

Reactions induced by triphenyl phosphite addition during melt mixing of PET/PBT blends: chromatographic evidence of a molecular weight increase due to the creation of bonds of two different natures

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A detailed chromatographic investigation has been carried out on the influence of triphenyl phosphite addition in molten poly(ethylene terephthalate) or poly(ethylene terephthalate)/poly(butylene terephthalate) blends. The observed molecular weight evolution corresponds to torque and viscosity observations and fully confirms the occurrence of high temperature reactions between polyester and phosphite. The reaction mechanisms deduced from model compound studies are successfully applied to polymers. The formation of bonds of different types is verified: phosphite reactions with hydroxyl chain ends lead to the incorporation of significant quantities of phosphorus into the polyester backbone. A high sensitivity of these phosphorus containing links towards water, phenol or *m*-cresol has been observed. Subsequent carboxyl chain end attack on the phosphorus linkages leads to stable ester bonds. © 1997 Elsevier Science Ltd.

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INTRODUCTION

The reactive processing of poly(ethylene terephthalate) (PET) with triphenyl phosphite (TPP) has been studied by Aharoni *et al.*¹. The mechanism described involves selective reactions between polymer chain ends and the phosphite. An increase in the polyester intrinsic viscosity was observed as a consequence of new ester bond formation.

The extension of this reaction to PET/poly(butylene terephthalate) (PBT) blends has been investigated in this work. Due to the similarity of the polymer backbones and the nature of their chain ends, the phosphite addition is assumed to act similarly and therefore to promote block copolymer formation. Moreover, transesterification reactions are presumed to be greatly reduced by the presence of a phosphite²⁻⁶. Such achievement of a molecular assembly could allow a fine control of the microstructure.

In a preceding paper⁷, different experiments were reported, confirming an alternative reaction mechanism. Torque values recorded during Brabender mixing, representative of the polymer melt viscosity, greatly increase after TPP addition. Confirmation has been

obtained by intrinsic viscosity measurements. A detailed study of the reactions occurring between polyesters and phosphite requires direct molecular weight observations. The perfecting of an accurate chromatographic procedure, appropriate for polyester/phosphite systems, highlighted several problems concerning polymer degradation, particularly on heating in solution^{7,8}. The creation of chemical bonds of different nature has been suggested. Furthermore, an investigation carried out on model compounds⁹ revealed the possible formation of reactive links including phosphorus atoms.

Reliable polyester molecular weight values are now available via the detailed chromatographic study reported in this paper and allow us to extend to polymers the reaction mechanisms found between model molecules.

As a simultaneous study on the physical behaviour of a PET/PBT (75/25 w/w) blend was underway in our laboratory, the present research has been conducted on this particular blend. However, experiments carried out on PET have confirmed the validity of the proposed reaction scheme for pure polyesters.

EXPERIMENTAL

Materials

PET was B73L supplied by ICI. PBT was Celanese 2000 supplied by Hoechst/Celanese. Concentrations of chain ends were measured by infra-red (i.r.) spectroscopy,

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Table 1 Polyester hydroxyl and carboxyl chain end concentrations and absolute number-average molecular weights, determined by infrared spectroscopy on polyesters as received, and calculated values for PET/PBT (75/25, w/w) blends. Weight-average molecular weights of polyesters as received and of 75/25 blend, measured with chromatographic conditions described in text and expressed in polystyrene equivalents

	PET	PBT	PET/PBT (75/25)
$[-\text{OH}]$ (eq g ⁻¹ · 10 ⁶ g)	68	26	58
$[-\text{COOH}]$ (eq g ⁻¹ · 10 ⁶ g)	38	44	39
\bar{M}_n^a	18 900	28 600	20 600
\bar{M}_w	49 800	49 000	49 100
			(measured)

^a Assuming only -OH and -COOH end groups are present

and absolute number-average molecular weights were calculated⁷. Both are displayed in *Table 1*. Values for PET/PBT (75/25) blends are extrapolated from measurements conducted on pure polyesters. The weight-average molecular weights of polyesters as received and of 75/25 blends measured by gel permeation chromatography (g.p.c.) are expressed in polystyrene equivalents.

