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Transesterification and ringed spherulites in blends of butylene terephthalate–ε-caprolactone copolyester with poly(ε-caprolactone)

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The miscibility, transesterification and formation of ringed spherulites in blends of poly(ε-caprolactone) (PCL) with butylene terephthalate–ε-caprolactone (BCL) copolyester have been studied by d.s.c. and polarizing microscope. When the BT contents in copolyesters are below 60%, copolyesters are miscible with PCL. The compatibility between components in the blends has a certain correspondence with the weakening of PCL crystallization ability in the blends. The transesterification can easily occur in the blends at 530 K. The transesterification depends on the miscibility between components and the BT content of the copolyesters, though the BT content plays a more important role in the trans-reaction. Both copolyesters and transesterified copolyesters can evidently improve the formation of ringed spherulite in PCL/BCL copolyester blends. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: miscibility; transesterification; formation of ringed spherulite)

INTRODUCTION

Many research papers[1–8] have been devoted to the study of the transesterification reaction occurring in molten polyester blends. The understanding and characterization of such trans-reactions are of great scientific and practical importance, but these authors have mainly investigated the trans-reactions in blends between aromatic polyesters.

To study blends of polyester or copolyester with aliphatic polyester may also provide some important information about the morphology and properties of the blends as shown in the work of Ma *et al.*[9]. In our laboratory a series of butylene terephthalate–ε-caprolactone copolyesters (BCL) have also been synthesized. Here, we show that transesterification can evidently occur in blends of BCL copolyesters with poly(ε-caprolactone) (PCL). In such blends the transesterification depends on not only the miscibility between components, but also the hard segment content of the BCL copolyester. Furthermore, it is especially interesting that the copolyester and transesterified copolyester can have a large influence on the formation of normal and ringed spherulites.

EXPERIMENTAL

The parameters of the series of BCL copolyesters synthesized by us are listed in *Table 1*. The synthesis was divided into two steps: the first involved the esterification of terephthalic acid and butanediol; the second was polycondensation of butylene terephthalate (BT) with caprolactone (CL) in the presence of a catalyst. The copolyesters were purified by precipitation in methanol from a 5% chloroform solution. Their BT 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. PCL used in this research work was supplied by Scientific Polymer Products with $M_w = 40\,000$. The PCL/BCL copolyester blends were prepared by casting films from a chloroform solution at room temperature. The resulting films were dried in a vacuum oven at a temperature of 323 K until they reached constant weight.

The d.s.c. measurements were conducted with a Perkin Elmer DSC-2C apparatus equipped with a TADS microcomputer and an intercooler II. The d.s.c. 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.

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Table 1 Parameters of the copolyester samples

Copolyester	Content of hard segments: Stoichiometric (wt%)	Content of hard segments: n.m.r. (wt%)	$[\eta]^a$ (dl g^{-1})	T_g (K)	T_m (K)
BCL80	80	80	0.93	260	449
BCL60	40	60	1.04	246	397
BCL46	35	46	0.94	227	341
BCL39	10	39	1.12	218	

[a] Measured in *m*-cresol at 30°C

apparatus, the samples were first heated at a rate of 20 K min^{-1} to 490 K and maintained at that temperature for 1 min. Thereafter, the samples were quenched at a rate of 160 K min^{-1} to 190 K and kept at 190 K for 1 min, then reheated at a rate of 20 K min^{-1} to 490 K. Again, the samples were maintained for 1 min at that temperature, then underwent cooling at a rate of 20 K min^{-1}. The cooling curves show the sample's crystallization behaviour. The transesterification of the blends was also directly observed by d.s.c. The samples were treated at 530 K for a certain length of time and quenched to 190 K, then reheated at a rate of 20 K min^{-1} and the T_c, T_g and T_m were determined.

The morphology of the PCL spherulites in the blends was observed by a polarizing microscope manufactured by Olympus Limited, Japan. The specimen was sandwiched by cover glasses. The condition of isothermal crystallization of each sample was as follows: first melted in an oven at a temperature of 490 K for 1 min, then moved immediately on to a thermostat and crystallized at a selected temperature for 12 h. To study the effect of the transesterification on the formation of spherulites, each sample was treated at 530 K, then transferred to a thermostat and crystallized at a selected temperature for 12 h.

