Studies on the Role of Organophosphites in Polyester Blends: II. The Inhibition of Ester-Exchange Reactions

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Synopsis

Ester-exchange reactions during melt extrusion of polyarylate, polycarbonate, and polyethylene terephthalate ternary blends result in a decrease of the melting point and the heat of fusion of the poly(ethylene terephthalate). When an organophosphite is used to suppress the ester-exchange reactions, it was found that whenever the phosphite is converted into a phosphonate, there is little change in both the melting point and the heat of fusion of the polyethylene terephthalate during prolonged exposure to high temperature in the blends. [31]P nuclear magnetic resonance is employed to investigate the chemical changes and differential scanning calorimetry to evaluate the thermal stability of the blends. The organophosphite appears to be transformed through side-chain hydrolysis into other phosphorous species, such as diphosphonate in order to be an effective suppressant of the ester-exchange reactions.

INTRODUCTION

Ester-exchange reactions at high temperature in polyester blends have been extensively reported in the literature.[1–11] Transesterified copolymers may exhibit some advantages such as higher tensile strength as discussed by Mondragon and Nazabal in the polycarbonate/polyarylate blends.[12] However, the same blend displays poor impact properties as reported by Golovoy et al.[13]

Because ester-exchange reactions affect mechanical properties, their inhibition is a crucial element of the polymer blends technology. Control of processing conditions to minimize the extent of exchange reactions was discussed by Mondragon and Nazabal.[12] Iwakura et al. used diisocyanate to couple polyesters having terminal hydroxyl end groups to avoid exchange reactions in the preparation of polyester–urethane block copolymers.[14] Devaux et al. found that residual polymerization catalyst caused ester-exchange reactions.[15] Organophosphite was useful to inhibit the ester-exchange reactions by forming an octahedral complex with the catalyst. However, Droscher and Schmidt reported ester-exchange reaction of polyethylene terephthalate even in the absence of catalyst.[16] Other organophosphorus compounds has been reported to suppress the exchange reactions.[17]

In a recent article, we reported the results of inhibiting the ester-exchange reactions by organophosphites in a polyarylate/polycarbonate/poly(ethylene terephthalate) (PAr/PC/PET) ternary blend.[18] In subsequent tests, it was observed that merely adding the organophosphite to the blend is not sufficient. Conditions that promote conversion of the phosphite were found to be necessary.

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In this article we report a possible route for the inhibition of the exchange reactions by organophosphites. The phosphites appear to be transformed into phosphonates, which are effective inhibitors for the exchange reactions. Solid-state ^{31}P NMR was employed to investigate the chemical changes and differential scanning calorimetry (DSC) to evaluate the effectiveness of the stabilizer.

EXPERIMENTAL

Raw Materials. Polyarylate was received from Amoco Performance Products under the trade name Ardel D-100. Polycarbonate was acquired from Dow Chemical Co. (Calibre 300-3 and Calibre 300-15), and poly(ethylene terephthalate) (Cleartuf 1006B) was supplied by Goodyear Co. Ultranox 624 (bis(2,4-di-*t*-butylphenyl) pentaerythritol diphosphite) was supplied by Borg-Warner Chemicals. Stabaxol P-100 (polycarbodiimide) and Stabaxol KE 7646 (15% of Stabaxol P-100 in PET) were supplied by Mobay Corporation.

Stabilizer Concentrates. The stabilizers were incorporated into the blend by first preparing concentrates. The conditions of drying the resins for preparing the concentrates are summarized in Table I. A 10% by weight of Ultranox concentrate was designed. All the Ultranox used was fresh from sealed bottles. Polycarbonate concentrate was prepared by a twin-screw extruder; details of concentrate preparation have already been given. PET concentrates (with Stabaxol P-100) were used as received.