TPP (Janssen, 99⁺%) and phenol (Janssen, 99%) were used as received. 1,1,2,2-Tetrachloroethane (TCE) (Aldrich, 99%) and acetone (technical grade) were distilled before use.

Processing conditions

PET and PBT, previously dried overnight at 120°C under vacuum, were kneaded in a Brabender plastograph equipped with an electrically heated mixing device W50EH. The mixing speed used was 30 rev min⁻¹. The temperature was regulated in the range 275–280°C. The atmosphere was controlled by blowing nitrogen above the mixing chamber. Temperature and torque were continuously recorded during the mixing process.

Different TPP quantities were added to the polyester blends: 0, 1, 2 or 5%. Phosphite concentrations are always reported in amount of additive per weight of base polymer. In all Brabender experiments, the polymers were premixed during 5 min in order to obtain an homogeneous polyester melt before adding the TPP. The zero time corresponds to the introduction of the TPP into the mixer, a reference sample being withdrawn just before. Other samples were withdrawn for analysis after different mixing times ranging from 1 to 30 min.

To establish the correlation between torque and molecular weight in polyester/phosphite systems, data were extracted from different experiments. In order to avoid an accuracy loss due to possible friction differences between experiments, only data corresponding to torque values above 100 g m⁻¹ were taken into account.

Polyester samples, previously frozen in liquid nitrogen, were finely ground in a crushing mill from IKA. The purification was achieved by extraction with distilled acetone during 72 h in a Soxhlet-type apparatus and drying afterwards at 120°C under vacuum overnight.

Phosphorus elemental analysis

The samples (0.5 g of each) were heated in 5 ml of concentrated sulfuric acid, followed by oxidation/heating with hydrogen peroxide until a clear solution was obtained. The solution was then diluted to 50 ml with purified water. This method of sample preparation is often referred to as wet oxidation.

Phosphorus was determined by inductively coupled plasma optical emission spectrometry using a Perkin-Elmer Plasma II instrument. The instrument was calibrated using solutions containing 0, 10, 20, 30 ppm of P in 10% (v/v) sulfuric acid. The P concentrations were calculated from the emission intensities of the samples. The relative standard deviation of the measurement was typically 1% for three replicates.

G.p.c.

The g.p.c. was performed at 50°C with a phenol/tetrachloroethane (3/2, w/w) eluent using a Waters 150C high temperature chromatograph with a refractive index detector. Two Shodex columns from Showa Denko (Ref: AT-80M/S) and one Ultrastaygel column (500 Å from Waters) were used in series. The flow rate was 0.5 ml min⁻¹.

Polyesters (8–10 mg of each) were dissolved at room temperature in 2 ml of the same batch of solvent as the eluent phase. Approximately 120 µl was injected. The run time was fixed to 90 min. The eluent was maintained in a thermostatic bath at 30°C in order to prevent phenol crystallization.

The results were analysed on a Digital Micro Vax 2000 computer. The chromatograph was calibrated with 12 polystyrene standards supplied by Waters and ranging from 1250 to 2 700 000 g mol⁻¹. Molecular weight values are therefore expressed in polystyrene equivalents (PS g mol⁻¹). The precision inherent to chromatographic measurements is better than 10%.

After conditioning the chromatographic columns during 15 days with the eluent phase at 50°C, the retention time stability of the polystyrene standards was verified. Nevertheless, new PS calibrations were regularly conducted in order to prevent any modification of the system. Very good molecular weight reproducibility with time was observed. It was also verified that the polyester holding time in solution in phenol/tetrachloroethane at 50°C does not have any influence on the measured molecular weight.

RESULTS

Polyester processing and corresponding molecular weight values

Unless otherwise stated, chromatographic molecular weight measurements carried out on polyesters after reaction with phosphite were performed on purified samples. As explained hereafter, this means that, immediately after processing, polyester/TPP systems are refluxed with distilled acetone. This treatment is efficient and prevents any degradation caused by undesirable reaction by-products. All samples were then dried in order to avoid hydrolysis. Since these analyses were conducted on blends, all chromatographic values are expressed as polystyrene equivalents.

