the ring width between successive concentric rings became. The gradual decrease of ring-band width with the increasing amount of amorphous content is due to the periodical twisting of the lamellae during crystallization. In the growing spherulite of PCL, owing to miscibility and intimate contact between the polymer chains, the amorphous component was easily trapped in the crystalline lamellae of PCL, thus causing twisting of the lamellae. When the ternary blends contained a greater fraction of amorphous material, more amorphous polymer chains would get into the PCL spherulites leading to more discontinuous bright ring bands and to the smaller width of those bands in the crystalline lamellae. Figure 3 (bottom) shows the ternary PCL/PBzMA/SAN-17 (60/20/20) blend with the most loosely arranged ring-banded spherulites of PCL in the blends. Apparently, the interlamellar domain is populated with PCL amorphous chains intermingled with an amorphous as well as miscible PBzMA and SAN chains in the figure. During the latter stages of crystallization, the spherulites impinged on their neighbors according to observations from POM. In the ternary blends, the boundaries between spherulites became straight because the spherulites of PCL nucleated simultaneously at the crystallization temperature ($T_c = 45°C$) [15].

Similarly, the morphology of the spherulites of the PCL/PBzMA/SAN-25 blend had an extinction ring like that of the PCL/PBzMA /SAN-17 ternary blend. After being examined, the ring patterns of the miscible PCL/PBzMA/SAN-25 blend system with higher wt% of AN contents in SAN copolymer were compared with those of the miscible PCL/PBzMA/SAN-17 system. Figure 4 shows the interference ring patterns of PCL spherulites in the PCL/PBzMA/SAN-25 blend sample with PCL contents of 70–90 wt% (Fig. 4, top three), and the radial spherulite of PCL found in the blend with PCL content of 60 wt% (Fig. 4, bottom) crystallized at 45°C. The ring bands and the spherulite of PCL in the PCL/PBzMA/SAN-25 blend were irregular and smaller in comparison with those in the PCL/PBzMA/SAN-17 blend. In the composition investigated (PCL = 60–90 wt%), the extent of distortion of ring patterns changed with the increasing amount of an amorphous polymer in the PCL/PBzMA/SAN-25 blends. The bright ring bands in the PCL/PBzMA/SAN-25 blend samples are rough and discontinuous due to the amorphous components trapped among different crystalline lamellae of PCL. The sparse ring-banded spherulite of PCL is attributed to the reduction in chain mobility which results from an increase of T_g, the dilution of the crystallizable component at the growth front, changes in free energy of nucleation from specific interactions, and competition between the advancing spherulitic front and the diffusion of the noncrystallizable component into interlamellar and interfibrillar regions [8]. Interestingly, the spherulite morphology in the ternary blend with a PCL content 60 wt% is dramatically different from that observed in the PCL/PBzMA/SAN-25 system. It could be concluded that bright spherulites of PCL result from the low-miscible molecule or from the micro-phase separation in the blend with lower wt% of PCL contents in the ternary system. Obviously, the morphology of spherulites of PCL depends not only on the components, the ratio of composition, and wt% of AN content in the copolymer, but also on the molecular interactions among the components.

Figure 5 shows the composition dependence of the band period of the extinction rings in the PCL spherulites in the PCL/PBzMA/SA-17 blends (Fig. 5, top) in comparison with those in the PCL/PBzMA/SAN-25 (Fig. 5, bottom) blends. In estimating interference bands, the trends of the variation of the period of the successive ring bands were calculated. In the ternary blends, the period of interference rings decreased with the decreasing amount of PCL within the temperature range 35–50°C. In the ternary blends, the values of the period of the interference ring, however, increased apparently when the gradual increasing of the PCL content approached to 90 wt% at a high crystallization temperature ($T_c > 45°C$). The spherulites of PCL in the

