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Miscibility and spherulites in blends of poly(ϵ-caprolactone) with ethylene terephthalate–caprolactone copolyester

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The miscibility of blends between poly(ϵ-caprolactone) (PCL) and ethylene terephthalate–caprolactone copolyester (TCL) with different ethylene terephthalate (ET) contents has been studied by differential scanning calorimetry. When ET contents in the copolyesters are less than 30%, the copolyesters are miscible with PCL. The TCL48 and TCL58 copolyesters were partially miscible with PCL and had an evident influence on the formation of ringed spherulites of PCL in the blends. This means that the addition of a non-crystallizable component with partial miscibility is important for enhancing the formation of PCL ringed spherulites. Transesterification in PCL/TCL blends can also affect the formation of ringed spherulites. There is a best extent of transesterification under which the patterns of ringed spherulites are most distinct. Such a phenomenon may be related to the improvement of miscibility of PCL with TCL copolyesters and composition homogenization in the blends. Copyright © 1996 Elsevier Science Ltd.

(Keywords: ethylene terephthalate–caprolactone copolyester; poly(ϵ-caprolactone); ringed spherulite)

INTRODUCTION

In the family of polyesters, poly(ϵ-caprolactone) (PCL) exhibits a unique characteristic in that it can be miscible with many polymers, such as poly(vinyl chloride), polyhydroxyether of bisphenol A, polycarbonate of bisphenol A, poly(epichlorohydrin), nitrocellulose, cellulose propionate, cellulose butyrate and, styrene/acrylonitrile copolymer[1–13]. Generally, these blends show a single glass transition temperature (T_g) intermediate between those of the individual components at each composition. A melting point depression of PCL was also observed in these blends. The experimental results prove that some specific molecular interactions exist between constituents of the blends.

Recent publications[14–20] have shown that pure PCL exhibits a morphology of spherulites which, for crystallization tempertures below about 323 K, show simple extinction crosses under the polarizing microscope. Spherulites grown at higher crystallization temperatures additionally exhibit banding with large radial separations. However, after addition of miscible non-crystallizable polymers to PCL, the crystallization temperature at which spherulites demonstrate ringed extinction patterns becomes much lower. The ringed extinction patterns become very distinct.

In the present work, the miscibility and crystallization behaviour of blends of poly(ϵ-caprolactone) with ethylene terephthalate–caprolactone copolyesters (TCL) have been investigated. In particular, the study on the crystallization morphology of PCL in these blends yielded very interesting results. The formation of the ringed spherulites changes with the degree of miscibility and transesterification in these blends.

EXPERIMENTAL

PCL used in this research was supplied by Scientific Polymer Products Inc., and had $M_w = 40\,000$. The series of TCL copolyesters was synthesized in our laboratory and their parameters are listed in *Table 1*. The synthesis was divided into two steps: the first involved the esterification of terephthalic acid and ethylene glycol; the second was a polycondensation of ethylene terephthalate with caprolactone in the presence of a catalyst. The copolyesters were purified by precipitation in methanol from a 5% chloroform solution. Their ethylene terephthalate (ET) contents were determined by nuclear magnetic resonance (n.m.r.) spectroscopy from a 5% deuterated chloroform solution at room temperature with a JEOL Japan FX-90 Q spectrometer. The blend films were prepared by casting from a chloroform solution at room temperature, and dried in a vacuum oven at 323 K until they reached constant weight.

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Table 1 Description of synthesized TCL copolyesters

Acronym	ET content (wt%)[a]	T_g (K)[b]	$[\eta]$ (dl g^{-1})[c]
TCL82	82	306.0	0.84
TCL72	72	291.0	0.96
TCL58	58	261.7	0.85
TCL48	48	245.6	0.87
TCL28	28	219.0	1.20
TCL13	13	208.0	1.99

[a] ET content determined by n.m.r.