The polyester molecular weight evolution during mixing with various triphenyl phosphite amounts is presented in *Figures 1–3*. Corresponding torque values, recorded on the Brabender plastograph, are given in *Figure 4*. The observations resulting from these two different techniques corroborate the viscometry measurements previously reported⁷.

The polyester degradation which occurred during the time necessary to achieve adequate melting and mixing has already been observed by i.r. spectroscopy for chain

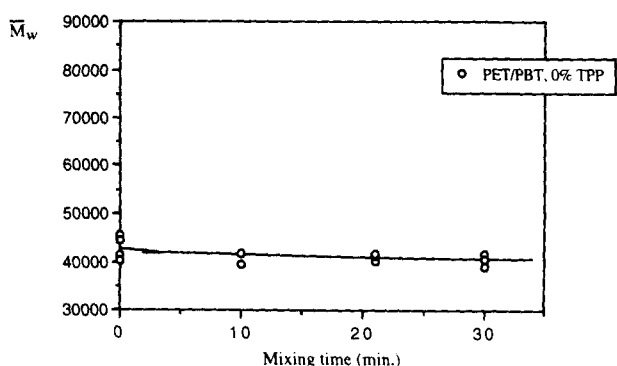


Figure 1 Weight-average molecular weight versus mixing time for a PET/PBT (75/25) blend without phosphite addition

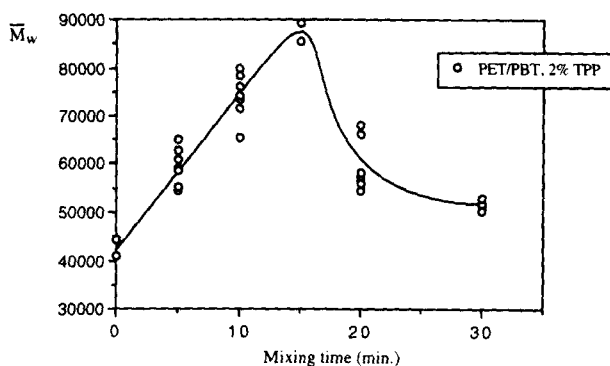


Figure 2 Weight-average molecular weight versus mixing time for a PET/PBT (75/25) blend with addition of 2% TPP

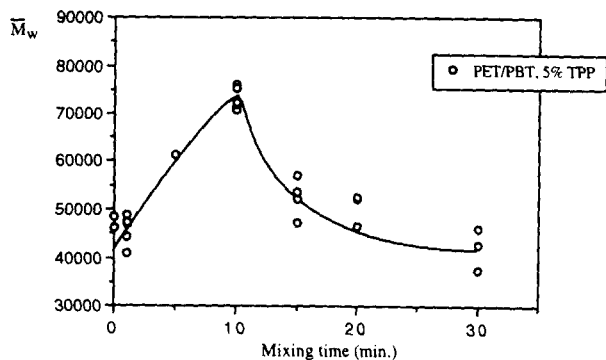


Figure 3 Weight-average molecular weight versus mixing time for a PET/PBT (75/25) blend with addition of 5% TPP

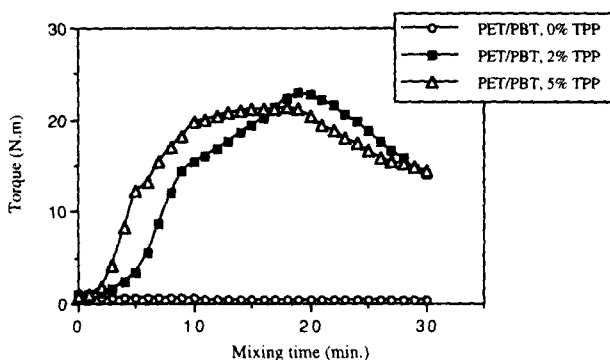


Figure 4 Torque versus mixing time for PET/PBT (75/25) blends with addition of 0, 2 or 5% TPP

ends⁷. In this work, all the g.p.c. measurements confirm the decrease of the molecular weight between the initial polymer pellets (Table 1) and the samples withdrawn just before phosphite addition, i.e. at $t = 0$.