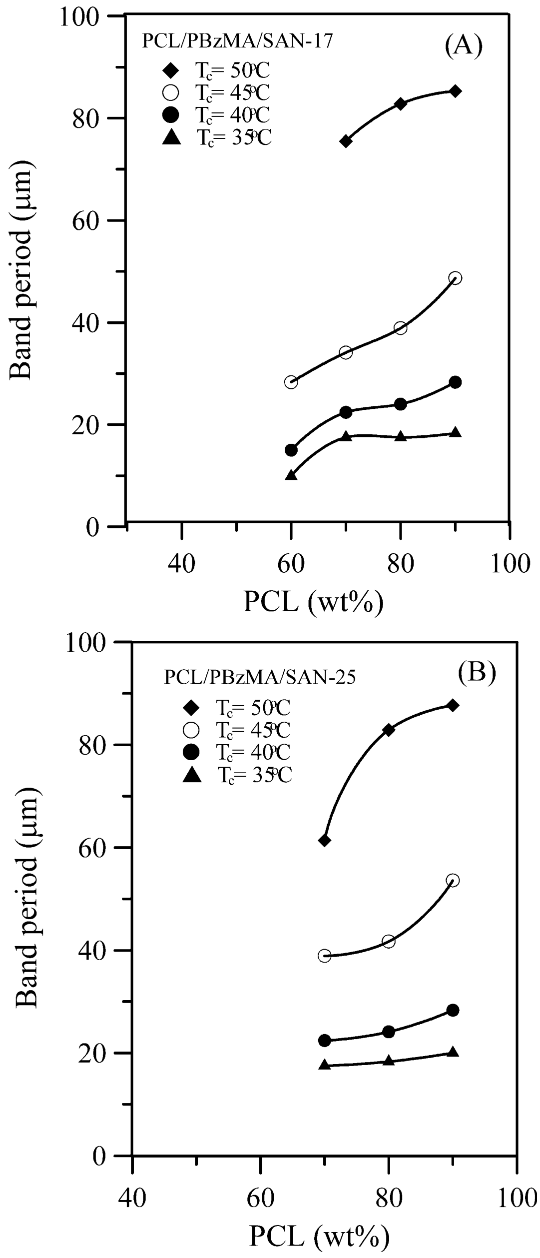


Fig. 5 Comparison between band periods of the PCL/PBzMA/SAN-17 blends (*top*) and those of the PCL/PBzMA/SAN-25 blends (*bottom*) at different crystallization temperatures

blends seemed to possess a maximum value at a high T_c. When the spherulites at the low crystallization temperature ($T_c = 35$°C) were in contrast with those at the high T_c ($T_c = 50$°C), both of their band periods increased slowly as the PCL content approached 70 wt% in the PCL/PBzMA/SAN-x ternary blends. In the figures, the interference rings of PCL in the PCL/PBzMA/SAN-17 blends are significantly smaller than those in the PCL/PBzMA/SAN-25 blends, and the ring-banded period increases with the elevation of the crystallization temperature and with the increase of wt% of PCL in the ternary blends. Owing to the observations from POM, the mechanism of inducing ring bands depended on the crystallization temperature (T_c), concentration of PCL, and wt% of AN in the SAN copolymer in the ternary blends. This suggests that in the POM morphology of the ternary blends, the size of PCL spherulites with interference rings is in proportion to the amount of PCL in the ternary blends. The increase of the amorphous polymer chain can cause more seeds of nucleation, which produces the simultaneous nucleation of crystallization. Consequently, smaller PCL spherulites are found. Additionally, in the same composition, the blends with 17 wt% of AN in the SAN copolymer have a larger PCL spherulite than those with 25 wt% of AN in the SAN copolymer. This phenomenon can be due to the effect of the repulsion force of the SAN copolymer, according to which the molecular interaction becomes strong between the amorphous and the crystallizable polymer chain in the PCL/PBzMA/SAN-17 miscible blends. Therefore, it could be concluded the amorphous component in the homogeneous blends may act as stereo-hindrance to the nucleation of PCL segments. In the blends, the molecular interaction among polymers not only can prompt miscibility of the blends but also can extend the time of nucleation of PCL crystallization and can reduce the number of seeds. That could explain why large PCL spherulites are found in the ternary blends. Apparently, not only the composition but also the wt% of AN in the SAN copolymer with the different repulsion forces among molecules have an influence on the nucleation rate of crystallization and on the morphology of PCL spherulites. This depression of the rate of nucleation is attributed to the dilution effect on the crystallizable components at the growth front of the PCL spherulites. In the previous study [11], cloud point data showed that owing to the repulsion force of the "copolymer effect", the ternary blends with 9 or 25 wt% of AN in the SAN copolymer have a weaker molecular interaction than the blends with 17 wt% of AN in the SAN copolymer. The polarized morphology also gives evidence to support the fact that the homogeneity in the PCL/PBzMA/SAN-25 blend is less than that in the PCL/PBzMA/SAN-17 blends.