Blend Preparation. Polyarylate (PAr), polycarbonate (PC), and poly(ethylene terephthalate) (PET) were predried for at least 16 h under vacuum at 115°C prior to compounding. A Haake mini extruder model 245 was used. Temperature setting for the extruder was 280/300/290°C and the die section was set at 280°C. All the blends described in this study have the same composition with PAr/PC/PET = 50/20/30 by weight. The stabilizers used were at 0.5% by weight of Ultranox 624 and 0.25% of Stabaxol P-100. Dry pellets were premixed and then charged to the hopper of the extruder.

Phosphorus MAS NMR. The details of acquiring the phosphorus-31 MAS NMR spectra were described in the first article of this series.[19]

Calorimetric Measurement. A Mettler TA3000 thermal analysis system was used to evaluate the effectiveness of the stabilizer system. Data were collected and analyzed using the Mettler TC10A processor. In the DSC measurements samples were scanned from 30 to 280°C at 5°C/min. In the isothermal test, samples were scanned to 300°C at 20°C/min and held isothermally at

TABLE I
Summary of Concentrate Preparation in Twin Screw Extruder

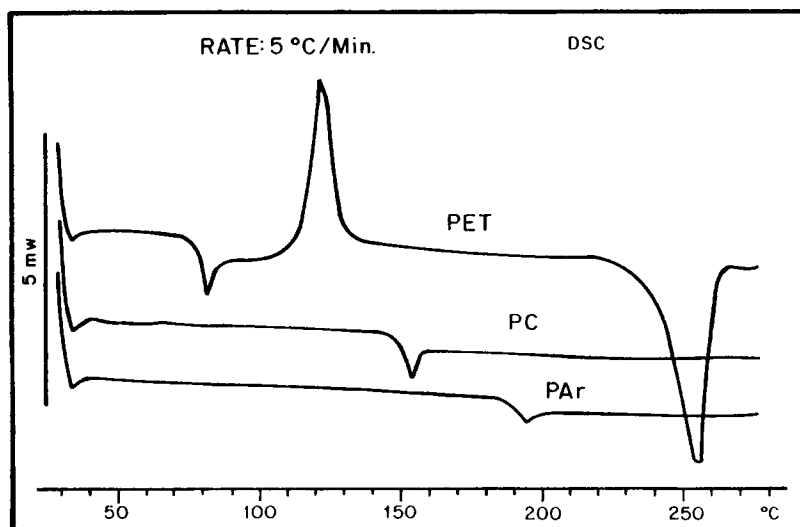| Concentrate[a] ID	Type of polymer	Drying condition	Compounding atmosphere
A	PC	4 h, 100°C	Ambient air
B	PC	18 h, 130°C	N₂ blanket
C	PET	18 h, 130°C	N₂ blanket

[a] Nominal 10% wt.

Fig. 1.   DSC scan of (a) poly(ethylene terephthalate), (b) polycarbonate; and (c) polyarylate.

30°C/min. The same sample cell was then cooled rapidly to 30°C (approximately 3 min) and rescanned to 280°C at 5°C/min.

Catalysts Analysis. Energy dispersive X-ray fluorescence spectrometry was employed to qualitatively detect the presence of metallic catalyst in the polymers.