[b] T_g determined by d.s.c. at a heating rate of 20 K min^{-1}

[c] Inherent viscosity measured in *m*-cresol at 303 K

Table 2 T_g of the PCL/TCL blends

TCL copolyester	PCL content (wt%)	T_g (K)[a]
TCL72	100	202
	90	280
	80	281
	70	281
	50	284
	20	290
	0	291
TCL48	100	202
	90	234
	80	234
	70	235
	50	235
	20	236
	0	246
TCL28	100	202
	70	204
	50	210
	30	215
	0	219
TCL13	100	202
	90	202
	80	202
	70	202
	50	205
	20	207
	0	208

[a] T_g determined by d.s.c. for the quenched samples at a heating rate of 20 K min^{-1}

Differential scanning calorimetry (d.s.c.) measurements were conducted with a Perkin–Elmer DSC-2C apparatus equipped with a TADS microcomputer and an intracooler II. The calorimeter was calibrated with ultrapure indium. The glass transition temperature (T_g) was determined by the half-height of the corresponding heat capacity jump. In the d.s.c. apparatus, the samples (preheated to 500 K, then quenched to a hot stage kept at 308 K to crystallize) were first cooled to 190 K and maintained for 1 min, then heated up at a rate of 20 K min^{-1} to 450 K to obtain T_g and the melting temperature (T_m). The samples were held at 450 K for 3 min, then cooled at a rate of 20 K min^{-1} to measure the crystallization temperature (T_c). The transesterification samples were first treated at a certain temperature for a certain time and quenched to 190 K, then reheated at a rate of 20 K min^{-1} to observe T_c, T_g and T_m.

The morphology of the poly(ϵ-caprolactone) spherulites in the blends was observed by a polarizing microscope and a phase contrast microscope (Olympus Co. Ltd, Japan). The specimen used in the observation was ~ 20 μm thick, and was sandwiched between two cover glasses. Each specimen was first melted at 500 K for 1 min, then immediately transferred into a hot stage kept at a certain temperature to grow the spherulites. To study the effect of transesterification on the formation of spherulites, each specimen was treated at 510 K for a different time and then quenched to room temperature.

RESULTS

Miscibility and spherulite morphology of PCL/TCL blends

The T_g values of the blends of poly(ϵ-caprolactone) with different ethylene terephthalate–caprolactone copolyesters are listed in *Table 2*. The T_g values of the PCL/TCL13 and PCL/TCL28 blends change regularly with composition as shown in *Figure 1*. The relationship between T_g and composition in PCL/TCL28 can be described by the Gordon–Taylor equation. This result means that the constituents in PCL/TCL28 and PCL/TCL13 blends are miscible. When ET contents in copolyesters are more than 30%, their blends with poly(ϵ-caprolactone) seem to be partially miscible or immiscible, since only one T_g approaching those of the pure TCL components was observed in the d.s.c. curves.

The melting peak T_m and the enthalpy of isothermally crystallized PCL (ΔH_m) in the blends are shown in *Table 3*. The values of T_m indicate that the melting point decreases with increasing TCL content for the first two blend systems. Such a phenomenon is due to miscibility and morphology effects in the blends. It is difficult to image the specific molecular interaction in these blend systems, so that the morphology effect may be an important factor in the melting depression. The melting behaviour of PCL in the PCL/TCL72 blends was different: except for the blend with composition 80/20, the melting temperature was almost equal to T_m of pure PCL.

The values of T_c were determined by d.s.c. with a cooling rate of 20 K min^{-1} for some blends after maintaining them at 450 K for 3 min. The results show that T_c decreases with increasing amount of TCL component in the blends (*Table 3*). This means that the