To understand the effect of the temperature on the morphology of PCL spherulites, the crystallization of the ternary blends was examined at different temperatures. A comparison of PCL spherulites in the PCL/PBzMA/SAN-17 (90/5/5) blend, which crystallized at different temperatures, is shown in Fig. 6. An apparent extinction ring with regular interference period was found within the range of crystallization temperatures. The size of PCL spherulites increased with the increasing of the crystallization temperature (T_c), and the boundaries of spherulites became straight and closely connected as a result of the effect of the low rate of crystallization and nucleation of PCL. At high crystallization temperatures, the coarse and discontinuous interference band appeared (Fig. 6, top two). The dark region interrupted the continuous bright ring bands, and

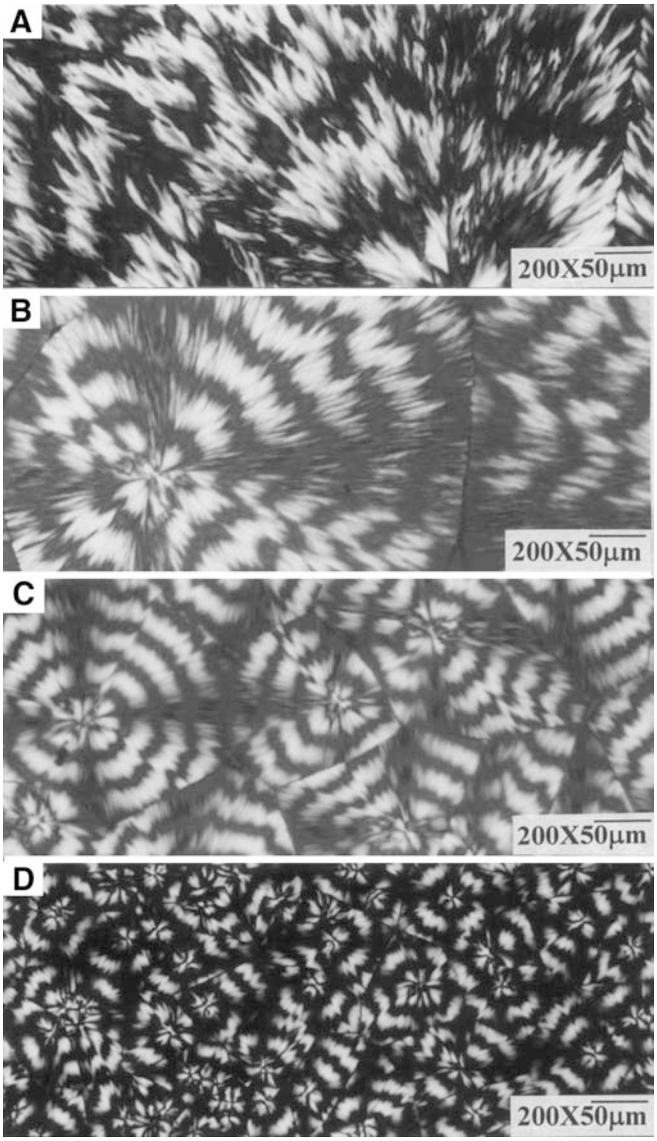


Fig. 6 Optical micrographs of the PCL/PBzMA/SAN-17 = 90/5/5 ternary blends at different crystallization temperatures (°C) from *top* to *bottom* 50, 45, 40, and 35

