

A Study on Blends of Liquid Crystalline Copolyesters with Polycarbonate. II. Transesterification Control

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SYNOPSIS

The inhibited and catalyzed ester exchange (transesterification) during melt blending of poly(bisphenol-A carbonate) (PC) and liquid crystalline poly(oxybenzoate-co-ethylene terephthalate) (POB-PET 40/60; P46) was investigated with differential scanning calorimetry. It was found that the ester exchange between P46 and PC was effectively inhibited for a 20% P46 blend at 240°C, as further confirmed by nuclear magnetic spectroscopy. When the blending temperature and P46 concentration increased, only the transesterification between the PET segment in P46 and PC took place under inhibition. The morphology of the blends was analyzed with scanning electron microscopy and displayed a disconnected interface between P46 and PC under inhibition. Conversely, the transesterification took place between the POB segment in P46 and PC when a catalyst was added.

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INTRODUCTION

Liquid crystalline polymer (LCP) blends have been studied extensively in recent years.^{1,2} The motivation was first to use the high-tensile modulus of the LCPs in the solid state to reinforce the matrix polymers. Second, the low viscosity of the LCPs can reduce the overall viscosity of the blend and is a good processing aid. In general, blending several percent to about 20% of LCP with matrix polymers would give the two mentioned advantages without incurring the high cost of the LCP.

The homogeneity of polymer blends depends on the compatibility or the interaction between polymers. The degree of interaction between two polymers is best described by the free energy of mixing, ΔG , which contains enthalpic (ΔH) and entropic (ΔS) contributions. For a blend to be a single phase, the necessary condition is $\Delta G < 0$. The entropy terms are usually small, and the enthalpy terms dominate the free energy of mixing in polymer blends. In general, the favorable (exothermic) heat of mixing resulted from some interaction between

the polymers. The introduction of interacting groups by chemical modification of a polymer or by copolymerization can result in a negative contribution to the enthalpy of mixing.

The enthalpy of mixing rigid-rod LCPs with a flexible-coil polymer was mostly positive. Consequently, phase separation of the LCP blend occurred during processing, where high stress and high temperature existed.³ Introducing some kind of interaction between these two dissimilar polymers is necessary to improve the compatibility of the two polymers. The previous work by our group⁴ was concerned with the compatibility by the transesterification between polycarbonate (PC) and liquid crystalline poly(oxybenzoate-co-ethylene terephthalate) (POB-PET) of composition 40/60, denoted as P46. The main result was that for blends containing more than 20% P46 the compatibility between the two polymers increased with the ester exchange reaction. As transesterification continues, the blends convert first to block copolymers and, finally, to random copolymers.⁵ When the blends are in the form of random copolymers, the benefits of adding LCP to the matrix will be lost. To have some transesterification between the liquid crystalline copolyester and the matrix polymer without losing the liquid crystalline characteristics becomes

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an important research goal. This work was intended to control the transesterification by using catalysts or inhibitors. The ideal situation is that the ester exchange reaction can be stopped at the point where mostly the PET segment was reacted with PC (for compatibility) and without proceeding to the POB segment (for liquid crystalline). In this way, the liquid crystalline characteristics of the P46 blend will be retained.

EXPERIMENTAL

Materials

Liquid crystalline poly(oxybenzoate-*co*-ethylene terephthalate) (POB-PET) was synthesized by adding *p*-acetoxybenzoic acid monomers to poly(ethylene terephthalate) (PET) following the method described in the literature.⁶ The intrinsic viscosity of the PET used in the synthesis was 0.6 dL/g. The *p*-acetoxybenzoic acid monomer was purchased from Shang Hu Corp. The composition of POB-PET was 40/60, and it was termed P46. P46 exhibited birefringence when it was heated up to 300°C and then cooled down. Polycarbonate (PC) was obtained from the Shin Kwang Corp. The number-average molecular weight of the PC was 17,000. The chemical structures of P46 and PC are shown in Figure 1.

Methods

The powder of the liquid crystalline P46 and PC pellets was dried at 110°C under vacuum for 8 h prior to the mixing. Thirty grams of the mixtures of P46 and PC in different weight ratios were put into a Brabender mixer. To study the effect of the inhibition, three sets of experiments of different composition were carried out: 20, 30, and 40% P46 in the matrix of PC. Triphenyl phosphate and tetrabutylorthotitanate (TBOT), both 0.5% by weight, were used as an inhibitor and a catalyst, respectively, for controlling the ester exchange between PC and P46. They were added to the mixture separately and dispersed with a spatula for 10 min. Then, the mixture was put into a Brabender. The speed of the roller blade was 50 rpm. The blending temperatures were set at 240, 250, and 260°C.