RESULTS

The DSC scan of PAr, PC, and PET is shown in Figure 1. All the polymers were annealed at 5°C below their glass transition temperature (T_g) for 2 h in order to enhance the transition region. A ^{31}P MAS NMR spectrum of an Ul-
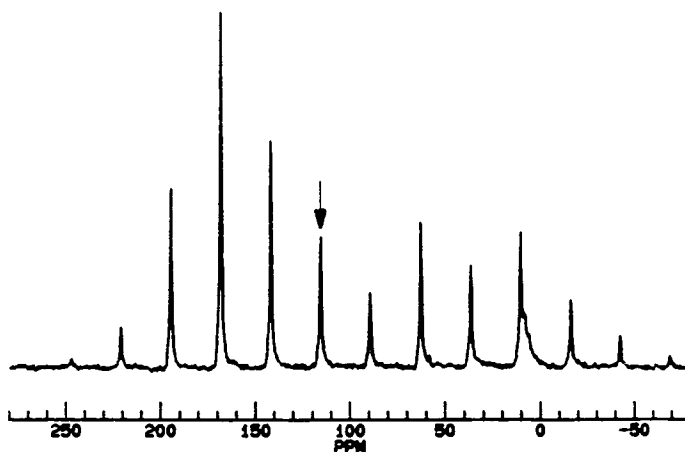
Fig. 2.   MAS NMR spectrum of Ultranox 624.
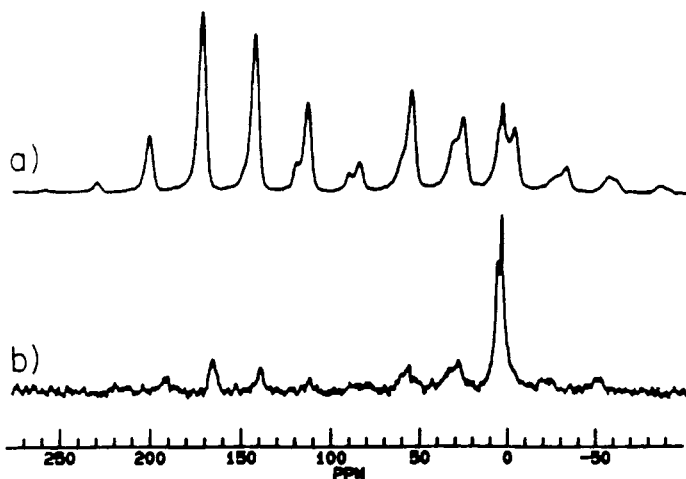
Fig. 3. MAS NMR spectrum of phosphite–polycarbonate concentrate (concentrate A): (a) as extruded; (b) after 16 h at 100°C.

tranox 624 is shown in Figure 2. The chemical shift of the phosphite is shown by the arrow. All the NMR peaks assignment are discussed in more detail in the first article of this series.[19] The NMR spectrum of the phosphite–polycarbonate concentrate (concentrate A) as extruded is shown in Figure 3a. After heating the concentrate at 100°C for 16 h in an air-circulating oven [Fig. 3(b)], it was observed that the material segregated into two types of pellets. One type of pellet stayed transparent while the other one became opaque. Their NMR spectra are shown in Figures 4(a) and 4(b), respectively. Both spectra of Figures 3(a) and 4(a) show the existence of phosphite with some phosphonate, while the spectra of Figures 3(b) and 4(b) show that the phosphite peak has
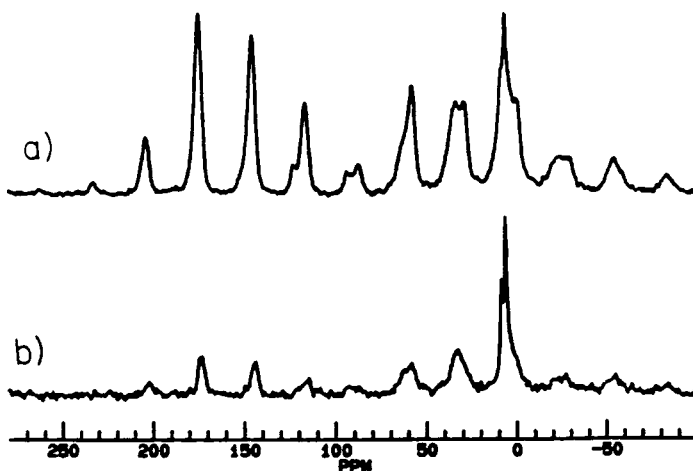