RESULTS

Miscibility and spherulite morphology of blends PCL/BCL copolyester

The d.s.c. curves of PCL/BCL39 copolyester blends with different compositions are shown in *Figure 1*. From the heating curves it can be seen that for each composition of the blend only one T_g exists. The d.s.c. curves of PCL/BCL39 copolyester blends in a narrow temperature range in *Figure 2* show that the T_g value of the PCL/BCL 39 blend changes regularly with composition. This means that the PCL/BCL39 blend is miscible. The T_g values of the blends of PCL with different BCL copolyesters are listed in *Table 2*. From the data shown in *Table 2* it can be seen that the PCL/BCL copolyester blends are miscible when the BT contents in the copolyesters are below 60 wt%.

Figure 3 shows the d.s.c. heating and cooling curves for PCL/BCL80 copolyester blends. After comparing these curves with curves of PCL/BCL39 blends shown in *Figure 1*, it can be seen that the crystallization ability of PCL in PCL/BCL80 copolyester blends decreases more slowly with increasing copolyester content in the blends. The weakening of the crystallization ability in the blends has some correspondence with the change of the miscibility in the blends. The better the compatibility

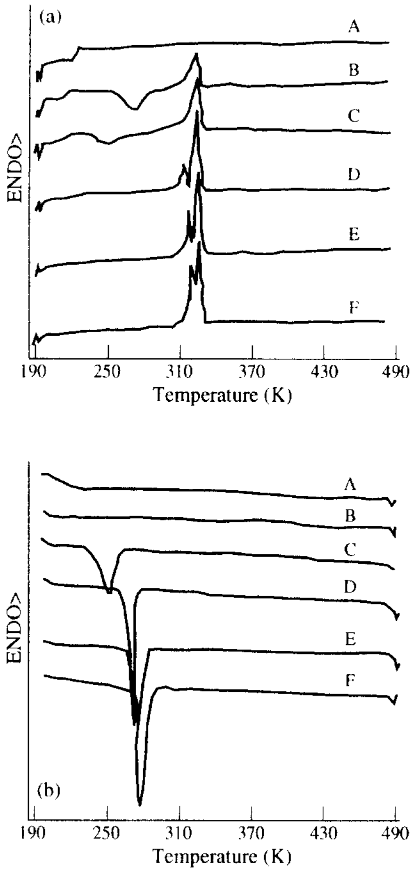

Figure 1 D.s.c. heating curves of PCL/BCL copolyester blends quenched from 490 to 190 K for different compositions (heating rate 20 K min^{-1}. (a) D.s.c. cooling curves of blends PCL/BCL copolyester cooled from 490 K at a cooling rate of 20 K min^{-1} for different compositions. (b) A: BCL39; B: BCL39 (80 wt%); C: BCL39 (70%); D: BCL39 (50%); E: BCL39 (30%); F: BCL39 (20%)

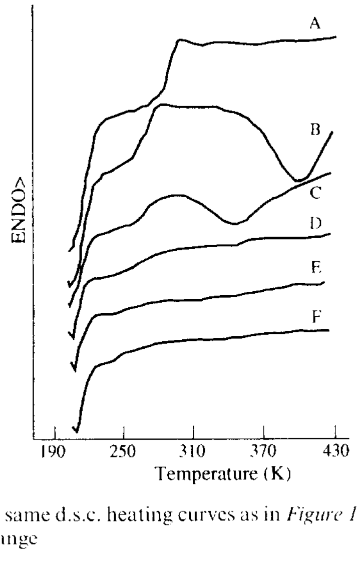

Figure 2 The same d.s.c. heating curves as in *Figure 1* only in a narrow temperature range

between components in the blends, the greater the weakening of the crystallization ability of crystallizable components in the blends.

It has been known that ethylene terephthalate–caprolactone (TCL) copolyesters can give evident influence on the formation of the PCL ringed spherulites in the PCL/TCL copolyester blends[9]. The spherulite patterns under a polarizing microscope for PCL in PCL/BCL copolyester blends are demonstrated in *Figures 4* and *5*. These patterns indicate that the PCL in the PCL/BCL copolyester blends can grow ringed spherulites at temperatures below 50°C. Moreover, the BCL46 copolyester in PCL/BCL copolyester blends can best produce the formation of PCL ringed spherulites.

Transesterification in blends PCL/BCL copolyester

The transesterification reaction in PCL/BCL blends can break the PCL macromolecule chain; therefore, the amount of pure PCL chains decreases as the reaction proceeds and the PCL chains become 'blocks' of different lengths. Such a reaction in the blends necessarily leads to a decrease in the PCL crystallization ability and the value of the reformed copolyester T_g. The d.s.c. experiments have shown such results as indicated in *Figures 6* and *7*. In d.s.c. heating curves, only the copolyester-rich component T_g was observed; moreover, the T_g shifts to a lower temperature with transesterification, and after a certain time the T_g becomes constant. At the same time, both the d.s.c. heating curves and the cooling curves show that the PCL (or both components in the blends) crystallization ability is weakened as transesterification proceeds.