The thermal analysis of the blends was carried out with a DuPont 2910 differential scanning calorimeter (DSC). The samples were heated up from 30 to 220°C at a heating rate of 20°C per min and were maintained at 220°C for 1 min. Then, the samples were quenched down to 0°C with liquid nitrogen. The samples were heated again from 0 to 300°C at the same heating rate. The DSC curves of the samples were taken the second time when the samples were heated up at the heating rate of 20°C per min. For the chemical structure analysis, the blends were dissolved in deuterated chloroform for 4 h;

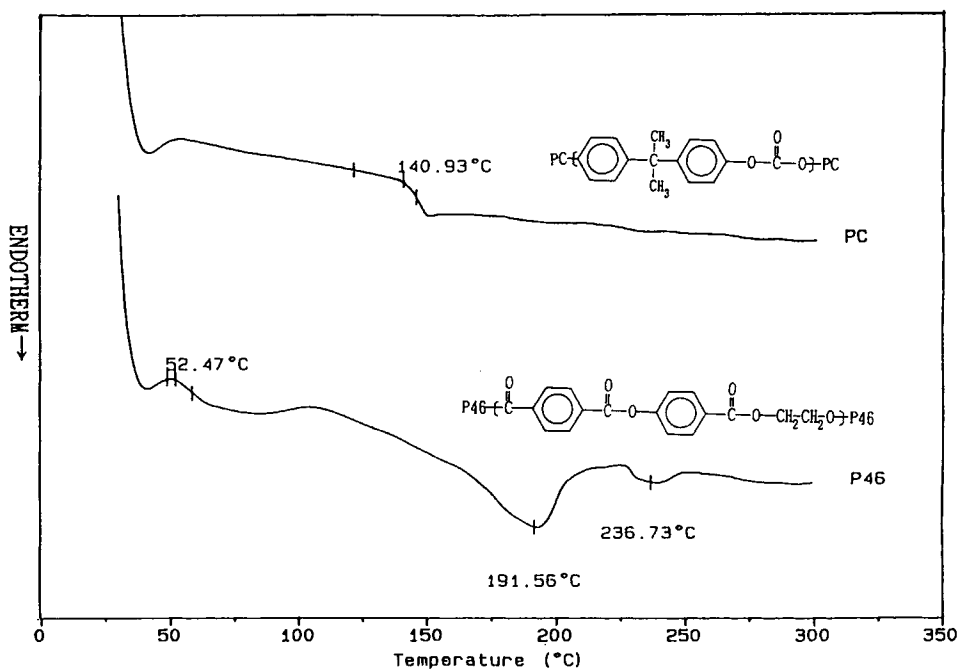


Figure 1 The chemical structures and the differential scanning calorimetry curves of PC and P46 at a heating rate of 20°C per min.

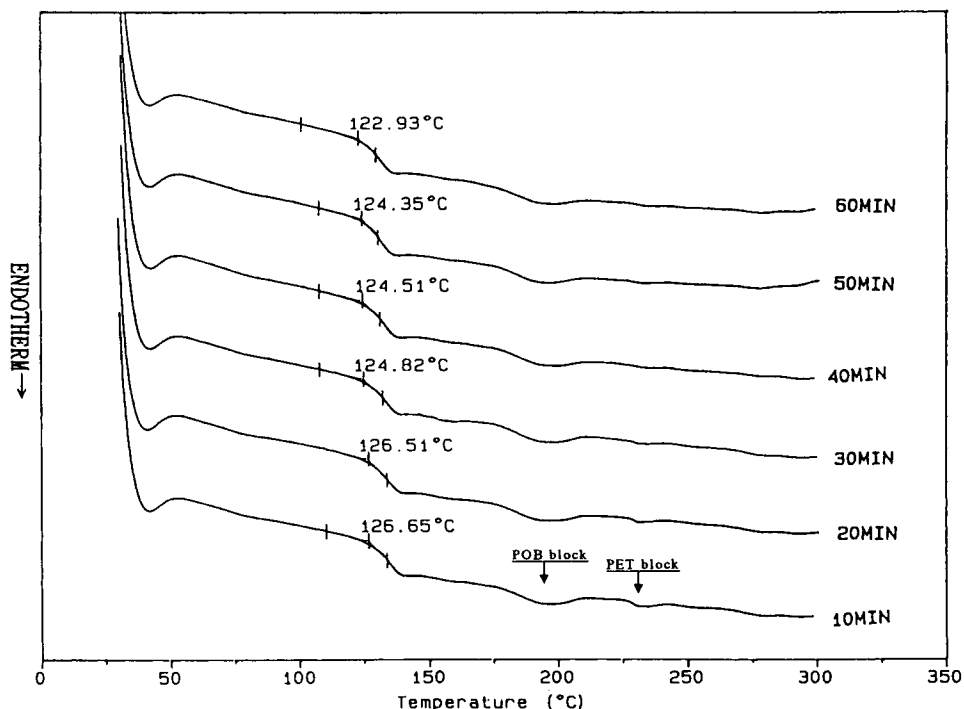


Figure 2 The differential scanning calorimetry curves of the blend containing 20% P46 after being mixed for different times at 240°C.

then, the undissolved particles were filtered with a syringe filter. Tetramethylsilane was added to the solution as an internal reference standard, and the liquid mixture was put in a nuclear magnetic resonance (NMR) tube. A Varian Fourier transformed NMR (unity-300) was used for this study. For the morphology analysis, the blends were put in the DSC and heated at a heating rate of 40°C per min to 220°C, remaining at 220°C for 1 min and air-cooled to room temperature. The samples were taken out of the DSC and quenched in liquid nitrogen. Then, the samples were fractured and coated with 10 nm-thick gold for scanning electron microscopy study. The trace of the residual catalyst was analyzed with a wavelength dispersive spectrometer (WDS), Microspec WDS 3 pc, attached to a Hitachi S-2500 scanning electron microscopy.