Fig. 4. MAS NMR spectra of phosphite–polycarbonate concentrate (concentrate A) after heating at 100°C for 16 h: (a) transparent portion; (b) opaque portion.
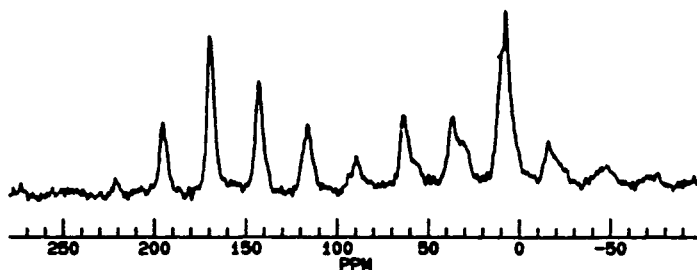
Fig. 5. MAS NMR spectrum of phosphite–polycarbonate concentrate (concentrate A) after 16 h *in vacuo* at ambient temperature.
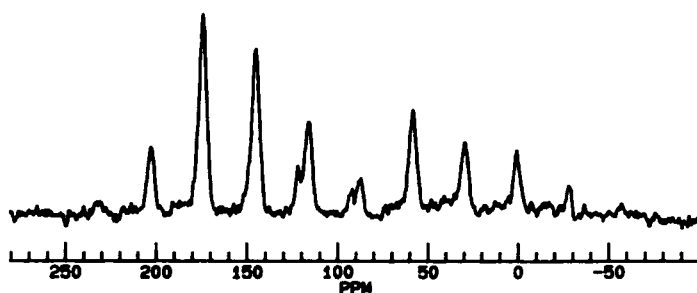

Fig. 6. MAS NMR spectrum of phosphite–polycarbonate concentrate (concentrate B) as extruded.
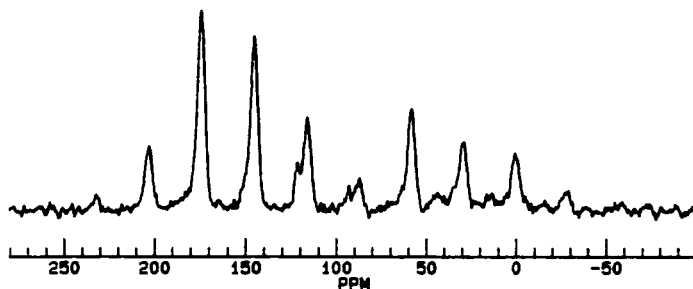

Fig. 7. MAS NMR spectrum of phosphite–polycarbonate concentrate (concentrate B) after heating at 100°C for 16 h.

essentially disappeared and only a signal with the chemical shift of a phosphonate remains. The existence of phosphonate in Figures 3(a) and 4(a) is also observed but at very low concentration.

In contrast to heating at 100°C, little transformation of phosphite to phosphonate occurs in concentrate A after drying in vacuuo for 16 h at ambient temperature as shown in Figure 5. Figure 6 shows the NMR spectrum of another PC–phosphite concentrate (concentrate B). The spectrum is similar to that of concentrate A [Fig. 3(a)] except around the broad peak centered at about 7 ppm. It is interesting to note that the phosphite in concentrate B remained
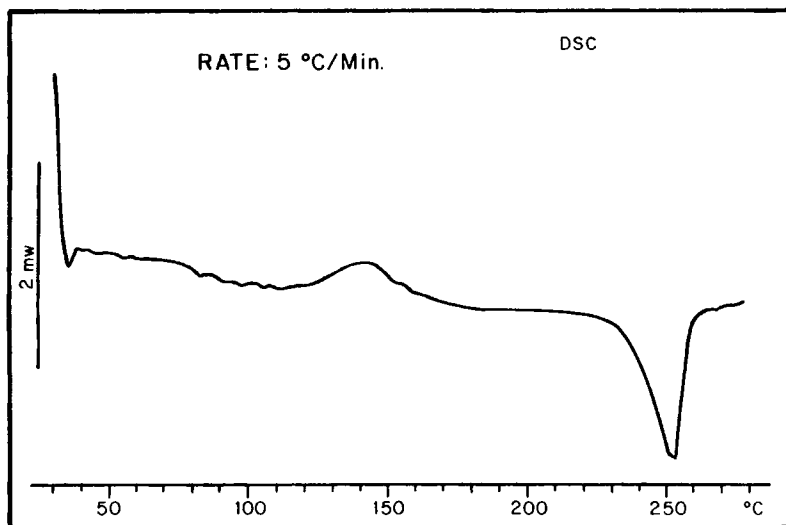
Fig. 8. Typical DSC scan of PAr/PC/PET ternary blend after melt extrusion.

intact even when subjected to a drying cycle of 100°C for 16 h (Fig. 7) in contrast to concentrate A [Fig. 3(b)].