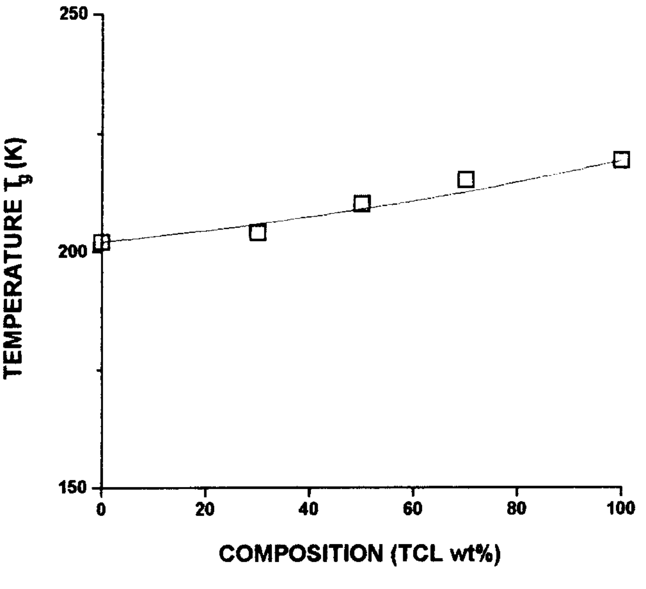

Figure 1 Dependence of T_g on composition for PCL/TCL28 blends

Table 3 ΔH_m and T_m of PCL/TCL blends after isothermal crystallization at 308 K

TCL copolyester	PCL content (wt%)	ΔH_m (exp.) (cal g^{-1})	ΔH_m (PCL) (cal g^{-1})	T_m (K)	T_c (K)[a]
TCL72	100	22.26	22.26	324	282
	90	18.49	20.54	323	273
	80	16.73	20.90	324	272
	70	14.42	20.61	324	272
	50	9.74	19.48	323	276
	20	3.79	17.45	320	277
TCL48	100	22.26	22.26	324	282
	90	19.11	21.23	323	281
	80	17.65	22.06	322	279
	70	15.01	21.44	322	278
	50	9.80	19.60	321	272
	20	4.58	22.90	319	270
TCL13	100	22.26	22.26	324	282
	90	21.08	23.42	323	279
	80	19.82	24.78	322	276
	70	16.84	24.06	322	275
	50	15.39	30.70	320	266
	20	1.99	9.95	314	262

[a] T_c determined by d.s.c. for the samples after maintaining at 450 K for 3 min with a cooling rate of 20 K min^{-1}

