Effect of Di-*n*-dodecyl Phosphate on the Transesterification Reaction in a Poly(butylene terephthalate)/Polycarbonate Blend

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ABSTRACT: The transesterification behavior of a poly (butylene terephthalate) (PBT)/polycarbonate (PC) blend with the addition of di-*n*-dodecyl phosphate was studied with differential scanning calorimetry (DSC) and infrared spectroscopy. The effects of triphenyl phosphate (TPP) and di-*n*-dodecyl phosphate on the suppression of transesterification were compared. The differences in the crystallization and melting temperatures during the two heating and cooling cycles in the DSC measurements were lower than those of the virgin PBT/PC blend, and di-*n*-dodecyl phosphate inhibited the formation of a random copolyester but did not suppress the formation of a block copolyester. The crystallization temperature of the PBT/PC blend in the presence of di-*n*-dodecyl phosphate was higher than that of the blend in the presence of TPP. Di-*n*-dodecyl phosphate was thus more effective than TPP in the inhibition of transesterification between PBT and PC. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1099–1104, 2008

Key words: polycarbonates; polyesters; esterification; crystallization

INTRODUCTION

Blends of poly(butylene terephthalate) (PBT) and polycarbonate (PC) constitute an important type of commercial polymer material in which semicrystalline PBT provides chemical resistance and thermal stability and amorphous PC provides impact resistance, toughness, and dimensional stability at elevated temperatures. Santos and Guthrie[1] reviewed the current knowledge of the physical, mechanical, and chemical properties of PBT/PC blends and concluded that PBT/PC blends may undergo three types of exchange reactions during melt processing:[2,3] acidolysis (reaction between the carboxyl end groups of PBT with the carbonate groups of the PC), alcoholysis (reaction between the hydroxyl end groups of PBT with the carbonate groups of PC), and direct transesterification (reaction between the ester groups of PBT with the carbonate groups of PC). Generally, direct transesterification is the major exchange reaction between PBT and PC.[4,5] The progressive transesterification reactions result in a transformation of the initial homopolymers into block copolymers and finally into random copolymers.[6] Pompe and coworkers[4,7,8] investigated the dependence of the transesterification behavior of a PBT/PC melt blend on the copolymer content by means of

differential scanning calorimetry (DSC) and nuclear magnetic resonance. On the one hand, the formed copolymers influence the compatibility of PBT and PC. The glass-transition temperature (T_g) values of the PBT-rich and PC-rich phases approach each other with increasing copolymer content.[9] If the formed copolymer is too limited, the interphase adhesion between the PBT-rich phase and PC-rich phase will be poor, leading to the brittleness of the blends. On the other hand, transesterification influences the melting behavior.[10–12] At the transition from the initial homopolymers to the final random copolymers, the crystallization ability of PBT vanishes; thus, the increase in the extent of transesterification degrades the mechanical performance as well as the solvent resistance, chemical resistance, and thermal stability.[13] Moreover, if the transesterification reaction is not well controlled, the properties of the blends will change with different thermal histories. Therefore, controlling the transesterification reaction is important for PBT/PC blends.

It has been proved that the transesterification reaction is catalyzed by titanium residues that are present in PBT,[14,15] and the transesterification rate increases with a residual titanium catalyst.[7,14–17] The activity of a residual catalyst can be inhibited by the addition of stabilizers.[15,18–25] Di-*n*-octadecyl phosphate[18] and triphenyl phosphate (TPP)[21,22] are widely used as efficient transesterification inhibitors. Devaux et al.[18] analyzed the evolution of solubility in methylene chloride (CH_2Cl_2) in a 50/50 PC/PBT

blend without and with di-*n*-octadecyl phosphate as a stabilizer. The solubility was observed to be constant up to times longer than 100 min in the stabilized blend. For the pure PC/PBT blend, for shorter reaction times, a sharp decrease in the solubility was observed, whereas for longer times, a completely soluble product was obtained. Xiong[23] investigated the effect of TPP on the transesterification between PBT and PC, and it was reported that the reaction was strongly inhibited by a 1% concentration of TPP. Yang and Zhang[24] evaluated the effects of different transesterification inhibitors on the physical and thermal properties of PBT/PC blends. The addition of sodium biphosphate can raise the impact strength and thermostability of the blends. Bai et al.[25] studied the effects of TPP and disodium diphosphate (DSDP) on the transesterification between PBT and PC. Both TPP and DSDP can increase the Vicat soft temperature of the blend.