RESULTS AND DISCUSSION

The chemical structures and the DSC curves of PC and P46 are shown in Figure 1. The glass transition temperatures are 141°C for the PC and 52.5°C for P46, respectively. Two melting peaks appeared for the P46 case. The one at 191.56°C represents the diluted melting point of the POB block in P46. The other one at 236.73°C is the melting point of the

PET block in P46. The P46 is, therefore, a block copolymer. In Figure 2, the DSC curves of different blending times of the 20% P46 blend at 240°C are shown. The glass transition temperature (T_g) of the PC and P46 decreased with blending time from 126.65°C at 10 min to 122.93°C at 60 min. The decrease of the T_g might be due to a partial plastizing and a partial ester exchange effect, as explained in our previous article.⁴ The melting peak of the PET block disappeared, and that of the POB block, after 60 min. When triphenylphosphate was added to the blend, the T_g of the blend decreased less with the blending time.

Additionally, the melting peaks of PET and POB were preserved with time, as shown in Figure 3. As the concentration of P46 in the blend increased to 30% and the blending temperature increased to 260°C, the T_g of the blend decreased dramatically to 108.83°C at 60 min blending time, as shown in Figure 4. In Figure 4, both the melting peaks of PET and POB almost totally disappeared after 60 min. In the case of inhibited blend, the T_g of the 30% P46 blend was retained around 123°C throughout the 60 min, as in Figure 5. In Figure 5, the melting peak of the PET block disappeared, and the melting peak of the POB block still existed after 60 min. This is an interesting effect in that the triphenylphosphate inhibited the ester exchange between the

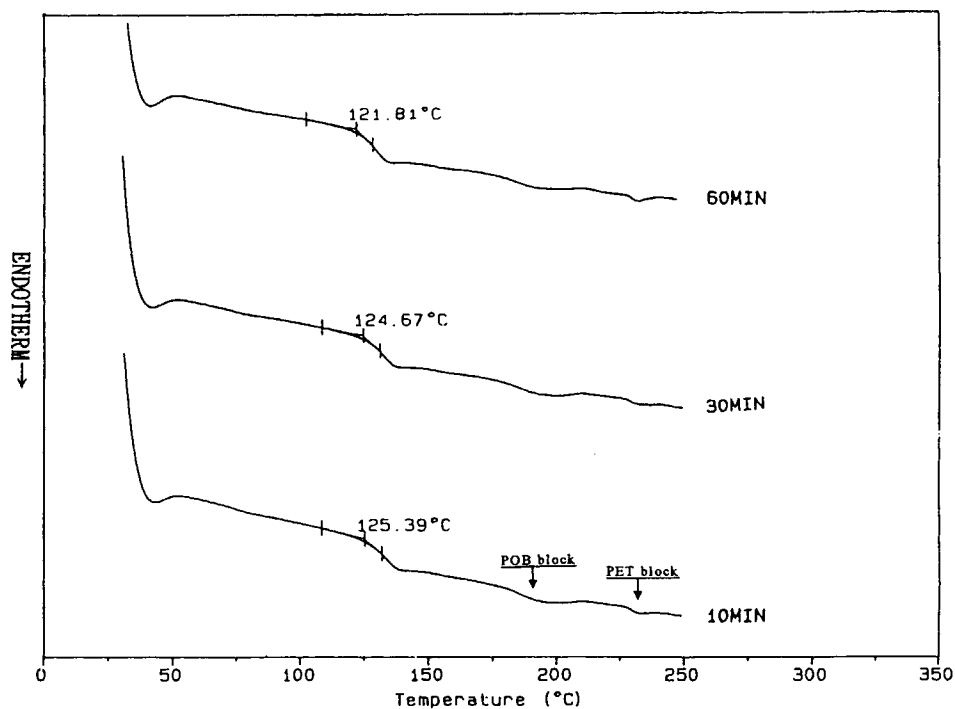


Figure 3 The differential scanning calorimetry curves of the blend containing 20% P46 and 0.5% triphenylphosphate after being mixed for different times at 240°C.