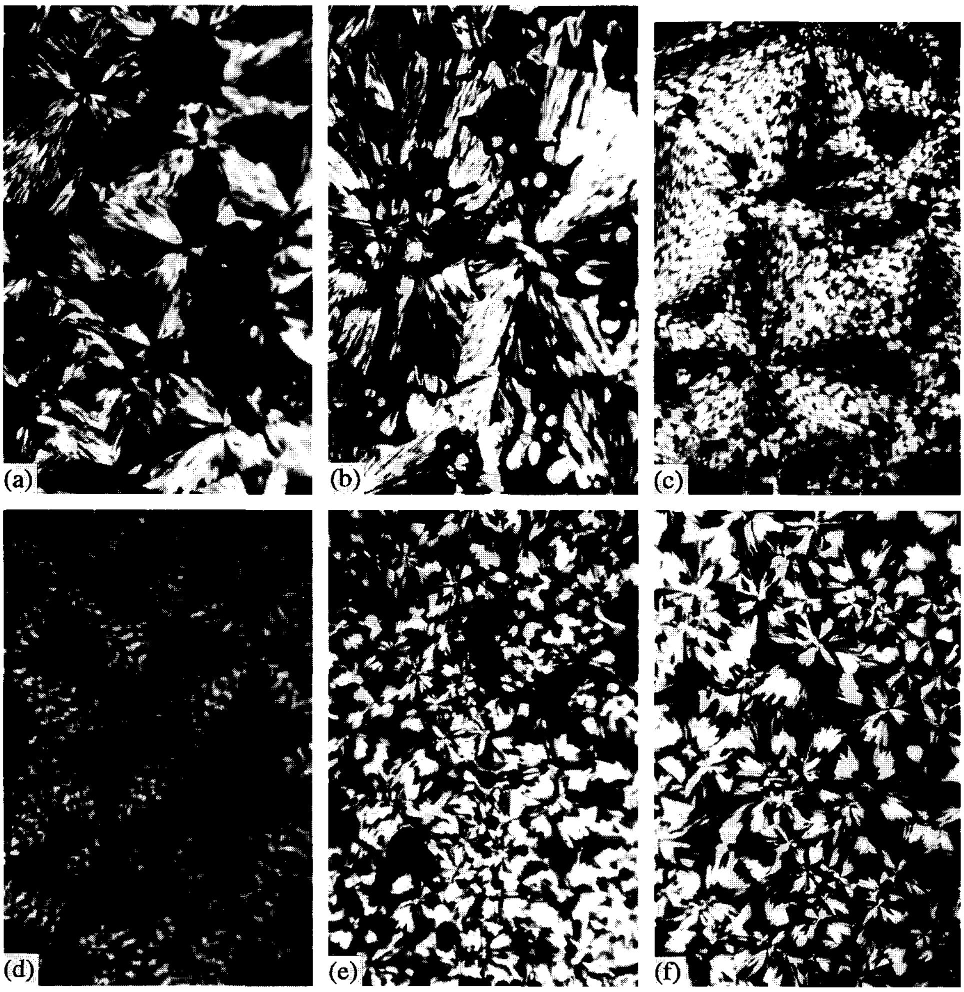

Figure 2 Polarized light micrographs of PCL/TCL (80/20) blends with different ET content isothermally crystallized at 313 K for 12 h: (a) PCL/TCL82; (b) PCL/TCL72; (c) PCL/TCL58; (d) PCL/TCL48; (e) PCL/TCL13; (f) PCL

crystallization of PCL in the blends is more difficult with increasing TCL content and needs higher supercooling. All of these observations support the conclusion about miscibility in the blends mentioned above. In addition, it is also found that (except for the 80/20 blend) the corresponding melting enthalpy of 100% PCL for the PCL/TCL13 blend increases with increasing amount of TCL13 copolyester. Such phenomena demonstrate that the caprolactone segments in TCL13 copolyester take part in the crystallization of poly(ε-caprolactone) and enhance the thermal effect of the PCL melting process.

The spherulitic morphology of pure PCL and PCL blends with different copolyesters, obtained using the polarizing microscope, is shown in *Figure 2*. It can be seen that the ringed spherulites in PCL/TCL48 and PCL/TCL58 blends have the clearest patterns in which the banding is more regular with smaller spacing. In the miscible blends of PCL/TCL13 and PCL/TCL28, the ringed spherulites can form only in the temperature range approaching to the temperature at which pure PCL can grow ringed spherulites (*Figure 3*). In the PCL/TCL72 blends the normal crystalline morphology of the PCL without ringed spherulites was observed in the temperature range considered.