In this study, the effect of di-*n*-dodecyl phosphate on the reaction between PBT and PC was investigated with DSC and Fourier transform infrared (FTIR). For comparison, the effect of TPP was also included.

EXPERIMENTAL

Materials

The polymers used in this study are listed in Table I. The PBT was Grisuplast U (Premnitz, Germany), which was synthesized with 1.4×10^{-4} mol % tetra(isopropyl) titanate as a catalyst. The PC was Lexan 161 (General Electric Plastics, The Netherlands). Before any experiment, PBT and PC were dried at 120°C *in vacuo* for at least 24 h. TPP was purchased from Aldrich (density = 1.19 g/cm^3, purity > 97%) and used as received. Di-*n*-dodecyl phosphate (purity > 97%) was purchased from Harbin Jinma Addition Agent, Ltd. (Harbin, China). CH$_2$Cl$_2$, 1,1,2,2-tetrachlorethane (C$_2$H$_2$Cl$_4$), phenol (C$_6$H$_5$OH), and methanol were all chemical-grade and were purchased from Tianjin Chemical Reagent Factory (Tianjin, China).

Sample preparation

PBT/PC blends with a weight ratio of 40 : 20 were prepared in a Haake Rheocord 90 torque rheometer (Haake, Germany). The rotor speed, mixing time,

and chamber temperature were maintained at 70 rpm, 10 min, and 250°C, respectively. Di-*n*-dodecyl phosphate was added to the blend at concentrations of 0.5, 1, 1.5, and 2%. For comparison, PBT/PC/TPP was also prepared at TPP concentrations of 0.5 and 1.5%. The PBT/PC/di-*n*-dodecyl phosphate and PBT/PC/TPP blends were prepared under the same blending conditions. To analyze the effects of di-*n*-dodecyl phosphate and TPP on the crystallization temperature (T_c) of PBT, PBT/di-*n*-dodecyl phosphate and PBT/TPP blends with a di-*n*-dodecyl phosphate or TPP concentration of 1.5%, respectively, were also prepared.

The samples obtained from the Haake rheometer were extracted in CH$_2$Cl$_2$ for 48 h at 55°C to make sure that no PC fraction was reserved in the non-solute part. CH$_2$Cl$_2$ was used because it is a good solvent for PC. The insoluble fraction was further extracted in the mixed solvent of C$_2$H$_2$Cl$_4$ and C$_6$H$_5$OH in a 40/60 (w/w) ratio, which is a good solvent for PBT, at room temperature for 48 h. The solute in C$_2$H$_2$Cl$_4$/C$_6$H$_5$OH and in CH$_2$Cl$_2$ was precipitated with methanol, and the precipitate was dried for 24 h before further analysis.

Characterization

The T_g, melting point (T_m), and T_c values of the samples from the torque rheometer were tested with DSC (DSC-7, PerkinElmer). A thin slice of each material ($\approx$0.5 mm thick) was encapsulated in a DSC pan. These pans were cycled in a differential scanning calorimeter at 10°C/min between 50 and 290°C, with a 1-min hold period at the minimum temperature and a 3-min hold period at the maximum temperature. T_g was obtained with the specific heat by the half-step method, which is similar to the method used by Pompe and Haubler.[4] T_m was determined as the peak maximum of the melting peak. The temperature corresponding to the peak of the crystallization exotherm was taken as T_c. T_m and T_c during the first heating and cooling cycles were called TM1 and TC1, respectively. Those during the second heating and cooling cycles were called TM2 and TC2, respectively. The sample weight was 5–7 mg.

The infrared spectra of pure PC, pure PBT, the solute in CH$_2$Cl$_2$, and the solute in C$_2$H$_2$Cl$_4$/C$_6$H$_5$OH were obtained with a Nicolet 510P FTIR spectroscopy instrument. The scanning wave number was from 500 to 4000 cm^{-1}, and the spectral resolution was 20 cm^{-1}. For each sample, 150 scans were taken to produce a spectrum, from which the background spectrum was subtracted. The precipitate from the solution of CH$_2$Cl$_2$ and C$_2$H$_2$Cl$_4$/C$_6$H$_5$OH was first compressed into a film with a diameter of 10 mm and then was used for FTIR analysis without further treatment.