It is interesting to note that the rates of the transesterification reaction are different for the blends with different copolyesters, as shown in *Figure 8*. The heating curves for PCL/BCL39 and blend PCL/BCL80 blends do not show a cold crystallization peak, but the heating curves for other blends exhibit an evident cold crystallization peak. This means that in the former case the PCL component in the blends has enough time to crystallize in quenching; however, in the latter case the PCL component only partly crystallizes in quenching, i.e. the crystallization ability of the PCL component in the blends is weaker. The transesterification in PCL/BCL46 and PCL/BCL60 blends are carried out more quickly. In fact, the transesterification is most rapid in PCL/BCL60 copolyester blend and slowest in PCL/BCL39 copolyester blend.

Formation of ringed spherulite in the transesterified blends

It is natural to ask how the transesterification can influence the formation of PCL ringed spherulites in the

Table 2 D.s.c. data for the PCL/BCL copolyester blends

Copolyester	PCL content (wt%)	T_g (K)	T_m (K) PCL	T_m (K) BCL	T_c (K) PCL	T_c (K) BCL
BCL80	0	260		449		411
	20	256	320	449	270	409
	30	248	321	449	272	409
	50	248	317	447	282	410
	70	246	318	447	282	408
	80	245	319	447	282	408
	100	199[a]	325			
BCL60	0	246		397		334
	20	229	321	397	275	338
	30	225	317	392	277	341
	50	223	319	394	280	333
	70	220	318		281	338
	80	216	319		280	334
	100	199[a]	325			
BCL46	0	227				
	20	220	316			
	30	219	319			
	50	215	321		264	
	70	215	321		269	
	80	211	322		277	
	100	199[a]	325			
BCL39	0	218				
	20	215	318			
	30	213	319		253	
	50	212	321		270	
	70	210	322		273	
	80	209	323		276	
	100	199[a]	325			

[a] From ref. 10

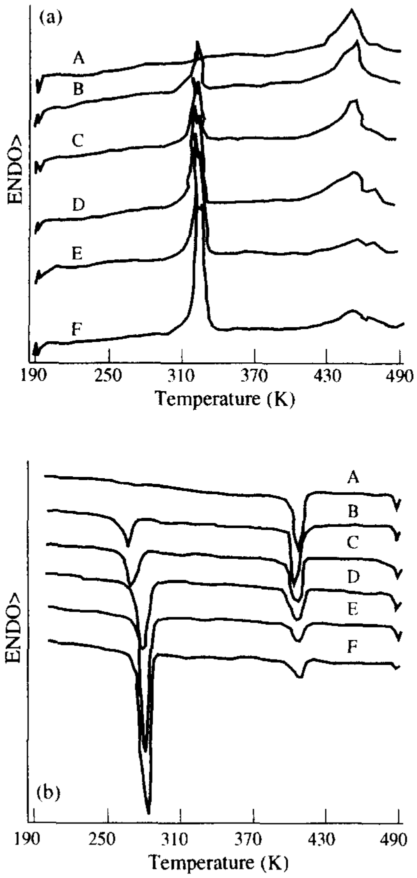

Figure 3 D.s.c. heating curves of PCL/BCL copolyester blends quenched from 490 to 190 K for different compositions (heating rate 20 K min^{-1}). (a) D.s.c. cooling curves of PCL/BCL copolyester blends cooled from 490 K at a cooling rate of 20 K min^{-1} for different compositions. (b) A: BCL80; B: BCL80 (80 wt%); C: BCL80 (70%); D: BCL80 (50%); E: BCL80 (30%); F: BCL80 (20%)

blends. *Figures 9* and *10* show the polarizing micrographs of PCL components in the transesterified PCL/BCL copolyester blends. From the polarizing micrographs it can be seen that the change of the ringed spherulite patterns in the blends has two stages: first, the ringed spherulite patterns become better (more regular and thinner) as transesterification proceeds; second, after maximum improvement of the ringed spherulite patterns, the extinction rings and crosses become worse—in the end, the PCL component in the blends cannot even grow any spherulite. Through comparing the changes of ringed spherulite patterns in PCL/BCL39 and PCL/BCL60 blends it can also be seen that the rate of change of the extinction patterns is most rapid in the PCL/BCL60 blend and slowest in the PCL/BCL39 blend. These rates have a correspondence with the transesterification rates in the same blends.