A typical DSC scan of the PAr/PC/PET ternary blend after melt extrusion is shown in Figure 8. The criteria for evaluating the resistance to ester-exchange reactions of the ternary blend is based on the retention of the melting point and the heat of fusion of the PET as we have reported previously.[18] The same criteria were also discussed by Kimura and co-workers.[5,6] The DSC result of blend using concentrate A (predried at 100°C for 16 h) after being isothermally
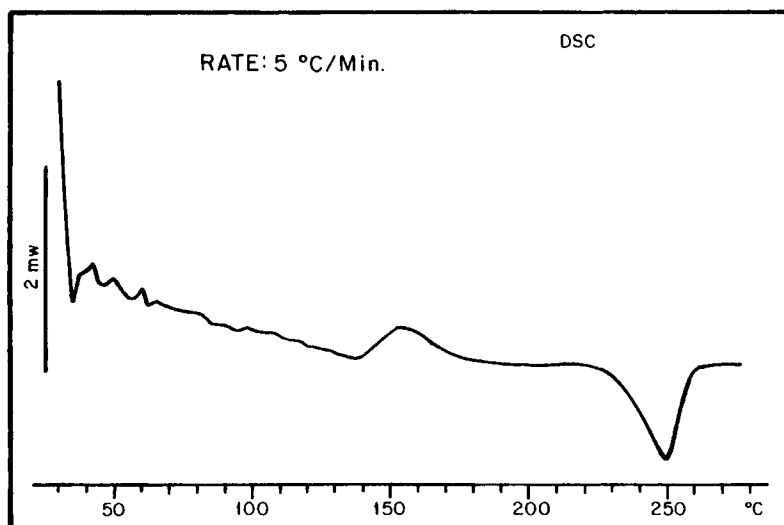
Fig. 9. DSC scan of PAr/PC/PET ternary blend with concentrate A (predried at 100°C for 16 h), after isothermally held for 30 min at 300°C.
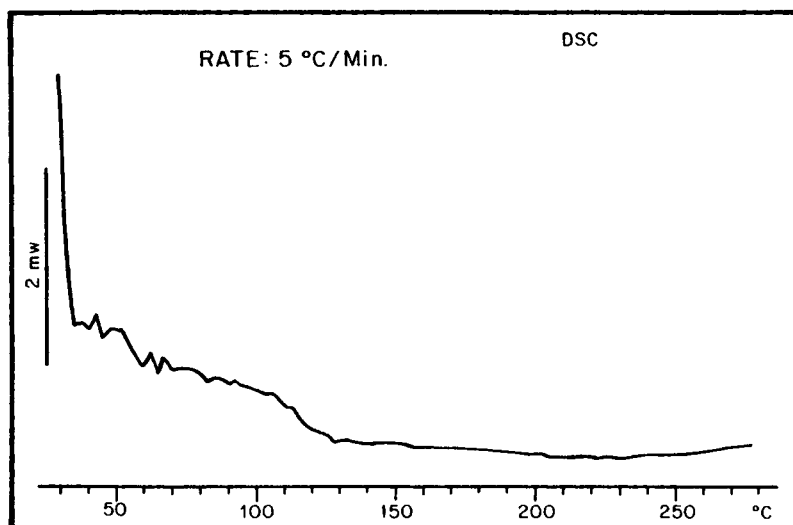
Fig. 10. DSC scan of PAr/PC/PET ternary blend with concentrate A (predried in vaccuo at ambient temperature for 16 h), after isothermally held for 30 min at 300°C.