TABLE I
Characteristics of the Polymers Used in This Study

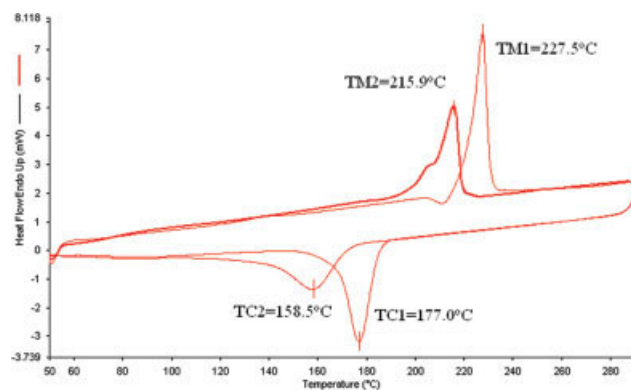|	M_w (kg/mol)	T_g (°C)	T_c (°C)	T_m (°C)
PBT	110.0	41.0	180.6	225.6
PC	36.5	148.9	—	—

Figure 1 DSC curves of the pure PBT/PC blend at a heating/cooling rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Figure 1 shows the DSC curves of the pure PBT/PC blend at the heating and cooling rate of 10°C/min. For clarity, T_g for the PC-rich phase in the blend is shown in Figure 2. T_g is 129.9°C, lower than that of pure PC, the value of which is 148.9°C, as listed in Table I. This means that there exists a certain kind of reaction between PBT and PC, the result of which acts as a compatibilizer to improve the compatibility of PBT and PC. Our observation is in agreement with the results of Porter and Wang.[9] In Figure 1, the PBT/PC blend during the secondary heating stage shows a double melting endotherm, with the main peak at 215.9°C and a smaller shoulder at 208.9°C. The smaller shoulder may be ascribed to the melting of thin lamellae formed during the cooling stage within the first time of the heating and cooling scan, as found by Hsiao et al.[26] TC1 is 177.0°C, 3.6°C lower than that of pure PBT. The fall of T_c results from the introduction of PC because of
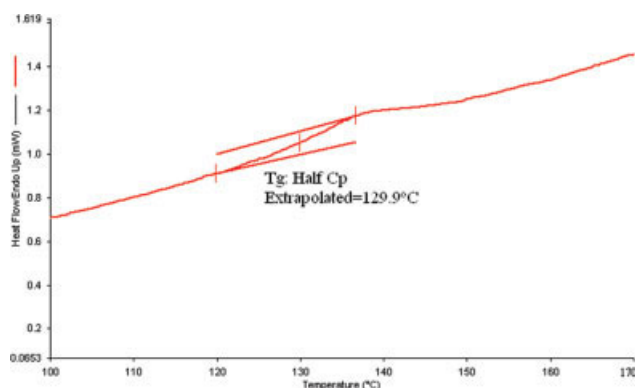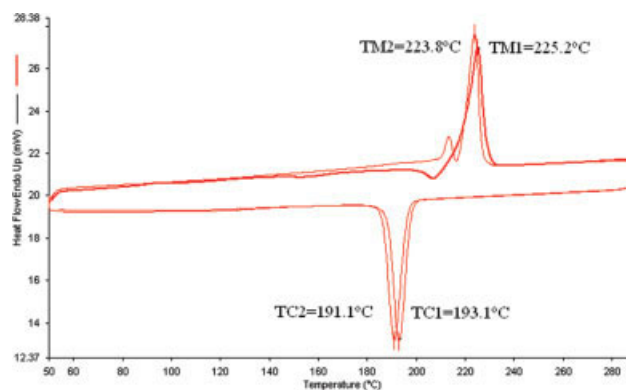

Figure 3 DSC curves of the PBT/PC blend at a di-*n*-dodecyl phosphate concentration of 1.5% and at a heating/cooling rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

its plasticizing effect. Also, the transesterification between PBT and PC during the blend compounding can lead to the fall. The values of TM2 and TC2 are lower than those of TM1 and TC1. The peak heights of TM2 and TC2 become shorter compared with those of TM1 and TC1. The occurrence of the transesterification reaction between PBT and PC during the heating and cooling cycles results in the decrease of the crystallinity of PBT.[13,14] In DSC, this is seen as a decrease in the melting peak, that is, the heat of fusion, as well as a decrease in the melting peak temperature.[20] Therefore, the differences of the melting temperature ($\Delta T_m = TM1 - TM2$) and crystallization temperature ($\Delta T_c = TC1 - TC2$) can be used to denote the extent of the transesterification reaction during the DSC scanning cycles.