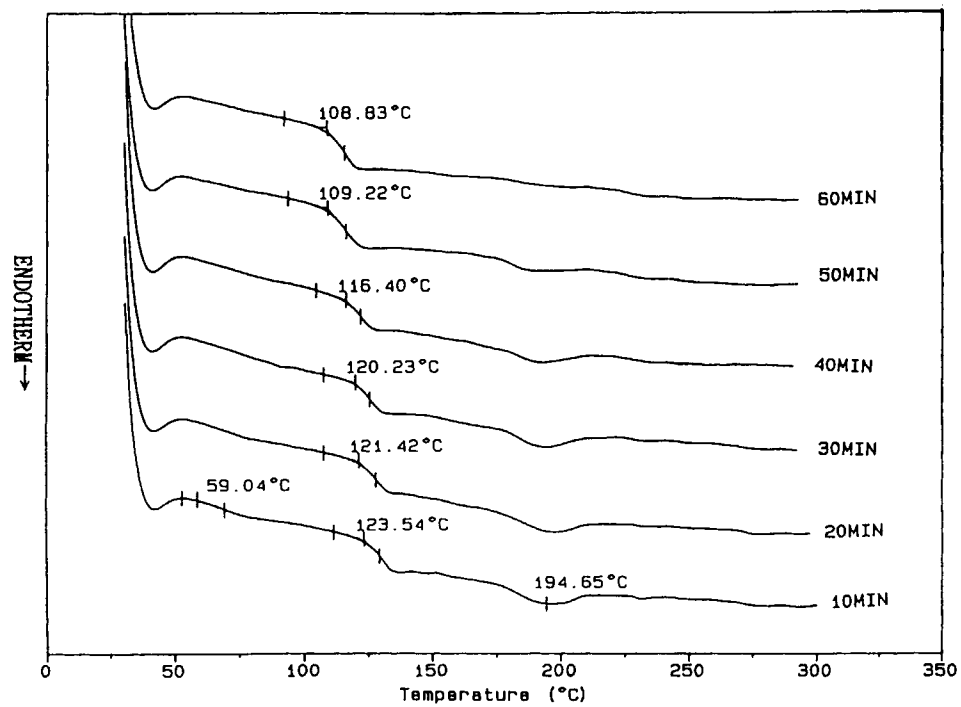


Figure 4 The differential scanning calorimetry curves of the blend containing 30% P46 after being mixed for different times at 260°C.

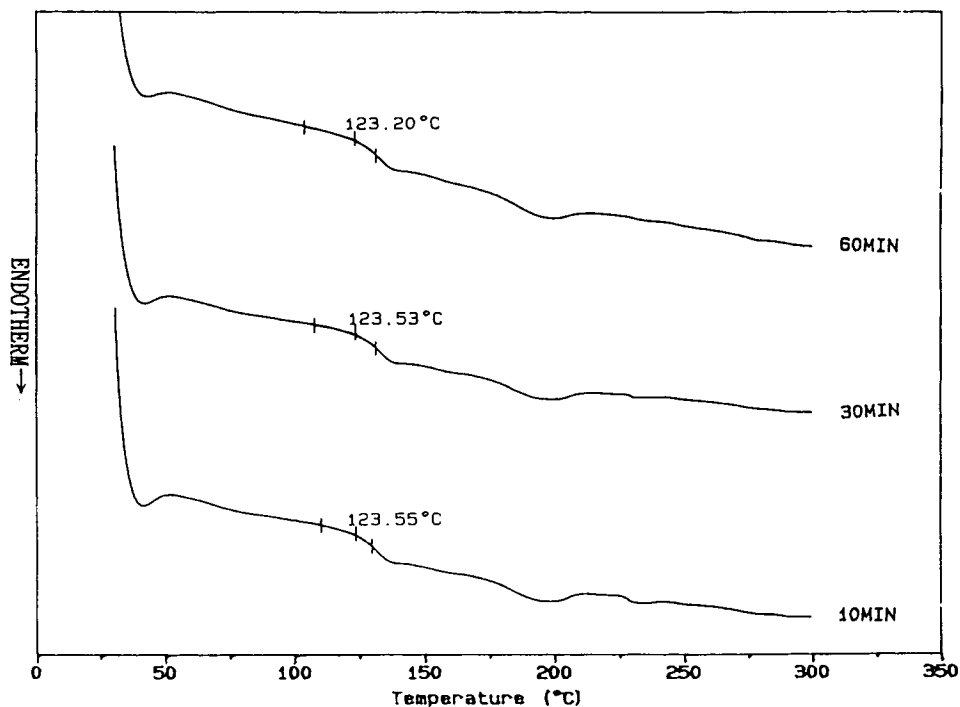


Figure 5 The differential scanning calorimetry curves of the blend containing 30% P46 and 0.5% triphenylphosphate after being mixed for different times at 260°C.