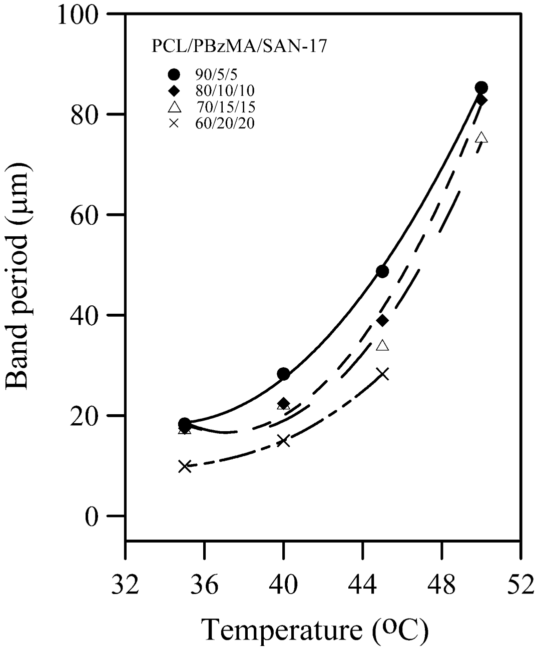


Fig. 7 Band periods of the PCL/PBzMA/SAN-17 ternary blends at different crystallization temperatures (35–50°C)

the bright region was scattered in the dark region in the PCL/PBzMA/SAN-17 ternary blends at the high crystallization temperature ($T_c = 50°C$ and 45°C). The discontinuity and the dispersion of ring bands in PCL spherulites may be attributed to the reduction of chain mobility. At a higher crystallization temperature, the high-T_g amorphous polymers ($T_{g,\mathrm{PBzMA}} = 54.3°C$, $T_{g,\mathrm{SAN\text{-}17}} = 109.5°C$) have good flexibility and chain mobility in the advancing spherulitic front, and the noncrystallizable components can diffuse easily into the interlamellar and interfibrillar regions of PCL during the process of crystallization.

The effect of composition and temperatures on the band period of the extinction rings measured in the PCL spherulites of the PCL/PBzMA/SA-17 blend is shown in Fig. 7. The period of interference rings increased with increasing crystallization temperature (T_c). In addition, the PCL-rich compositions had a comparatively wide band-period. It could be presumed that the band period of PCL in the blends becomes larger with the rise of the crystallization temperature. Apparently, the dilution and the stereo-hindrance of an amorphous can affect the extinction rings of the PCL spherulites. Specific interactions among the components in the blends containing PCL, PBzMA, and SAN significantly alter the mobility of both crystallizable and noncrystallizable components passing through amorphous components with a higher T_g. A SAN copolymer in the blends can surely influence the spherulitic morphology of PCL by changing the overall mobility of the segments in the mixture.

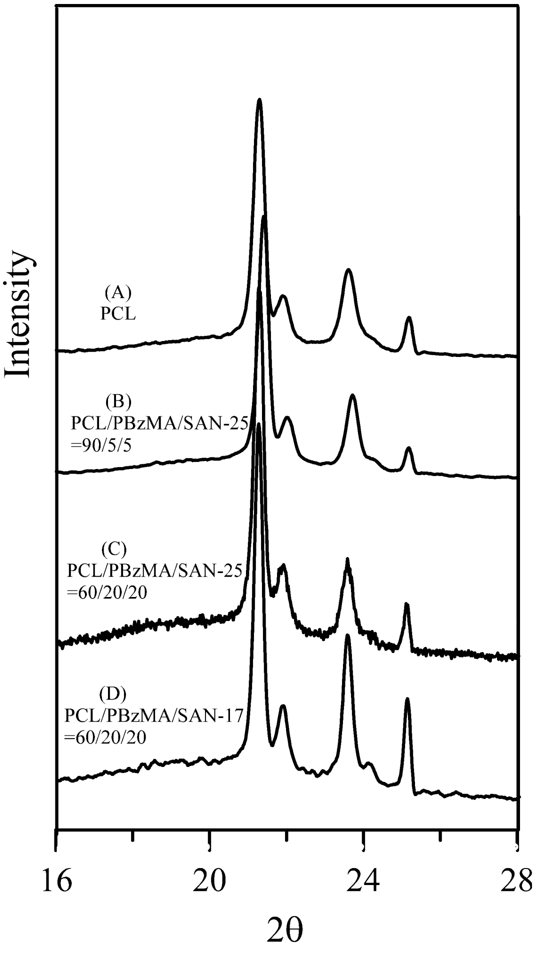


Fig. 8 Wide-angle X-ray diffraction patterns of the PCL/ PBzMA/ SAN-25 blends with various composition (from *top* to *bottom*): PCL, PCL/PBzMA/SAN-25 = 90/5/5, PCL/PBzMA/SAN-25 = 60/ 20/20, and PCL/PBzMA/SAN-17 = 60/20/20 ($T_c = 45°C$, 8 h)