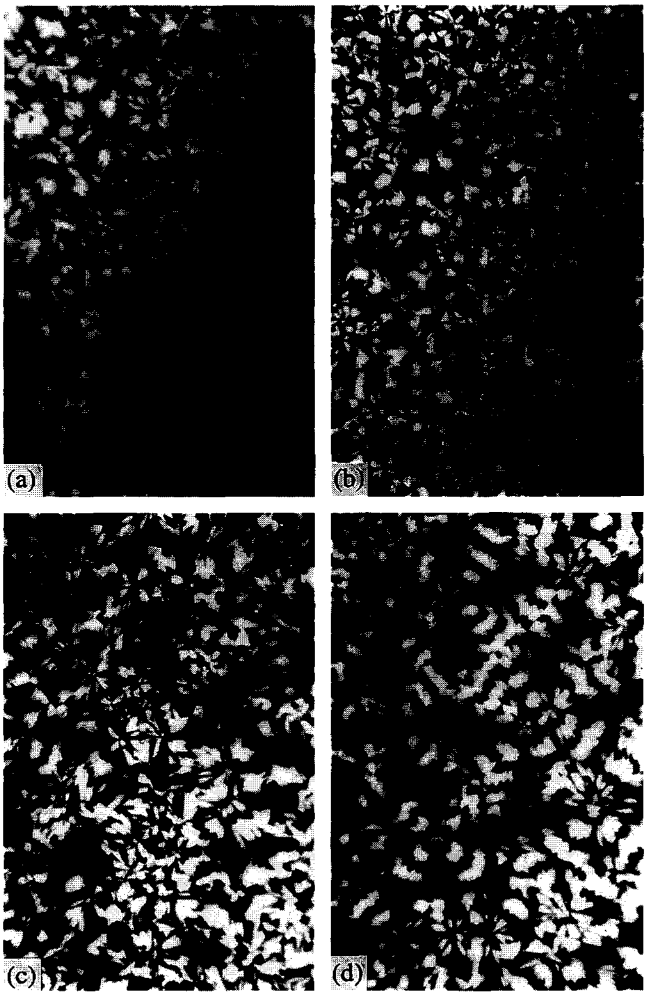

Figure 3 Polarized light micrographs of PCL/TCL13 (80/20) blend isothermally crystallized at different temperatures for 12 h: (a) 308 K; (b) 313 K; (c) 318 K; (d) 321 K

Transesterification and formation of ringed spherulites

It is evident that, when the blends of TCL copolyesters with PCL are heated to a high enough temperature (e.g. 510 K) for a suitable time, the components in the blends undergo transesterification. *Figure 4* shows the d.s.c. curves of PCL/TCL48 (80/20) blends after different annealing times at 510 K. With increasing annealing time, the glass transition temperature shifts to lower temperatures. The melting peak also undergoes a corresponding change, the peak moving to lower temperatures and its area becoming smaller. After-annealing for 40 min, the T_g reached a constant value. The PCL/TCL82 blend is immiscible, and should exhibit two T_gs before thermal treatment. However, because of

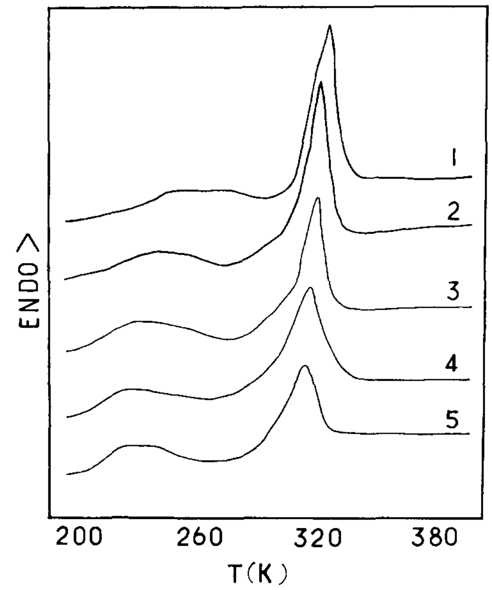

Figure 4 D.s.c. curves of PCL/TCL48 (80/20) blend annealed at 510 K for different times: (1) original sample; (2) 10 min; (3) 20 min; (4) 40 min; (5) 60 min

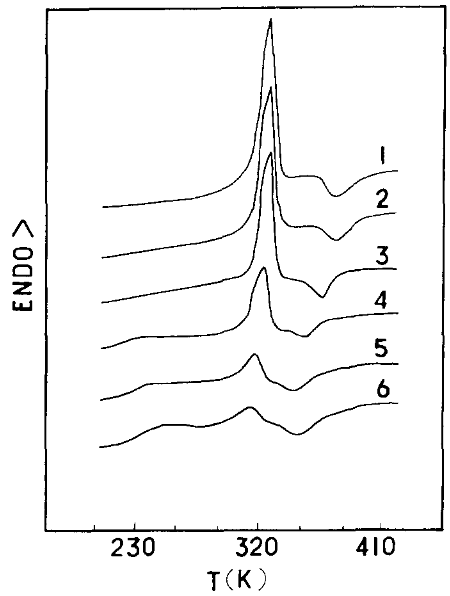

Figure 5 D.s.c. curves of PCL/TCL82 (50/50) blend annealed at 510 K for different times: (1) original sample; (2) 10 min; (3) 30 min; (4) 60 min; (5) 90 min; (6) 120 min