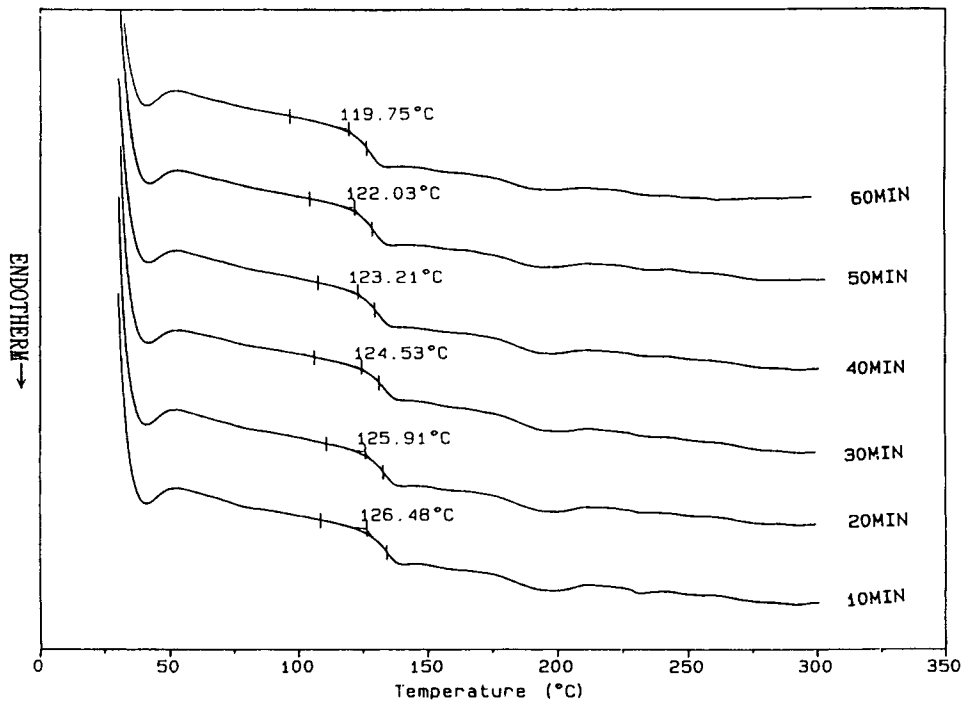


Figure 6 The differential scanning calorimetry curves of the blend containing 20% P46 after being mixed for different times at 250°C.

PC and the POB block more than that between the PC and the PET block in P46. In Figure 6, the T_g of the 20% P46 blend decreased to 119.75°C after 60 min at 250°C. Moreover, the melting peak of the PET block disappeared and the melting peak of the POB block remained. When the catalyst was added to the mixture, the T_g of the blend decreased just a little faster than that in the case of the blend without adding the catalyst, as in Figure 7. Also, the melting peak of the POB block disappeared, and the melting peak of the PET block remained. This is contrary to the case of the inhibited blend.

The micrographs of 20% P46 blends from scanning electron microscopy study are shown in Figure 8. In Figure 8(a), it is shown that after 60 min mixing at 260°C there were only a few 0.5 micron droplets left. On the contrary, there were quite a few 1 micron droplets left in the case of the inhibited blend under the same blending conditions, as shown in Figure 8(b). For the 30% P46 blend, droplets of less than 1 micron appeared after 40 min at 260°C. In the inhibited case, there were P46 droplets larger than 2.5 microns and the droplets seemed disconnected from the PC matrix, as shown in Figure 8(c) and (d). As the blending time increased, the 30% P46 blend became more homogeneous. In the inhibited case, there were still 1.5 micron droplets left. The same blend morphology trend can be observed

for longer blending times and higher P46 concentration in the blend, as in Figure 9. After being mixed at 260°C for 60 min, there were only a few 1 micron droplets left in both the 30 and 40% P46 blend, as shown in Figure 9(a) and (c), whereas, the inhibited blends displayed distinctively two phases with 1.5 micron P46 droplets dispersed in the PC matrix.

Further evidence on the effect of inhibition can be found in the nuclear magnetic resonance (NMR) study. Figure 10(a)–(c) represents the ^{13}C -NMR spectra of PC, the 20% P46 blend with inhibition, and the 20% P46 blend, respectively. The ethylene peak from the PET block appeared at 63 ppm and the ester peak from P46 appeared at 165 ppm clearly for the case of 20% P46 blend, as in Figure 10(c). This is an indication that the ester exchange took place and the two functional groups were attached to the PC molecule. For the inhibited case, in Figure 10(b), the two peaks are much smaller. Therefore, the inhibitor, triphenylphosphate, was effective in the case of the 20% P46 blend.

As mentioned in the literature,⁷ there were residual catalysts such as the titanium compound or Sb_2O_3 left after the polymerization of PET. A wavelength dispersive spectrometer (WDS) analysis on the PET used in the synthesis of P46 was carried out. There was about 0.064% Sb metal found in the PET. A possible explanation on the