DISCUSSION

Influence of BCL copolyester on the formation of PCL ringed spherulites in the blends

As shown in the previous work[9], it does not appear that the better the compatibility between components in the blends, the larger the influence of the added copolyester TCL component on the formation of PCL ringed spherulites in the blends. The same conclusion can be obtained from the results mentioned above, i.e. BCL46 and BCL39 copolyesters are miscible with PCL; moreover, the compatibility of BCL39 copolyester with PCL is better, but BCL46 copolyester, in which both BT segments and CL segments are non-crystallizable, can give a more evident influence on the formation of PCL ringed spherulites in the blends. This means that to improve the PCL ringed spherulite pattern, only a certain compatibility of the second component with PCL is important. Studying the morphological changes in polyesters induced by blending with small

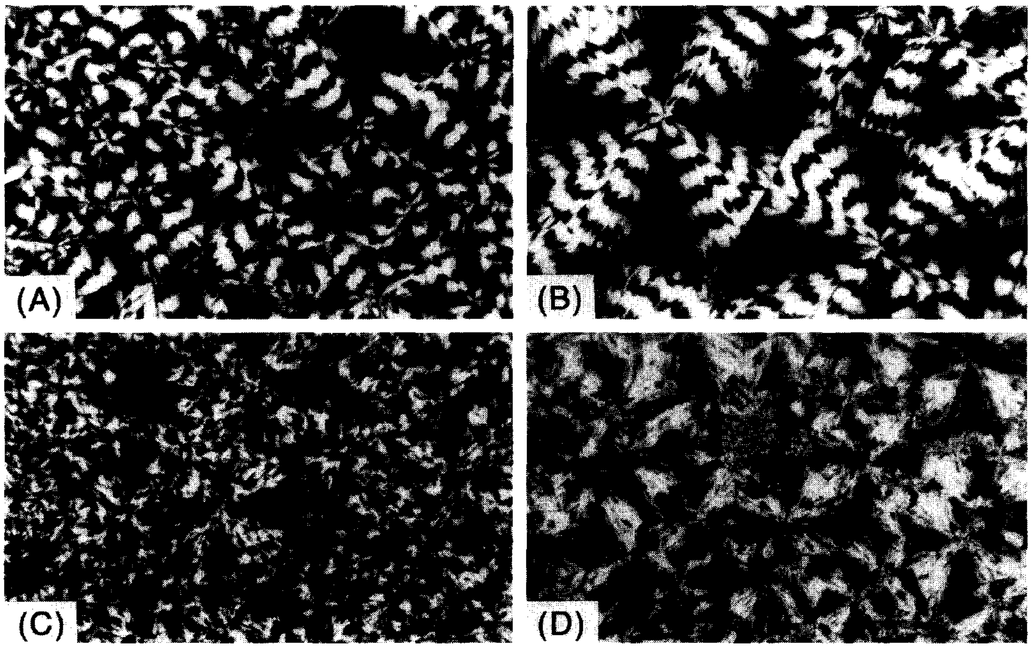

Figure 4 Polarized light micrographs of PCL/BCL copolyester blends (4/1) with different BT content copolyesters isothermally crystallized at 35°C: (A) PCL/BCL39; (B) PCL/BCL46; (C) PCL/BCL60; (D) PCL/BCL80