Crystallization structure of PCL

The wide-angle X-ray diffraction (WAXD) patterns of the PCL and the PCL/PBzMA/SAN-x blends whose samples crystallized at 45°C are displayed in Fig. 8. Sharp peaks at $2\theta = 21.4$, 21.9, 23.7, 24.1, and 25° are characteristic of the diffraction of the crystalline lamellae. However, the positions of the reflection peak are almost independent of the composition and the effect of copolymer in the blends. It is obvious that the WAXD patterns reveal the similar crystallization structure of lamellae in the PCL and the PCL/PBzMA/SAN-x ternary blends. Although the spherulitic morphology was dependent on the composition, the crystallization temperature, and wt% of AN in the SAN copolymer in the PCL/PBzMA/SAN blends, similar crystalline lamellae was obtained in the WAXD patterns. Apparently, it is not crystalline lamellae but the molecular interactions between different polymers that affect the ring bands of PCL spherulites in the ternary blends.

Depression of the melting point of PCL components

Nishi and Wang [16] used the Flory–Huggins approximation to treat the melting thermodynamics of the mixing in polymers. In the blend, the molar volume of the amorphous component (V_1) and the molar volume of the crystallizable polymer repeat unit (V_{2u}) cannot be assumed to be equal. Besides, the interaction between the crystallizable polymer and the amorphous component needs to be taken into account. The depression of the melting point of the polymer can be calculated by the following equation:

$$\frac{1}{T_{\mathrm{m}}^{0}}-\frac{1}{T_{\mathrm{mb}}^{0}}=-\frac{RV_{2\mathrm{u}}}{\Delta H_{2\mathrm{u}}V_{1\mathrm{u}}}\chi_{12}(1-V_2)^2 \qquad (3)$$

where, with the subscripts 1 and 2 indicate the amorphous and crystalline polymers, respectively; $T_{\mathrm{m}}{}^{0}$ and $T_{\mathrm{mb}}{}^{0}$ represent the melting point of the polymer blend and the equilibrium melting temperature, respectively; V and V_{u} represent the volume fraction of components and the molar volume of the repeat units, respectively; R is ideal gas constant; and $\Delta H_{2\mathrm{u}}$ is the molar enthalpy of fusion of the polymer blend at $T_{\mathrm{m}}{}^{0}$. The fact that the depression of the melting point occurs is only on condition that χ_{12} is negative for the miscibility of the amorphous/crystallizable blends. Therefore, the following equation shows how the polymer–polymer interaction parameter (χ_{12}) is taken into consideration in the factors resulting in the depression of the melting point of crystallization in polymer mixtures [16, 24]:

$$\chi_{12}=\frac{BV_{1\mathrm{u}}}{RT} \qquad (4)$$

where B is the interaction energy density characteristic of the polymer pair, and $V_{1\mathrm{u}}$ is the molar volume of the repeat units.

In the PCL/PBzMA/SAN-x ternary system, the crystallizable polymer is PCL with a molar volume $V_1=\Phi_{\mathrm{PCL}}$, and the amorphous components include PBzMA and SAN ($V_2=\Phi_{\mathrm{PBzMA}}+\Phi_{\mathrm{SAN}}$). Replacement of the molar volume of PCL in Eq. (3) and combination of Eqs. (4) and (3) yield the following linear relationship between $T_{\mathrm{m}}{}^{0}-\mathrm{T}_{\mathrm{mb}}{}^{0}$ and $(1-\Phi_{\mathrm{PCL}})^2$:

$$T_{\mathrm{m}}^{0}-T_{\mathrm{mb}}^{0}=-B\frac{V_{\mathrm{PCL}}}{\Delta H_{\mathrm{PCL}}}T_{\mathrm{m}}^{0}(1-\Phi_{\mathrm{PCL}})^2 \qquad (5)$$

DSC was used to study the variation of the observed melting temperatures of pure PCL and PCL crystals in the blends at different crystallization temperatures. Figure 9 shows the effect of crystallization temperature (T_{c}) on the observed melting temperature ($T_{\mathrm{m}}{}^{0}$) of PCL and several PCL/PBzMA/SAN-17 blends. As we know, these effects result from morphological contributions such as the degree of perfection and the finite size of crystals. Generally speaking, the crystallization of the polymer blends tends to melt below $T_{\mathrm{mb}}{}^{0}$ because the crystals are small and all of them are very imperfect.