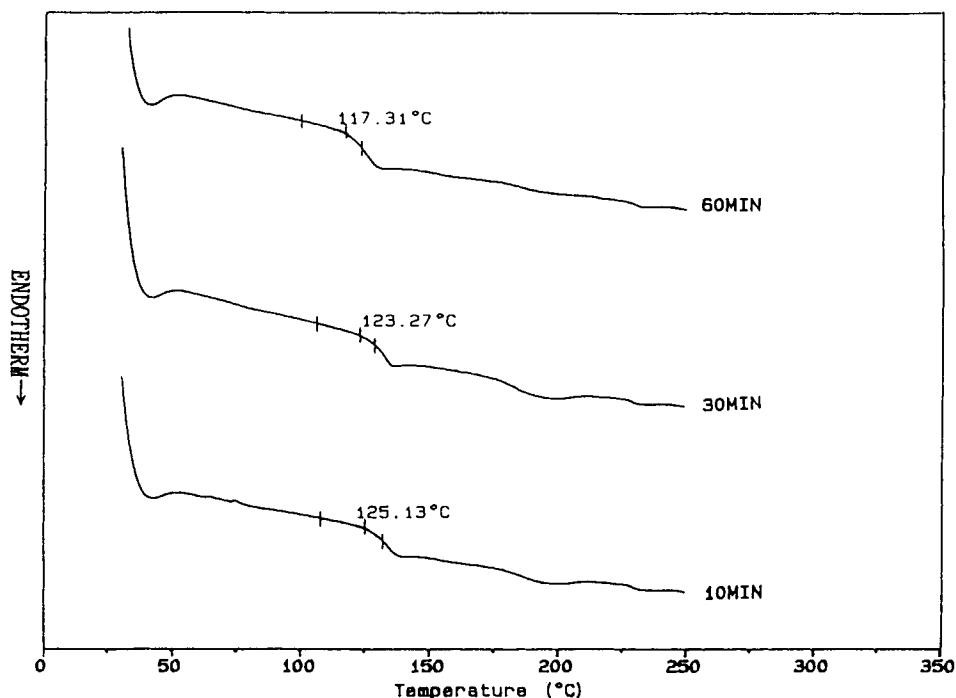


Figure 7 The differential scanning calorimetry curves of the blend containing 20% P46 and 0.5% TBOT after being mixed for different times at 250°C.

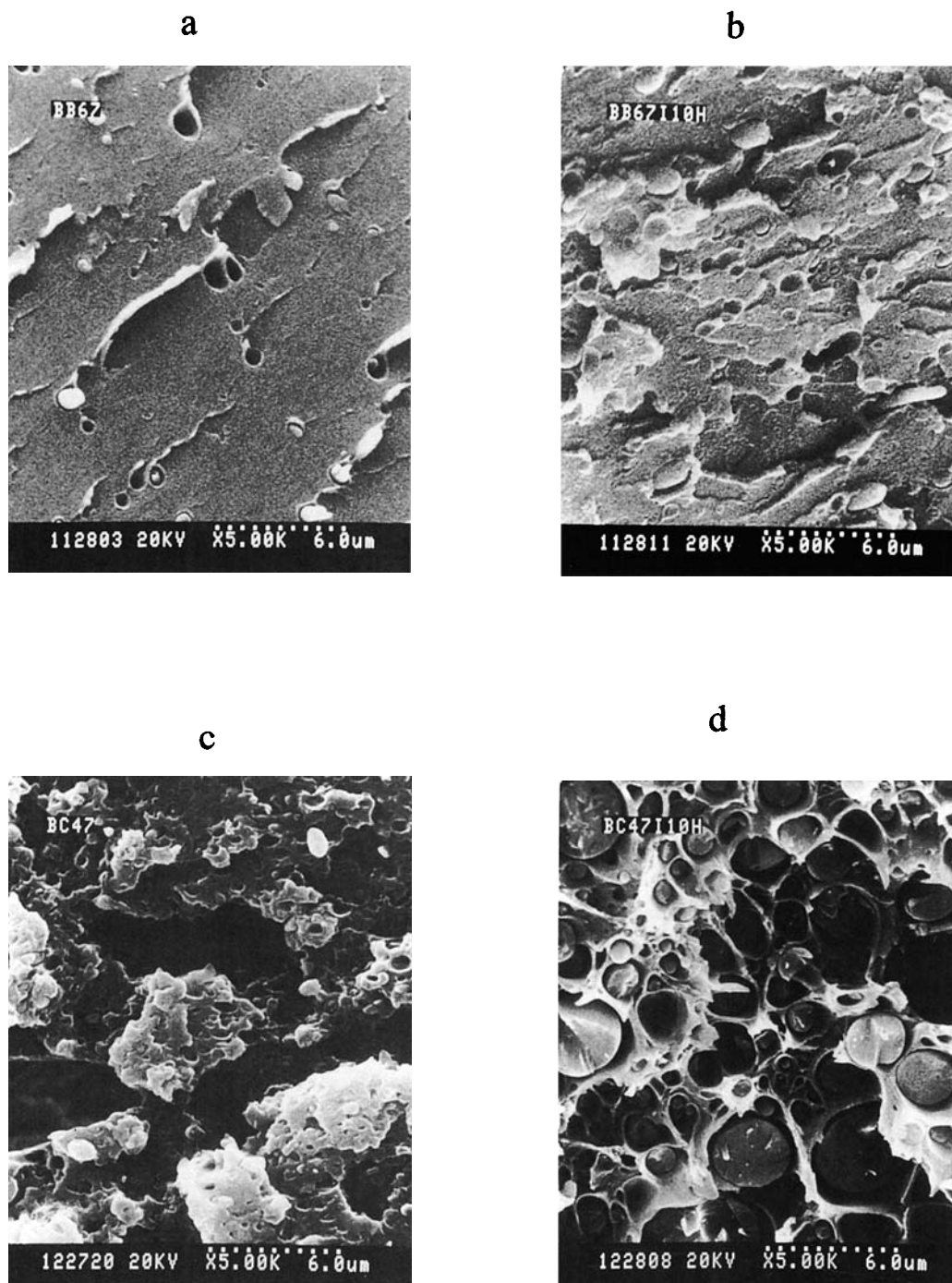


Figure 8 SEM micrographs of (a) 20% P46 blend mixed at 260°C for 60 min, (b) inhibited 20% P46 blend mixed at 260°C for 60 min, (c) 30% P46 blend mixed at 260°C for 40 min, and (d) inhibited 30% P46 blend mixed at 260°C for 40 min.