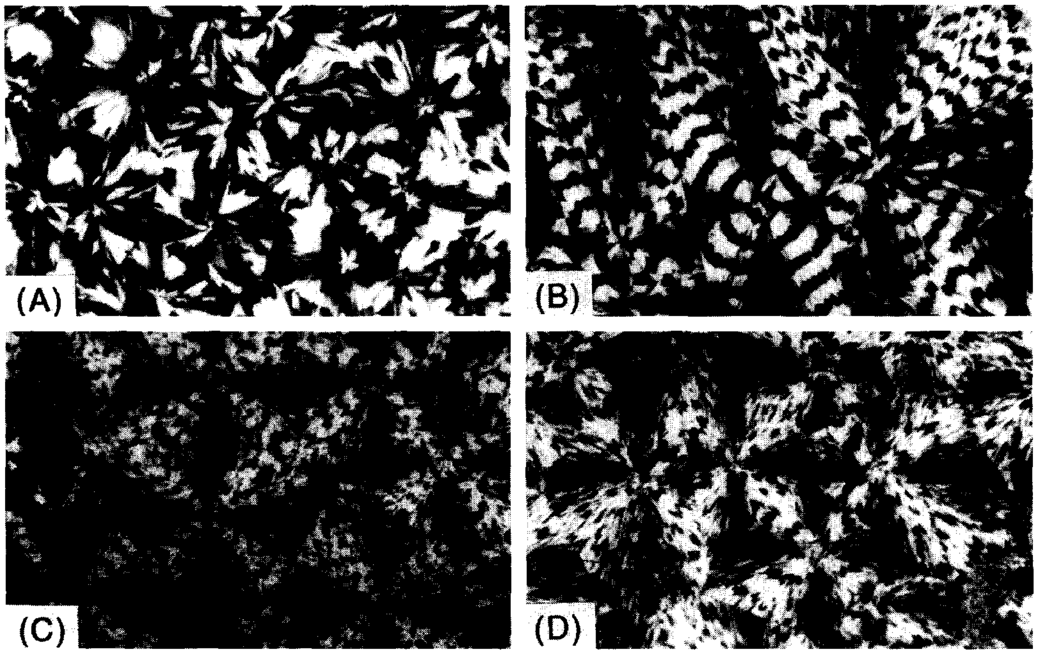

Figure 5 Polarized light micrographs of PCL/BCL copolyester blends (4/1) with different BT content copolyesters isothermally crystallized at 40°C: (A) PCL/BCL39; (B) PCL/BCL46; (C) PCL/BCL60; (D) PCL/BCL80

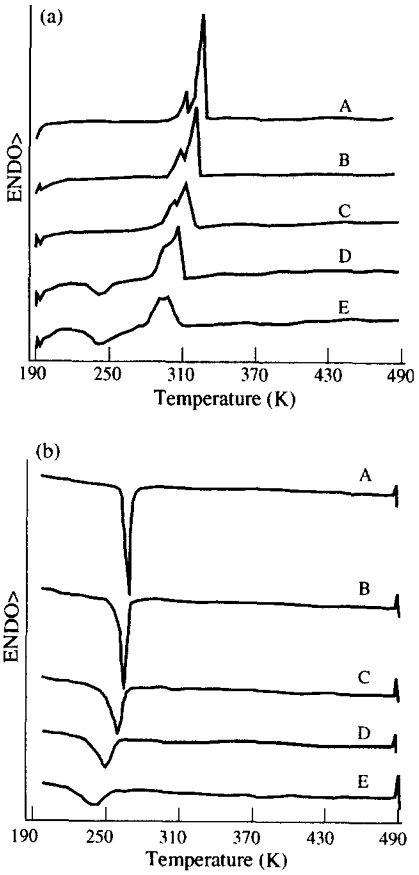

Figure 6 D.s.c. heating curves of PCL/BCL39 copolyester blends (4/1) quenched after treating at 530 K for different transesterification times (heating rate 20 K min^{-1}) and d.s.c. cooling curves of PCL/BCL39 copolyester blends (4/1) after treating at 530 K for different transesterification times (cooling rate 20 K min^{-1}): (A) 0 min; (B) 5 min; (c) 10 min; (D) 30 min; (E) 60 min

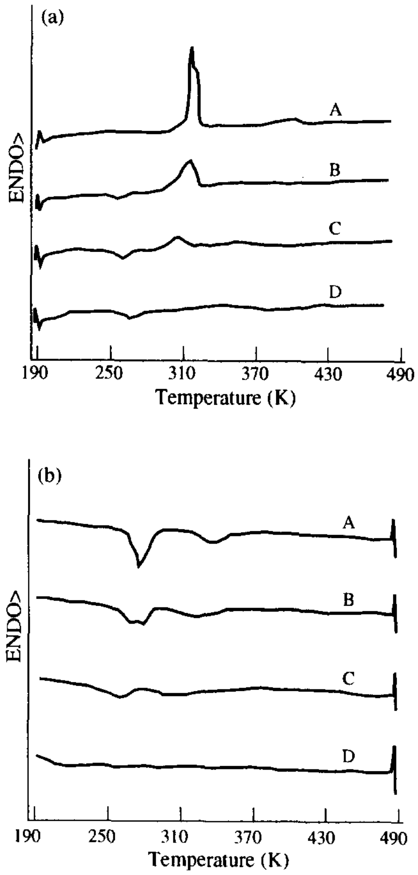

Figure 7 D.s.c. heating curves of PCL/BCL60 copolyester blends (4.1) quenched after treating at 530 K for different transesterification times (heating rate 20 K min^{-1}) and d.s.c. cooling curves of PCL/BCL60 copolyester blends (4/1) after treating at 530 K for different transesterification times (cooling rate 20 K min^{-1}): (A) 0 min; (B) 5 min; (C) 10 min; (D) 20 min