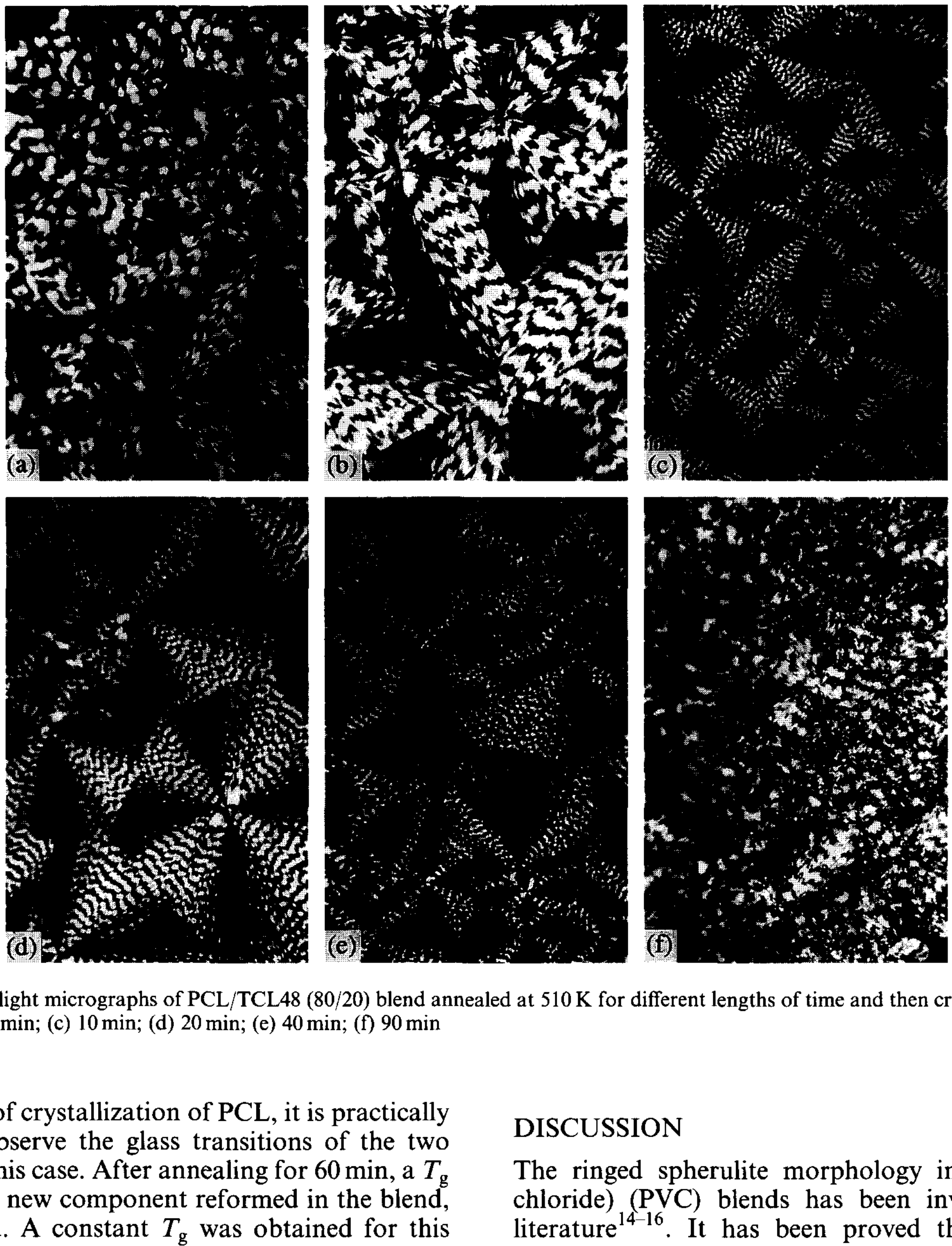

Figure 6 Polarized light micrographs of PCL/TCL48 (80/20) blend annealed at 510 K for different lengths of time and then crystallized at 313 K for 12 h: (a) 1 min; (b) 5 min; (c) 10 min; (d) 20 min; (e) 40 min; (f) 90 min

the high degree of crystallization of PCL, it is practically impossible to observe the glass transitions of the two components in this case. After annealing for 60 min, a T_g belonging to the new component reformed in the blend, can be observed. A constant T_g was obtained for this blend after annealing for 90 min as shown in *Figure 5*. These results demonstrate that transesterification has occurred in the annealed blends, making them homogeneous. The crystallization ability of the components became weaker and weaker in these annealed blends.