selective inhibition of the ester exchange between the POB–PET and the PC was as follows: First, one assumed that the phosphate inhibitor was dispersed homogeneously in the blend. Then, the phosphate reacted with the residual catalyst Sb_2O_3

in the PET segment. While in POB segment, the phosphate remained. Therefore, the ester exchange took place between the PET segment and the PC first. In the case of the catalyzed blend, the concentration of TBOT in the POB segment,

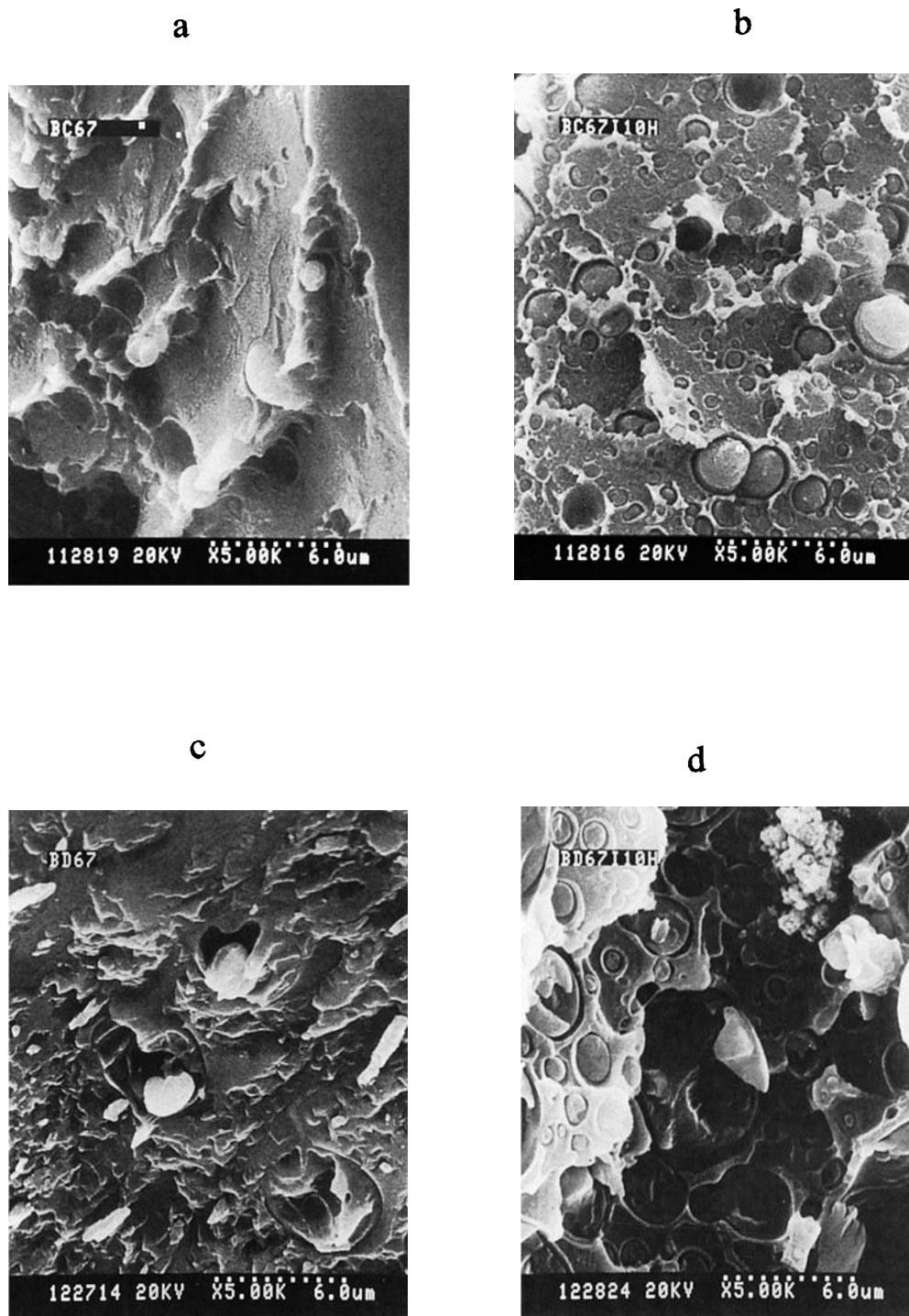


Figure 9 SEM micrographs of (a) 30% P46 blend mixed at 260°C for 60 min, (b) inhibited 30% P46 blend mixed at 260°C for 60 min, (c) 40% P46 blend mixed at 260°C for 60 min, and (d) inhibited 40% P46 blend mixed at 260°C for 60 min.

0.5%, was higher than that of the Sb_2O_3 already existing in PET segment. Therefore, the ester exchange took place first between the POB segment and PC.