concentrations of polymer diluents, Keith *et al.*[11] showed that 'the role of diluents (miscible second component) is not a passive one associated with conventional ways with segregation of an uncrystallizable species during crystallization. Rather there appears to be an interaction between host and diluent polymers strong enough to cause significant modification of crystal growth processes on a molecular scale. This interaction is presumably polar in origin and may well require true thermodynamic compatibility between host and diluent'. However, in our case both BCL and TCL copolyesters cannot have any intimate specific molecular interaction with PCL in the blends. Nojima *et al.*[12] also showed that in binary blends of PCL and CL–butadiene diblock copolymers, in which there is not any intimate specific molecular interaction between components in the blends, PCL can grow very regular ringed spherulites. Such a fact implies that the said specific molecular interaction is not a necessary condition for improving the formation of PCL ringed spherulites in the blends.

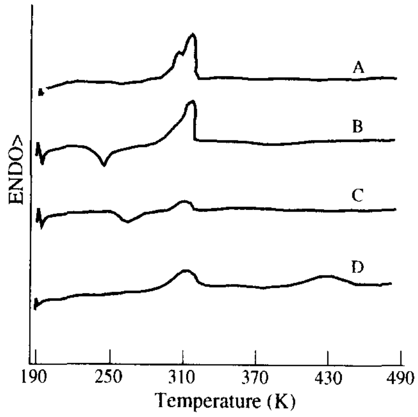

Figure 8 D.s.c. heating curves of PCL/BCL copolyester blends (4/1) with different copolyesters quenched after treating at 530 K for 10 min (heating rate 20 K min^{-1}): (A) PCL/BCL39; (B) PCL/BCL46; (C) PCL/BCL60; (D) PCL/BCL80

What is the main factor which determines the transesterification?

The miscibility (or good compatibility) should be favourable for occurrence of transesterification between components in the blends. The high BT content certainly also is a favourable condition for quickening transesterification in the blends. The PCL/BCL39 copolyester blend has the best compatibility between components in the blend, but the transesterification in this blend is the slowest. In such a case it should be understood that the higher BT content in BCL copolyesters is playing a more important role in quickening the transesterification. However, the most rapid transesterification does not occur in the PCL/BCL80 copolyester blend; on the contrary, the transesterification reaction in the