Figure 3 presents the DSC curves of the PBT/PC blend with a di-*n*-dodecyl phosphate concentration of 1.5%. In contrast to those in Figure 1, apparently the peak heights and width of TM2 and TC2 are
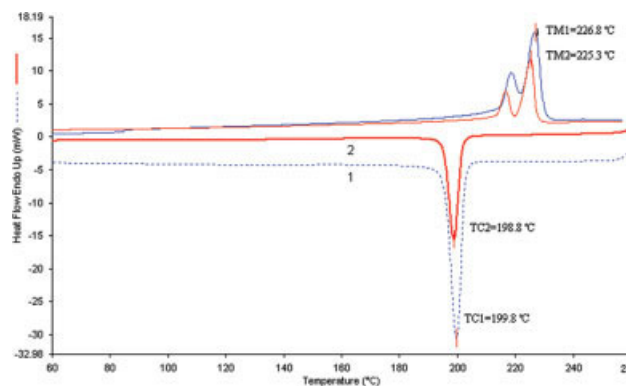

Figure 2 Determination of T_g corresponding to the PC-rich phase. C_p is the specific heat capacity. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 4 DSC curves of PBT with the addition of di-*n*-dodecyl phosphate and TPP: (1) di-*n*-dodecyl phosphate and (2) TPP. The concentration of di-*n*-dodecyl phosphate and TPP was 1.5%. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Effect of the Di-n-dodecyl Phosphate Content on the T_g, T_c, and T_m Values

Di-n-dodecyl phosphate content (%)	T_g (°C)	TM1 (°C)	TM2 (°C)	ΔT_m (°C)	TC1 (°C)	TC2 (°C)	ΔT_c (°C)
0	129.9	227.5	215.9	11.6	177.0	158.5	18.5
0.5	131.5	225.3	223.8	1.5	192.9	191.0	1.9
1	131.6	225.0	223.6	1.4	193.0	191.1	1.9
1.5	131.8	225.2	223.8	1.4	193.1	191.1	2.0
2	131.9	225.0	223.7	1.3	192.7	190.9	1.8

T_g is the temperature corresponding to the PC-rich phase in the PBT/PC blend.

similar to those of TM1 and TC1. The values of ΔT_m and ΔT_c are lower than those in Figure 1 for the pure PBT/PC blend. The introduction of di-n-dodecyl phosphate decreases the extent of transesterification during the DSC test cycles. TC1 in PBT/PC/di-n-dodecyl phosphate is 193.1°C, higher than that of pure PBT/PC. Furthermore, the value of TC1 is higher than that of pure PBT, the value of which is 180.6°C. In the PBT/PC blend, both the introduction of PC and the transesterification between PBT and PC can reduce the crystallization ability of PBT. Theoretically, the value of TC1 cannot be higher than that of pure PBT. Our experimental results may be due to the crystallization promotion behavior of di-n-dodecyl phosphate for PBT. Figure 4 gives the DSC curves of PBT with the addition of di-n-dodecyl phosphate or TPP at a concentration of 1.5%. The introduction of di-n-dodecyl phosphate increases T_c, which is 199.8°C and higher than that of pure PBT. Di-n-dodecyl phosphate can promote the crystallization behavior of PBT. The value of TC1 of the PBT/PC/di-n-dodecyl phosphate blend is lower than that of PBT/di-n-dodecyl phosphate with the same di-n-dodecyl phosphate content. The reason is that although di-n-dodecyl phosphate is an effective transesterification inhibitor, complete transesterification inhibition cannot be obtained. This point has been proved by Pompe and Haubler.[4] Also, the plasticizing effect of PC cannot be neglected.