held at 300°C for 30 min is shown in Figure 9. It is believed that this temperature and time duration are sufficient for evaluating the resistance to ester-exchange reactions in this blend.[18] The result of using the ambient temperature vacuum dried concentrate A in the ternary blend, subjected to the same isothermal test, is shown in Figure 10. It is obvious that after 30 min at 300°C the exchange reactions are so advanced that a copolymer is formed and crystallization is no longer possible. The use of concentrate B in the blend gave essentially the same
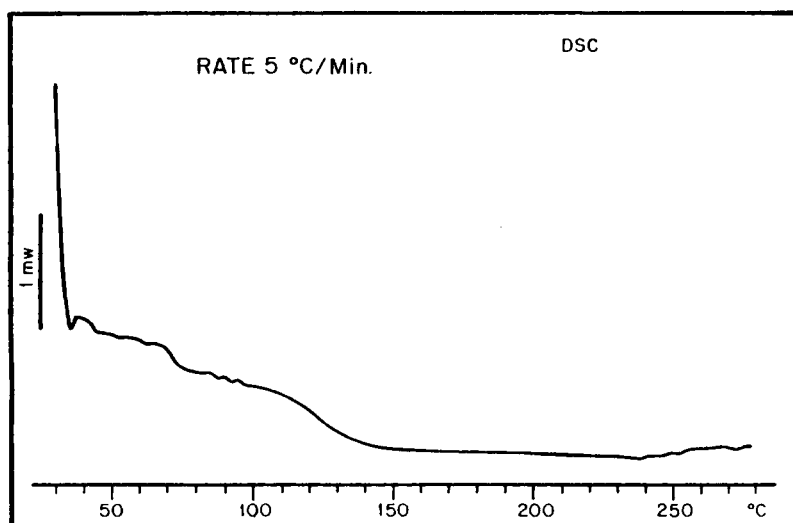

Fig. 11. DSC scan of PAr/PC/PET ternary blend with concentrate B (predried at 100°C for 16 h), after isothermally held for 30 min at 300°C.
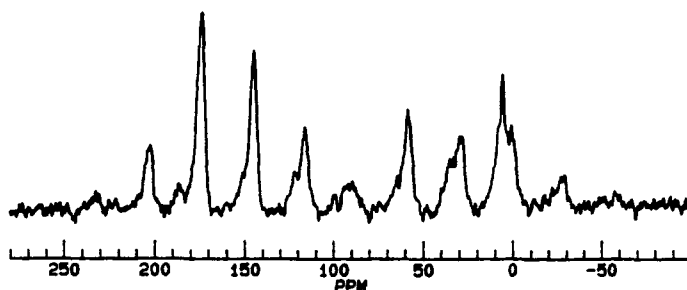
Fig. 12.   MAS NMR spectrum of phosphite–poly(ethylene terephthalate) concentrate (concentrate C).

results, as is shown in Figure 11. Another concentrate, using PET (concentrate C) instead of PC, gave positive results. The NMR and DSC spectra are shown in Figures 12 and 13, respectively.

Figure 14 shows the NMR result of an Ultranox 624 that had been heated in a furnace at 270°C for 10 min and then subsequently heated for 16 h at 100°C.[19] A trace amount of water was also added to a Ultranox 624 sample and heated under the same condition in the furnace. The spectrum is shown in Figure 15.[19] In both cases the phosphite was transformed into phosphonate as depicted by the NMR spectra.

The only metallic catalyst residual found by the energy dispersive X-ray fluorescence spectrometry experiment was antimony, which is present in the PET. Both PAr and PC were found to be metallic catalyst free.