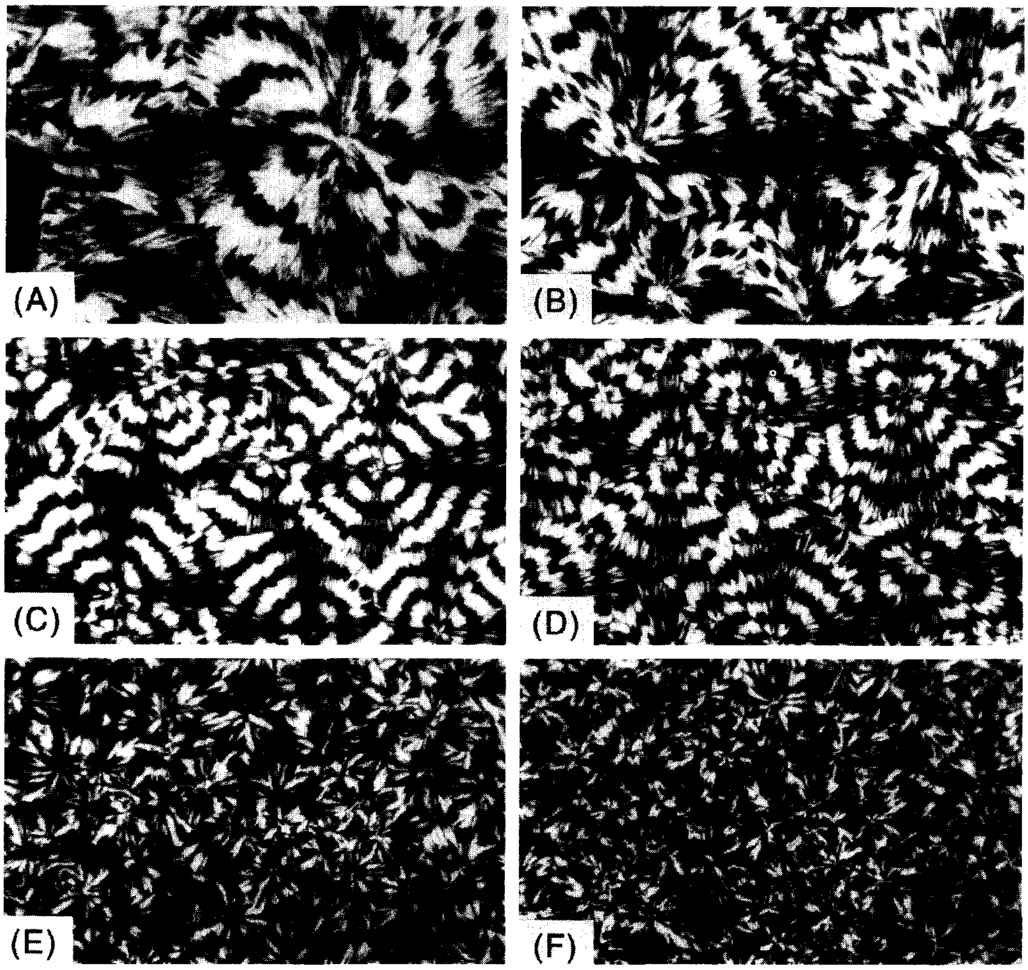

Figure 9 Polarized light micrographs of PCL/BCL39 copolyester (4/1) isothermally crystallized at 40°C after treating at 530 K for different times: (A) 1 min; (B) 2 min; (C) 5 min; (D) 40 min; (E) 60 min; (F) 120 min

PCL/BCL60 copolyester blend has the maximum reaction rate. Such experimental results exhibit that, despite the highest BT content in BCL80 copolyester, it is less compatible with PCL than BCL60 copolyester; therefore, the transesterification in PCL/BCL80 copolyester blend is less rapid than that in PCL/BCL60 copolyester blend. Both better compatibility and sufficiently high BT content are simultaneously favourable for the trans-reaction in PCL/BCL60 copolyester blend.

How should the two stages of the ringed spherulite formation in the transesterified PCL/BCL blends copolyester be understood?

In the first stage the PCL ringed spherulite patterns in the transesterified blends become better. How can such a phenomenon be explained? Since the high BT content in BCL copolyesters is a more important factor for the transesterification of the PCL/BCL copolyester blends. In the first stage the transesterification should mainly occur between the high BT content copolyester and pure PCL macromolecules. It is difficult to imagine that the breaking of PCL molecular chains is favourable for the formation of ringed spherulites in the PCL/BCL copolyester blends. In fact in any copolyester there is a compositional heterogeneity, i.e. any low BT content copolyester includes a part of the high BT content components. The BT contents in *Table 1* show the average BT contents in corresponding BCL copolyesters. Therefore, in the first stage of transesterification in any PCL/BCL copolyester blend the average BT content decreases and simultaneously the BT contents between the different copolyester macromolecules become more or less homogeneous. Just such a result for the transesterification in the blends may be an important influence on the formation of the ringed spherulites in the blends.

Of course, in the first stage all along the requisite amount of pure PCL chains or long PCL blocks should be retained to grow the spherulites or ringed spherulites in the PCL/BCL copolyester blends. Here, it should be noted that up to now the mechanism for the formation of ringed spherulites still remained unclear including the reason why a compositionally homogeneous copolyester component in the PCL/BCL copolyester blends can improve the ringed spherulite patterns so evidently.

In the second stage the PCL ringed spherulite patterns in the transesterified blends become worse. Such a phenomenon is easily understood, because, in the process of transesterification, PCL macromolecular chains are continuously broken, and such results certainly lead to decreasing the PCL crystallization ability to grow spherulites. In the end the spherulites are observed with difficulty.

The two stages of the ringed spherulite formation are closely linked with the two stages of the transesterification in the PCL/BCL copolyester blends.