Table II gives the T_g, TM1, TM2, TC1, and TC2 values of PBT/PC blends with different di-n-dodecyl phosphate contents. ΔT_c and ΔT_m are also shown. T_g corresponding to the PC-rich phase of the PBT/PC/di-n-dodecyl phosphate blend is higher than that of pure PBT/PC and does not change much with the increase in the di-n-dodecyl phosphate content. The values of TC1, ΔT_c, and ΔT_m also change little with the increase in the di-n-dodecyl phosphate content. The 0.5% concentration of di-n-dodecyl phosphate is enough for the transesterification reaction inhibition in the PBT/PC blend. Devaux et al.[6,18] discovered that the transesterification reaction can be controlled by additives capable of complexing the titanium catalyst residues in PBT. The extent of control is a func-

tion of the phosphate type and its concentration. Fortunato et al.[27,28] reported that one or more acidic OH groups in the molecule of the phosphorous additive permit the formation of adducts with Ti atoms, which can be considered inactive as a catalyst. Di-n-dodecyl phosphate involves one acidic OH group in the molecule and hence offers the control of the transesterification reaction between PBT and PC.

For comparison, the effect of TPP on the transesterification behavior is also examined. Table III lists the T_c and T_m values of the PBT/PC blend at the TPP concentrations of 0.5 and 1.5%. At the 1.5% concentration of TPP, the value of TC1 is 190.1°C. TC1 of the PBT/PC/TPP blend is higher than that of pure PBT/PC. The values of ΔT_m and ΔT_c for PBT/PC/TPP are lower than those of pure PBT/PC. TPP is an effective transesterification reaction inhibitor for the PBT/PC blend during blend compounding and during thermal treatment in DSC, as observed by Delimoy et al.[21]

A comparison of Tables II and III reveals the difference between di-n-dodecyl phosphate and TPP in the transesterification reaction inhibition. At a transesterification reaction inhibitor concentration of 1.5%, di-n-dodecyl phosphate produces a TC1 increase of 3.0°C in comparison with TPP, whereas at 0.5%, TC1 for di-n-dodecyl phosphate is 7.6°C higher than that for TPP. As shown in Figure 4, both di-n-dodecyl phosphate and TPP can promote the crystallization behavior of PBT, and T_c with di-n-dodecyl phosphate is 1°C higher than that with TPP. For the PBT/PC/di-n-dodecyl phosphate and PBT/PC/TPP blends, as the concentration of PC is the same, the effect of PC on the crystallization behavior of PBT is

TABLE III
Effect of TPP on the T_c and T_m Values

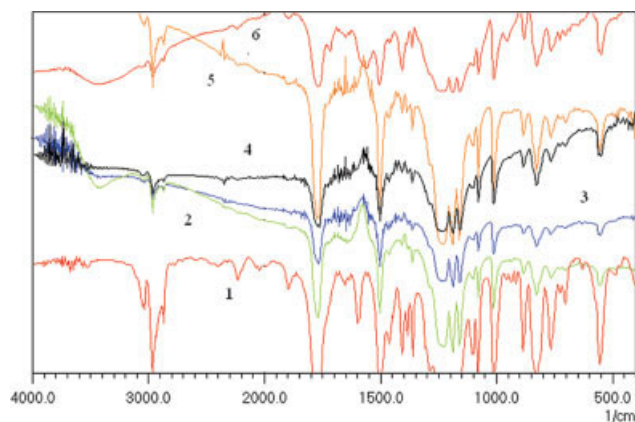| TPP content (%)	TM1 (°C)	TM2 (°C)	ΔT_m (°C)	TC1 (°C)	TC2 (°C)	ΔT_c (°C)
0	227.5	215.9	11.6	177.0	158.5	18.5
0.5	225.9	222.4	3.5	185.3	183.6	1.7
1.5	224.9	223.6	1.3	190.1	188.6	1.5

Figure 5 FTIR results of the solute in CH_2Cl_2: (1) PC, (2) 0.5% di-*n*-dodecyl phosphate, (3) 1% di-*n*-dodecyl phosphate, (4) 1.5% di-*n*- dodecyl phosphate, (5) 2% di-*n*-dodecyl phosphate, and (6) the pure PBT/PC blend. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 6 FTIR results of the solute in $C_2H_2Cl_4/C_6H_5OH$: (1) 2% di-*n*-dodecyl phosphate and (2) pure PBT. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the same. From this point of view, di-*n*-dodecyl phosphate is more effective than TPP for the inhibition of the transesterification reaction in the PBT/PC blend.