DISCUSSION

The results of the DSC tests indicate that whenever the phosphite is converted into phosphonate, the melting point and the heat of fusion of the PET
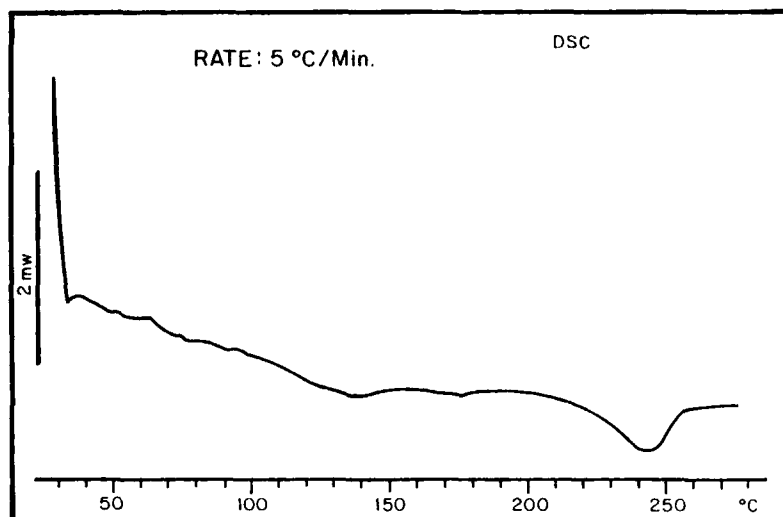

Fig. 13.   DSC scan of PAr/PC/PET ternary blend with concentrate C (predried at 100°C for 16 h), after isothermally held for 30 min at 300°C.
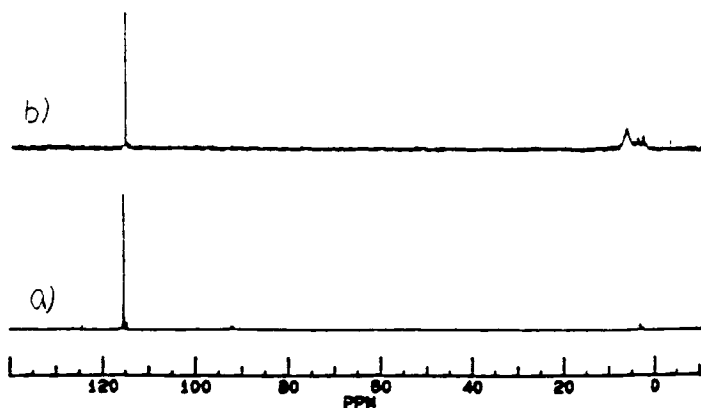
Fig. 14.   Solution state ^{31}P NMR spectra of Ultranox 624 (all solutions in CCl$_3$D): (a) untreated Ultranox 624; (b) after 10 min at 270°C followed by 16 h at 100°C.[19]

are stabilized. Concentrate B, in which the phosphite remains intact, gives blends with poor thermal stability.

The ternary blends that contain the converted phosphite, e.g., concentrate A and C, developed a gray color. The higher the extrusion temperature, the darker the color developed. On the other hand, blends obtained from using concentrate B did not develop any gray color. The gray color is likely to be a complex formed by the residual catalyst (antimony, in this case) used in the PET polymerization process and the phosphonate.[20]

These results indicate that the organophosphite may have reacted with the moisture from the environment during extrusion through side-chain hydrolysis and converted into the tricovalent phosphonic acid (H—O—P) and later tautomerized into the more stable pentacovalent form (H—P=O) as follows:
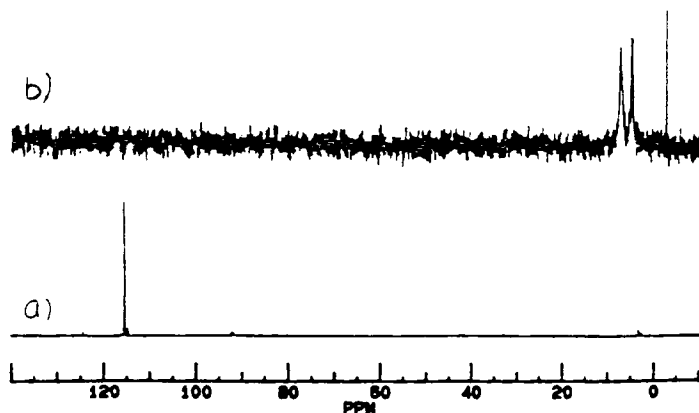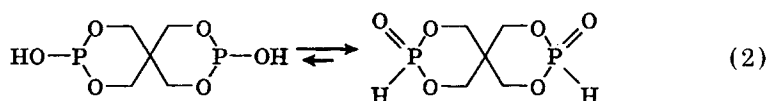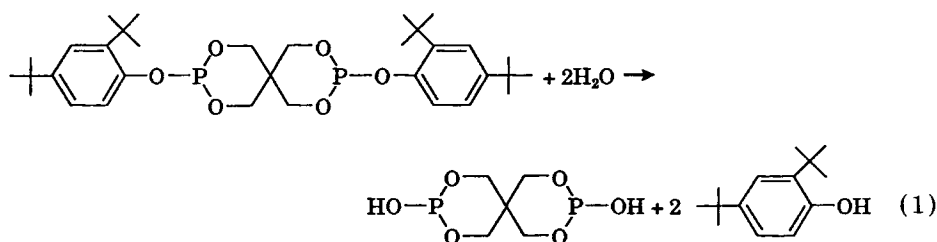