The transesterification not only makes the blends homogeneous, but also promotes the growth of ringed spherulites. During transesterification, the banding in the ringed spherulites becomes more regular and the band spacing becomes shorter. In *Figure 6*, the morphology of spherulites of PCL in PCL/TCL48 (80/20) blends, which have been annealed at 510 K for different times, is shown. It is evident that annealing for 40 min promotes the PCL to grow the most regular ringed spherulites with the shortest band spacing. After annealing for 90 min, the pattern of ringed spherulites was blurred. The micrographs obtained by the phase contrast microscope for spherulites of the PCL/TCL48 blend show the same ringed spherulites without extinction crosses. *Figure 7* shows polarized light micrographs for PCL/TCL82 blends (80/20). The annealing temperature was the same as that in *Figure 6*. After transesterification, regular ringed spherulites are observed clearly.

DISCUSSION

The ringed spherulite morphology in PCL/poly(vinyl chloride) (PVC) blends has been investigated in the literature[14–16]. It has been proved that this blend is miscible, and that hydrogen bond interaction exists between the carbonyl group in PCL and the α-hydrogen in PVC. Naturally such an interaction was imagined as the factor, and has an important influence on the formation of ringed spherulites in the blends. Moreover, in a study[17] on blends of PVC and CPE56.3 (the number refers to chloride content, CPE is chlorinated polyethylene) with PCL, completely different segregation behaviour was observed during the PCL crystallization process. The PCL in the PCL/PVC blend grew large and regular ringed spherulites, but the PCL in the PCL/CPE56.3 blend formed fibrillar textures in the spherulites. Such dissimilar segregation behaviour was attributed to the difference in T_g between both amorphous diluents. A higher T_g of the amorphous diluent is favourable for the formation of PCL ringed spherulites.

In blends of PCL with TCL, copolyester, there is no specific molecular interaction. The TCL copolyesters have lower T_g values than CPE polymers. Yet the TCL48 copolyester has an evident influence on the formation of ringed spherulites. These experimental results mean that it is difficult to say that specific molecular interaction and