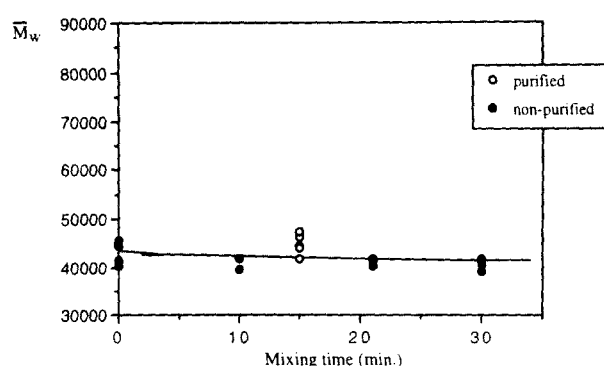


Figure 5 Weight-average molecular weight versus mixing time for a PET/PBT (75/25) blend without phosphite addition, purified or not by acetone washing

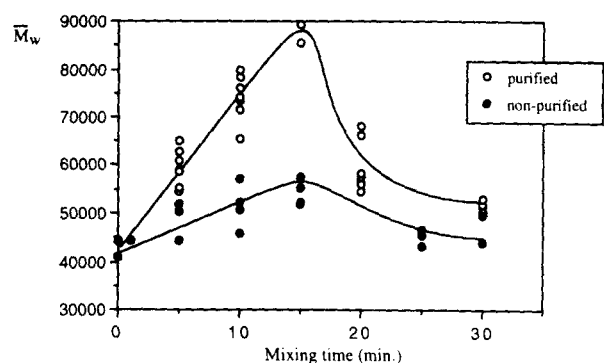


Figure 6 Weight-average molecular weight versus mixing time for a PET/PBT (75/25) blend with addition of 2% TPP, purified or not by acetone washing

By comparison with pure polyester behaviour, TPP addition induces large increases of the mixing torque (Figure 4), of the molecular weight (Figures 1–3) and of the viscosity⁷ as a function of the mixing time. The molecular weight values double and the torque increases by more than one order of magnitude. The curve maxima are observed to occur 10–20 min after the phosphite addition.

When the polymers reach high torques (and molecular weights), instabilities and large oscillations are observed and average values must be calculated. It was also experimentally observed that polyesters progressively behave as 'rubbery' materials, suggesting the possibility of branching. It therefore becomes meaningless to consider still the torque measurements as purely representative of the viscous flow for that part of the curves.

Influence of different treatments on measured polyester molecular weights

Purification of the samples. Optimum reliability of the g.p.c. procedure is obtained by preliminary purification of the polyester samples from all the reaction by-products. In order to check the influence of this procedure on the measured molecular weights, similar blends have been analysed twice, as prepared and after purification. Large differences are observed, as presented in Figures 5–7.

The molecular weight of pure polyester blends are not affected by the acetone reflux. Similar values are obtained for initial and purified samples. On the other hand, large differences are observed for polyesters which have reacted with phosphite. The advantage of the

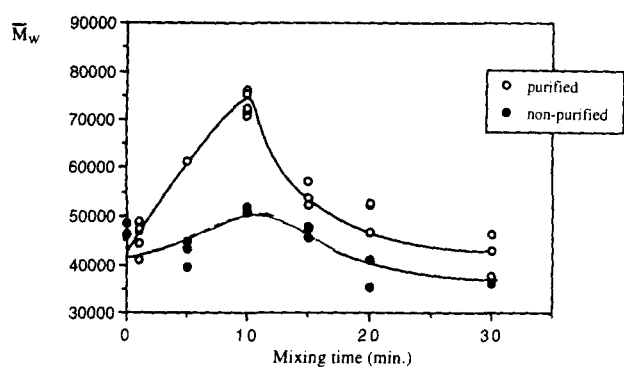


Figure 7 Weight-average molecular weight versus mixing time for a PET/PBT (75/25) blend with addition of 5% TPP, purified or not by acetone washing

Table 2 Weight-average molecular weight of a PET/PBT (75/25) blend with 0, 2 or 5% TPP, analysed immediately (A), purified by acetone washing (B) and dried (when indicated) during 16 h at 120°C

	0% TPP (15 min mixing)	2% TPP (15 min mixing)		5% TPP (20 min mixing)	
	B	A	B	A	B
Dried	45 100	54 300	87 400	38 200	51 100
Non-dried	47 600	87 400	76 500	63 300	60 200

purification procedure is obvious: the non-purified samples always present a molecular weight much lower or equal to those of the polyesters washed by acetone reflux. The molecular weight increase due to the phosphite addition is still observed for polyesters analysed immediately after mixing. However, the magnitude of the variations is much reduced in comparison with that of purified samples.