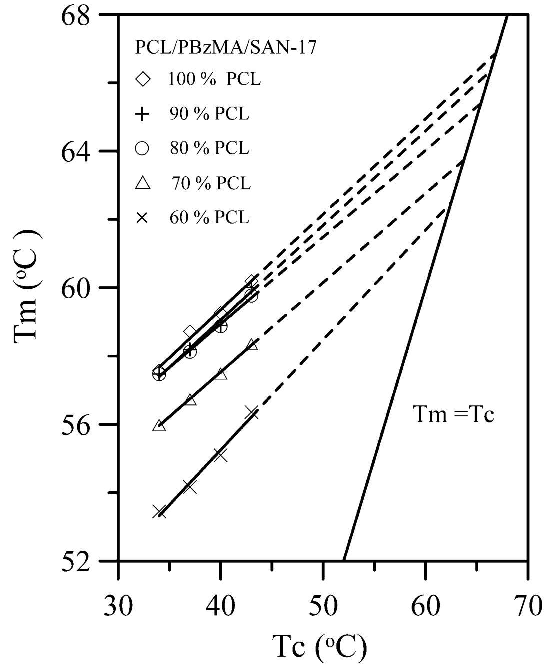


Fig. 9 Hoffman–Weeks plot of the PCL/PBzMA/SAN-17 blends with various composition (PBzMA/SAN = 1/1)

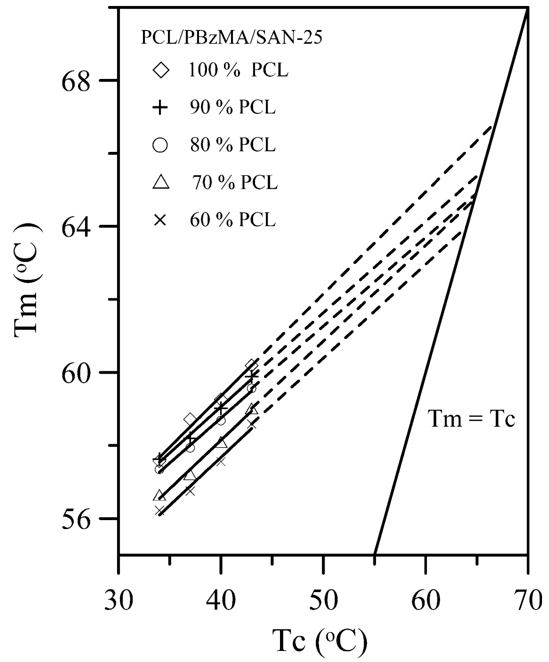


Fig. 10 Hoffman–Weeks plot of the PCL/PBzMA/SAN-25 blends with various composition (PBzMA/SAN = 1/1)

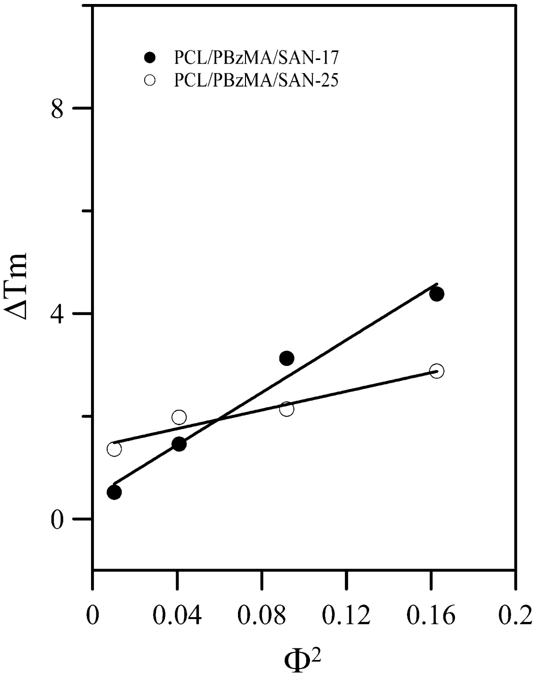


Fig. 11 The plot of the equilibrium melting point of the PCL/PBzMA/SAN-x blends versus the square of the volume fraction of amorphous (PBzMA/SAN = 1)