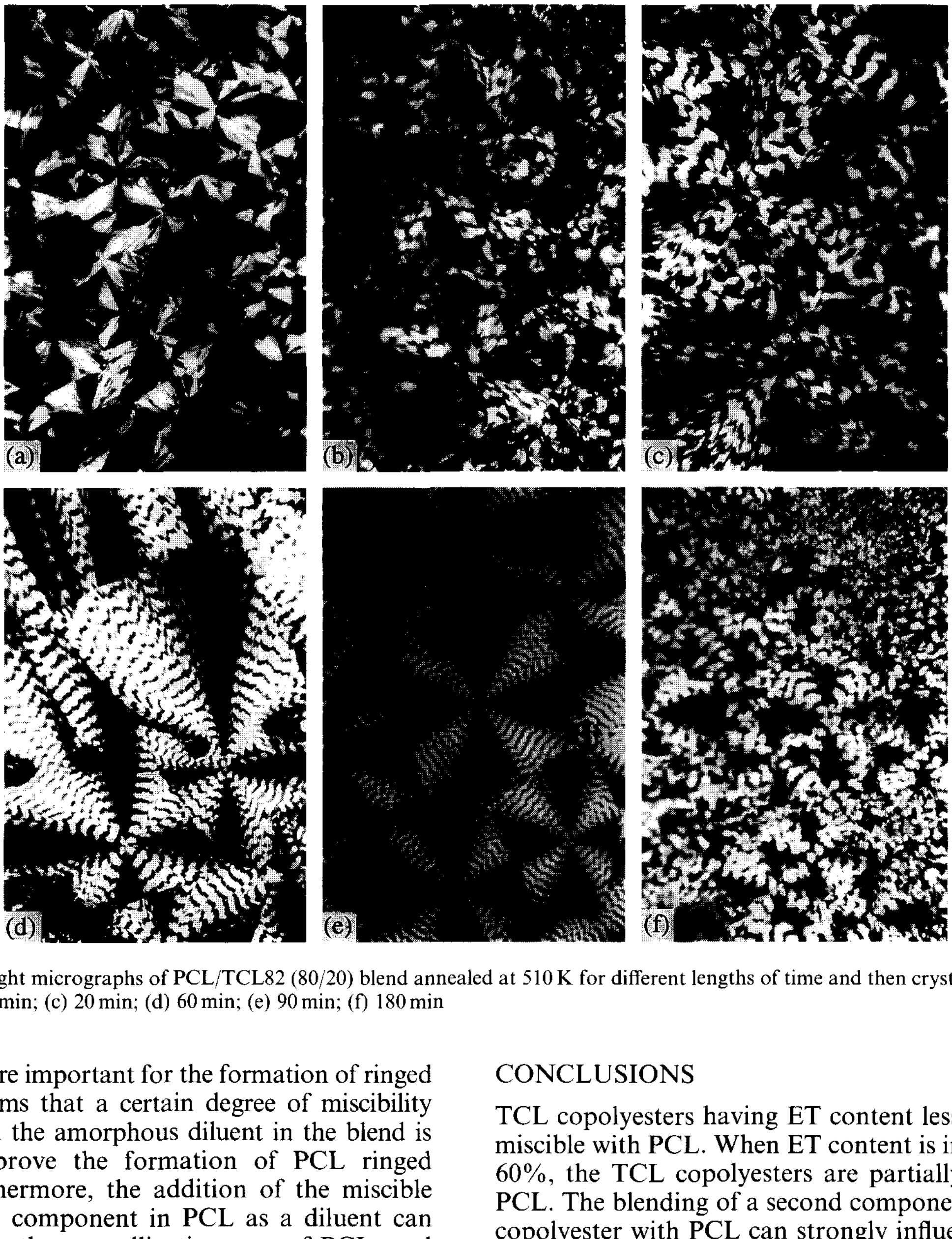

Figure 7 Polarized light micrographs of PCL/TCL82 (80/20) blend annealed at 510 K for different lengths of time and then crystallized at 313 K for 12 h: (a) 1 min; (b) 10 min; (c) 20 min; (d) 60 min; (e) 90 min; (f) 180 min

higher T_g values are important for the formation of ringed spherulites. It seems that a certain degree of miscibility between PCL and the amorphous diluent in the blend is necessary to improve the formation of PCL ringed spherulites. Furthermore, the addition of the miscible non-crystallizable component in PCL as a diluent can evidently decrease the crystallization rate of PCL, and this may be another important factor in the improvement of PCL ringed spherulite morphology.

It is well known that transesterification will break PCL molecular chains and improve the miscibility of the two components in these blends. The work in our laboratory[21] has demonstrated that reduced molecular chain length cannot improve the formation of ringed spherulites. Therefore the improvement of the ringed spherulite pattern by transesterification should be attributed to homogenization of the hard segment content of the TCL component in the blends. As the transesterification reaction proceeds, the content of pure PCL molecular chains decreases and the TCL copolyester content increases. At the end of transesterification, the blend will only contain TCL copolyester with less hard segment content. For this reason, the regularity of the ringed spherulites becomes worse and worse in the later stage of transesterification, eventually leading to the situation where normal spherulites cannot be formed.

CONCLUSIONS

TCL copolyesters having ET content less than 30% are miscible with PCL. When ET content is in the range 30–60%, the TCL copolyesters are partially miscible with PCL. The blending of a second component such as TCL copolyester with PCL can strongly influence the formation of PCL ringed spherulites. In such a case, the TCL copolyesters (in which both ET and caprolactone segments almost cannot crystallize) decrease the crystallization rate and favour the formation of ringed spherulites of PCL. In these blends, the reasons why TCL copolyesters influence the formation of the ringed spherulites remain to be unclear and further investigation is necessary.

Transesterification in PCL/TCL copolyester blends can lead to homogenization of composition, both of the copolyesters and of the blends as a whole, and this process can evidently affect the crystalline morphology of PCL in the blends. The blend films gave the most reglar ringed spherulites of PCL in the middle stage of transesterification.

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