Fig. 15.   Solution state ^{31}P NMR spectra of Ultranox 624 with trace amount of H$_2$O (all solutions in CCl$_3$D): (a) untreated Ultranox 624; (b) after 10 min at 270°C followed by 16 h at 100°C.[19]

$$+ 2H_2O \rightarrow$$

$$HO-P\quad P-OH + 2 \quad OH \quad (1)$$

$$HO-P\quad P-OH \rightleftharpoons \quad (2)$$

Heating the phosphite in a furnace also converts it into phosphonate as demonstrated by Figures 14 and 15. As for the PET concentrate (concentrate C), the carboxyl end groups in the PET can react with the diphosphite (Ultranox 624) and form the phosphonic acid (3) and subsequently transformed into phosphonate (2) as follows:

$$+ HOOC-PET \rightarrow$$

$$PET-COO \quad + HO-P\quad P-OH \quad (3)$$
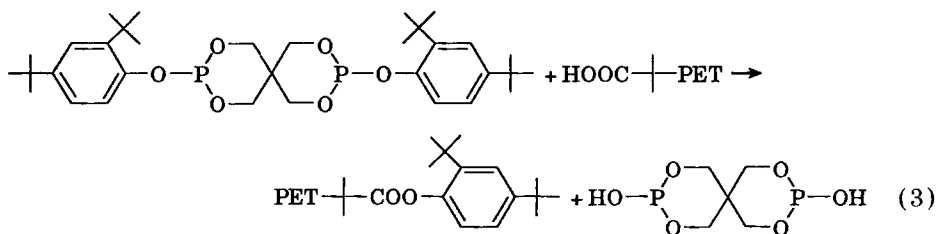
Aharoni and co-workers reported that the addition of triphenylphosphite at high temperature results in chain extension for the extruded PET.[21] Diphenylphosphite was the major extractable product detected by ^{31}P NMR measurement. The diphenylphosphite rapidly tautomerized from the tricovalently bonded diester of phosphorous acid to the more stable, pentacovalently bonded diester of phosphonic acid, diphenylphosphonate. Humphris and Scott also showed that the antioxidant and peroxidase activity of o-phenylene phosphites is not due to the phosphites themselves but to a catalytic species derived from them.[22] Furthermore, Smith, Barlow, and Paul used Irganox 1093, an organophosphonate to successfully suppress the ester-exchange reactions of a PC–copolyester blend at 277°C.[17]

The experimental results clearly suggest that organophosphites have to be transformed into other phosphorous species such as diphosphonate or diphosphate in order to be effective as an inhibitor of the ester-exchange reactions. As suggested by Devaux et al., the stabilizer may probably be linked to the catalyst in the form of a complex.[15] The results of our NMR studies, as presented in the first article of this series,[19] also suggest that a more rigid confirmation of the phosphonate is present in the final blend than that in the concentrate. We would like to propose that in order for the phosphite to form a complex with the catalyst, the tricovalent bond of phosphite or in this case the diphosphite (Ultranox 624) has to be converted into the pentacovalent bond through

side-chain hydrolysis and tautomerization to enhance the ability of forming the complex.

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