Thus, the crystallization temperature is usually lower because supercooling has a great influence on the melting point. The equilibrium melting points ($T_{mb}{}^{0} = 66.87°C$) of pure PCL are within the range of values (55–70°C) found in the literature [25, 26, 27, 28], and the $T_{mb}{}^{0}$ of pure PCL is higher than that of PCL crystals in the 60% PCL blends by about 4.3°C. Similarly, the crystallization of PCL in the PCL/PBzMA/SAN-25 blends has the same melting behavior shown in Fig. 10. A linear relationship is observed between T_c and T_m in Figs. 9 and 10. The melting point of PCL rose substantially after annealing or isothermal crystallization at elevated temperatures because of the more perfect crystals, which the polymer formed at a higher crystallization temperature. In addition, the depression of the melting temperature of PCL in the isothermally crystallized samples depended on the quantity of the amorphous component in the ternary blends. It also results from the dilution and the hindrance effects of PCL crystallization.

Judging from extrapolation of the experimental data shown in Figs. 9 and 10, the addition of an amorphous component (PBzMA/SAN-x) does not cause a drastic depression in the equilibrium melting temperature of PCL. Therefore, the depression of the melting point allows the estimation of the interaction energy density characteristic (*B*) of the ternary polymer blends. Figure 11 shows the plots to obtain *B* from Eq. (5) with, $\Delta H_{2u} = 3{,}690$ cal mol^{-1} and $V_{2u} = 105$ cm^{3} mol^{-1} [7]. The values found for *B* were −2.64 and −0.94 for PCL/PBzMA/SAN-17 and PCL/PBzMA/SAN-25 blends, respectively. The negative value of *B* verifies that the two PCL/PBzMA/SAN-x blend systems are miscible in the melting state, and the interaction parameter of the PCL/PBzMA/SAN-25 blends is greater than that of the PCL/PBzMA/SAN-17 blends. It implies that an AN content of 17 wt % in the SAN copolymer has stronger molecular interaction and results in more miscible blends. Comparing the values of *B* in the PCL/PBzMA/SAN-x blends obtained in this study, it was found that the interaction among the blends was dependent on the AN content in the SAN copolymer. Judging from the large negative value of interaction energy density characteristic, it can be concluded that the blend with an AN content 17 wt% of in the SAN copolymer surely has stronger molecular interaction to prompt the miscibility in the ternary blends.

Conclusion

In the ternary polymer blends, the specific interaction of the SAN copolymer results from the structure of styrene-*co*-acrylonitrile units. Apparently, the balance interaction between the polymers changes with wt% of AN contents in the SAN copolymer. The experiment reveals the fact that the copolymer with an optimum wt% of AN content can produce the maximum interaction in the ternary PCL/PBzMA/SAN-x blends. Additionally, the interaction has an apparent effect on the miscibility and the crystallization in the ternary polymer blends. In the study of the crystallization of the ternary polymer blends, a distinct pattern of the extinction rings instead of the Maltese cross occurs in the PCL spherulites because of the effect of the interaction in molecules. It is also found that the ring-banded PCL spherulites, the dilution effect, and the surface free energy are indispensable in forming a critical nucleus on the crystal surface, and the chain mobility also has an influence on the structure of PCL spherulites in the ternary blends. In the observation from POM, the spherulitic morphology is dependent on the composition, the crystallization temperature, and wt% of AN in the SAN copolymer in the PCL/PBzMA/SAN blends. Interestingly, similar crystalline lamellae are seen in PCL spherulites in the wide-angle X-ray patterns. Therefore, it is presumed that the SAN copolymer in the blends influences the spherulite morphology of PCL by changing the overall mobility of the segments in the mixture. Furthermore, the equilibrium melting temperature also indicates that the strength of the intermolecular interaction (*B*) in the PCL/PBzMA/SAN-17 blends is greater than that in the PCL/

PBzMA/SAN-25 blends. Good agreement is attained between the results of Flory–Huggins theory, the observed POM, and thermal behavior.

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