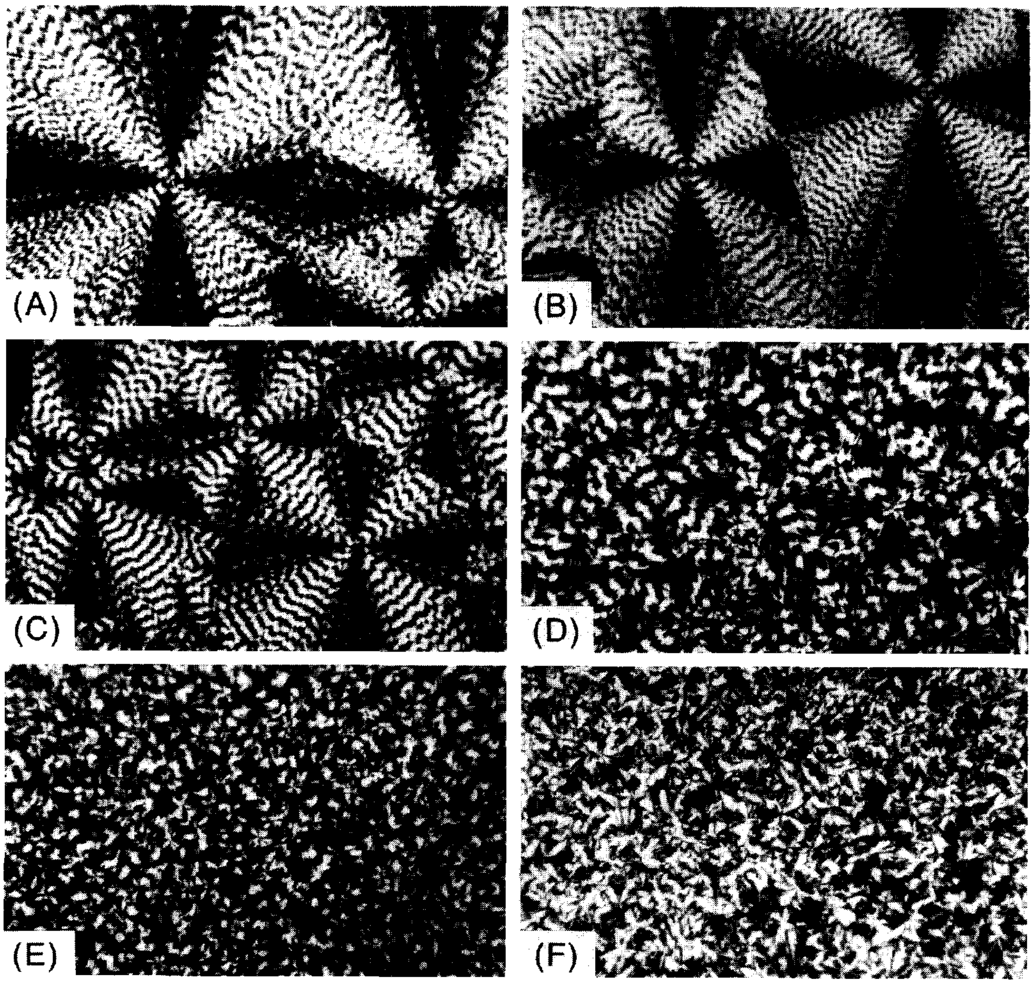

Figure 10 Polarized light micrographs of PCL/BCL60 copolyester (4/1) isothermally crystallized at 40°C after treating at 530 K for different times: (A) 2 min; (B) 5 min; (C) 10 min; (D) 20 min; (E) 30 min; (F) 60 min

CONCLUSION

The addition of non-crystallizable BCL copolyester in which both BT and CL segments cannot crystallize in the PCL/BCL copolyester blends can evidently influence the formation of ringed spherulites of PCL in the blends.

If the BCL copolyesters are miscible or compatible in some degree with PCL, it would slow down the crystallization of PCL and be favourable for the formation of the ringed spherulites.

It is not certain if the higher glass transition temperature of the second component in the blends is favourable for the formation of the ringed spherulites.

In PCL/BCL copolyester blends an intimate specific molecular interaction does not exist. It is necessary to investigate further the role of the specific molecular interaction or other interaction factors in the formation of the ringed spherulites in such kinds of blends.

The transesterification in the PCL/BCL copolyester blends depends on two factors: first, miscibility or compatibility between the components in the blends; second, BT content of the copolyester. The latter factor plays a more important role in the transesterification.

The transesterification in the PCL/BCL copolyester blends certainly leads to breaking of the PCL macromolecular chain; simultaneously, it decreases the average BT content of copolyesters and makes the copolyester component in the blends compositionally homogeneous. The results exhibit very evident improvement of the ringed spherulite patterns. The transesterification in some middle stage has the best influence on the morphology of ringed spherulites in the blends generally. However, the mechanism of such a process needs further investigation.

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