To further study the effect of di-*n*-dodecyl phosphate, samples from the Haake rheometer were extracted in CH_2Cl_2. Figure 5 presents the FTIR results of the solute in CH_2Cl_2. Without the addition of di-*n*-dodecyl phosphate, the FTIR curves of the solute exhibit a band at 1710 cm^{-1}, which is the special band of C=O in PBT.[7] With the addition of di-*n*-dodecyl phosphate, at 1710 cm^{-1}, no peak can be observed. The transesterification reaction between PBT and PC results in the formation of a block copolyester, which finally is transformed into a random copolyester. In the blend including random and block copolyesters, PC and the random copolyester can dissolve in CH_2Cl_2,[18] and the nonsolutes are PBT and the block copolyester. Figure 5 shows that no random copolyester is formed in the stabilized PBT/PC blend. Table IV gives the extracted solute fraction in CH_2Cl_2 of PBT/PC and PBT/PC/di-*n*-dodecyl phosphate. In our experiments, the blend ratio of PBT to PC is 60/40, and the PC weight fraction is 33.3%. The solute fraction should be 33.3% if the transesterification does not exist. As shown in Table

IV, for the pure PBT/PC blend, the solute fraction is 35.7%. The random copolyester is formed for the pure PBT/PC blend. For PBT/PC/di-*n*-dodecyl phosphate, the solute fraction is 21.3%. Part of PC is transformed into the block copolyester, and the random copolyester disappears. This means that di-*n*-dodecyl phosphate is an effective inhibitor for the formation of the random copolyester.

To minimize the effect of a possible PBT solute in CH_2Cl_2, the nonsolute in CH_2Cl_2 was further extracted in $C_2H_2Cl_4/C_6H_5OH$. Figure 6 presents the FTIR curves of the solute in $C_2H_2Cl_4/C_6H_5OH$. The solute exhibits a band at 1760 cm^{-1}, which is the special band of C=O in PC.[7] The solute does not include pure PC, which has been extracted by CH_2Cl_2. Therefore, the band is the band of the block copolyester between PBT and PC. It can here be concluded that di-*n*-dodecyl phosphate can inhibit the formation of the random copolyester but cannot completely inhibit the formation of the block copolyester.

In summary, although the block copolyester is present in the PBT/PC/di-*n*-dodecyl phosphate blends, di-*n*-dodecyl phosphate is still an effective transesterification inhibitor for the PBT/PC blend.

CONCLUSIONS

In this article, DSC results for PBT/PC/di-*n*-dodecyl phosphate and PBT/PC/TPP blends show that the crystalline temperatures of the two blends during the first cycle of heating and cooling in DSC are higher than those of the pure PBT/PC blend, and the differences in the crystalline temperatures of the two blends between the first and second heating and cooling cycles are lower than those of pure PBT/PC. Both di-*n*-dodecyl phosphate and TPP can suppress transesterification between PBT and PC. FTIR results

TABLE IV
Extracted Solute Fractions of Pure PBT/PC and PBT/PC/ Di-*n*-dodecyl Phosphate with a Di-*n*-dodecyl Phosphate Concentration of 2%

Sample	Solute fraction in CH_2Cl_2 (%)	Nonsolute fraction in CH_2Cl_2 (%)
Pure PBT/PC	35.7	64.3
PBT/PC/di-*n*-dodecyl phosphate	21.3	78.7

show that for the PBT/PC blend, the introduction of di-*n*-dodecyl phosphate can inhibit the formation of a random copolyester between PBT and PC but cannot completely suppress the transesterification between PBT and PC. At the same concentration of di-*n*-dodecyl phosphate and TPP, the crystalline temperature of PBT/PC/di-*n*-dodecyl phosphate is higher than that of PBT/PC/TPP. Therefore, compared with TPP, di-*n*-dodecyl phosphate is more effective for transesterification inhibition between PBT and PC.

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