During the sample drying procedure, a reaction involving the phosphorus by-products can occur. In order to check the influence of any eventual thermally activated degradation, some polyesters were analysed without drying. The results are presented in Table 2. The restricted accuracy observed is due to the reduced number of experiments and to the specific limitations of the g.p.c. method.

Drying after Brabender mixing and acetone washing has no influence on pure polyester blends: no molecular weight decrease due to hydrolysis is detected (Table 2). After phosphite addition, the molecular weight of undried polyesters is roughly similar to that of the corresponding blends after purification and drying. On the other hand, the samples dried without purification exhibit a large molecular weight decrease. However, the effects of phosphite addition still appear: even for degraded samples, the values obtained for polyester/phosphite systems are higher or roughly equal to those for the corresponding pure polyesters.

These results confirm that the presence of phosphite by-products, together with a sufficient heat exposure, leads to a molecular weight decrease. The stability of the polymer after washing by acetone emphasizes the purification efficiency.

Heating in solution. Previous results⁷ showed a large molecular weight decrease for polyester/TPP systems, even after purification by refluxing acetone, if the samples were held in phenolic solution at high temperature. This evolution has been interpreted as the scission of

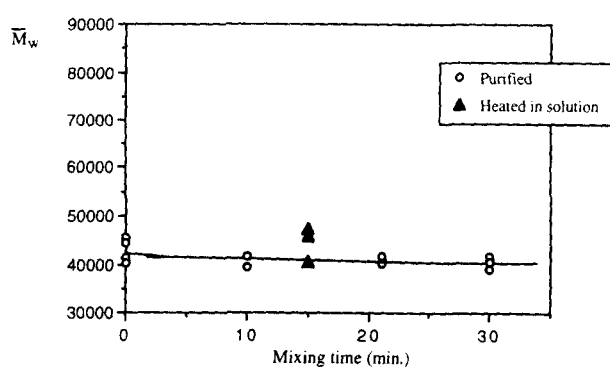


Figure 8 Weight-average molecular weight versus mixing time for a PET/PBT (75/25) blend without TPP addition, before (O) and after heating during 15 h (▲) at 120°C in a phenol/TCE (3/2) solution

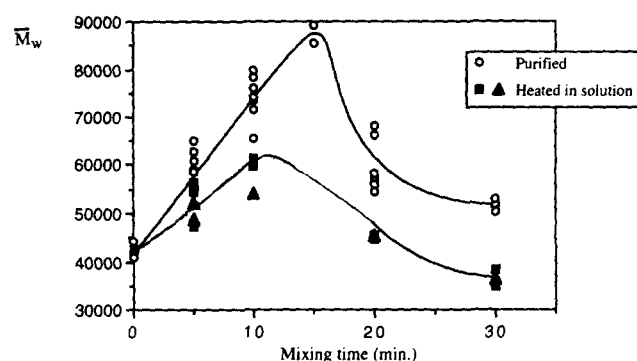


Figure 9 Weight-average molecular weight versus mixing time for a PET/PBT (75/25) blend with addition of 2% TPP, purified by acetone washing, before (O) and after heating at 120°C during 2 h (■) or 15 h (▲) in a phenol/TCE (3/2) solution