CONCLUSION

The transesterification between P46 and PC in a 20% P46 blend at 240°C was effectively inhibited

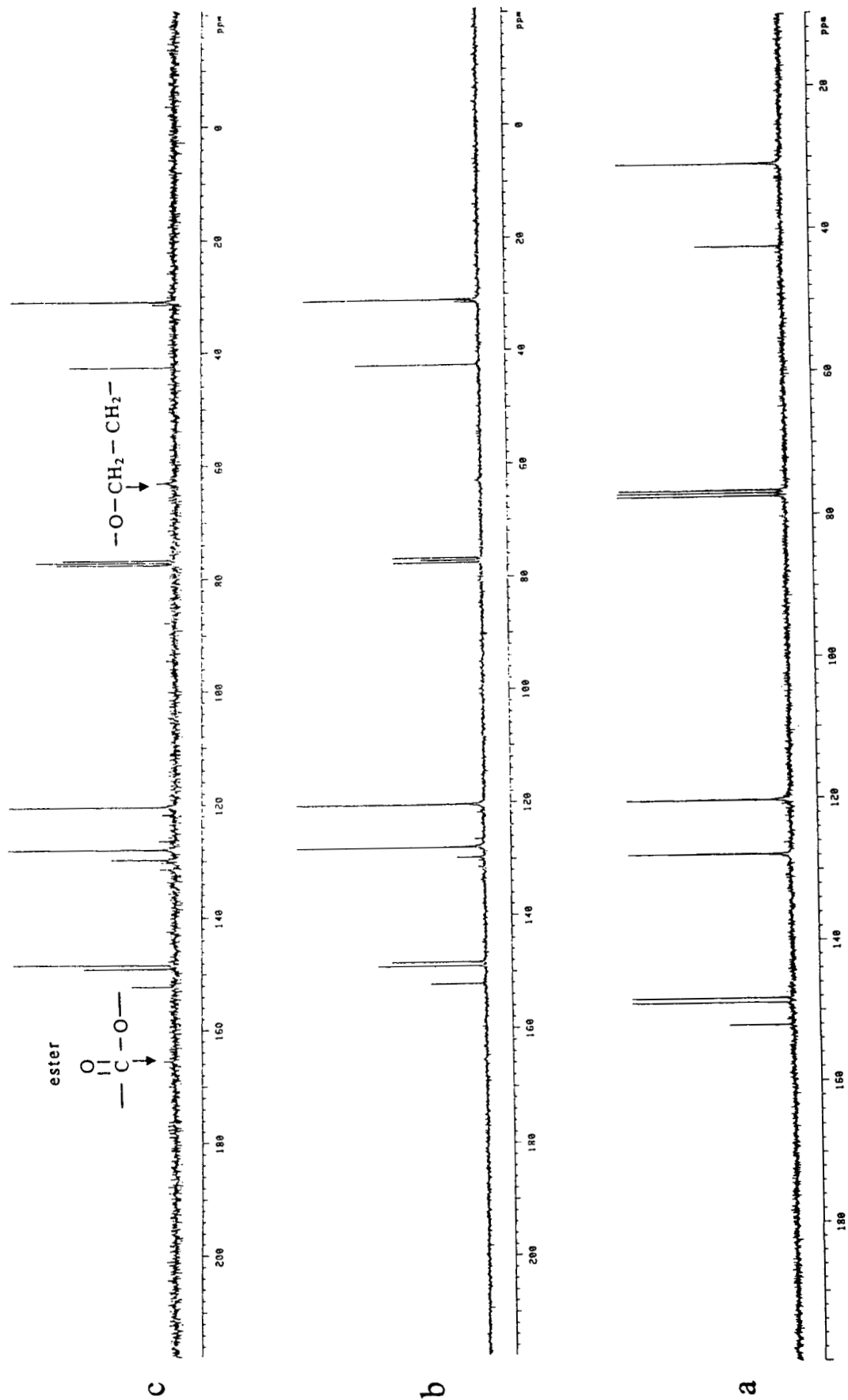


Figure 10 The ^{13}C -NMR spectroscopy of (a) PC, (b) inhibited 20% P46 blend mixed at 260°C for 60 min extracted with deuterated chloroform, and (c) 20% P46 blend mixed at 260°C for 60 min extracted with deuterated chloroform.

by adding the phosphate compound. When both the blending temperature and the P46 concentration increased, only the ester exchange between the PET segment in P46 and PC took place. Conversely, only the transesterification between the POB segment in P46 and PC took place when the tin compound was added as the catalyst. The selective ester exchange between P46 and PC resulted from the concentration difference between the residual catalyst from polymerization and the inhibitor or the catalyst used in this study.

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REFERENCES

1. G. Kiss, *Polym. Eng. Sci.*, **27**, 410 (1987).
2. A. Kolhi, N. Chung, and R. A. Weiss, *Polym. Eng. Sci.*, **29**, 573 (1989).
3. P. Tang, J. A. Reimer, and M. M. Denn, *Macromolecules*, **26**, 4269 (1993).
4. K. F. Su and K. H. Wei, *J. Appl. Polym. Sci.*, **56**, 79 (1995).
5. R. S. Porter and L. H. Wang, *Polymer*, **33**, 2019 (1992).
6. T. H. Thinn, J. Y. Chen, and C. C. Lin, *J. Appl. Polym. Sci.*, **47**, 1233 (1993).
7. A. Golovoy, M. F. Cheung, K. R. Carduner, and M. J. Rokosz, *Polym. Eng. Sci.*, **29**, 1226-1231 (1989).

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