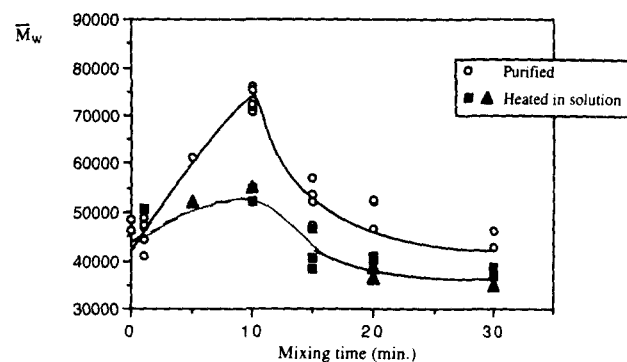


Figure 10 Weight-average molecular weight versus mixing time for a PET/PBT (75/25) blend with addition of 5% TPP, purified by acetone washing, before (O) and after heating at 120°C during 2 h (■) or 15 h (▲) in a phenol/TCE (3/2) solution

reactive links, created by the phosphite in addition to new ester bond formation. By taking advantage of this efficient way to break the most reactive bonds, it then becomes possible to follow the polyester molecular weight evolution caused only by the presence of stable bonds. Figures 8–10 show the behaviour of purified samples before and after heating at 120°C in a phenol/TCE (3/2) solution for different times.

Within the experimental g.p.c. accuracy, the observed changes after 2 or 15 h at 120°C in solution is quite similar, indicating that most of the degradation occurs rapidly. The molecular weight of pure polyester is not significantly modified by this treatment: no perceptible attack of the polymer backbone is detected. On the other hand, for blends reacted with TPP, heating in solution

Table 3 Weight-average molecular weight of PET/PBT (75/25) blends with 0 or 2% TPP, purified by acetone washing and held (where indicated) during 72 h in water at boiling temperature

	Purified	Heated in water
0% TPP (15 min mixing time)	45 400	47 400
2% TPP (20 min mixing time)	59 600	26 200

Table 4 Total phosphorus content (ppm) of different PET/PBT 75/25 blends with 2 or 5% TPP, withdrawn after different reaction times

	0 min	1 min	10 min	20 min	30 min
2% TPP	n.a.	n.a.	1540	1320	1440
5% TPP	65	4750	3470	3170	2880

induces a molecular weight decrease. First of all, it is important to point out that the large M_w increase resulting from the phosphite addition is much reduced, but still exists. However, for long mixing times, the measured molecular weight is below the value of the initial polyester.

Influence of hydrolysis. In order to verify the behaviour of the polyester/TPP blends in the presence of water, acetone purified polyester blends were maintained in water at boiling temperature for 72 h (Table 3).

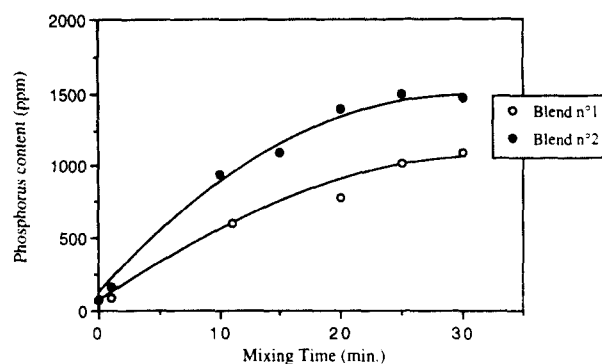
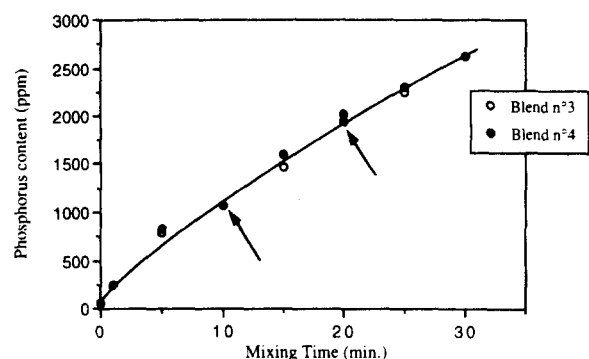
Table 3 shows that hydrolysis in boiling water is negligible for the pure polyester. On the other hand, the degradation observed for the samples containing phosphite goes beyond the scission of the links created by reaction in the molten state: its molecular weight falls far below the initial blend value.

Phosphorus elemental analysis

Chromatographic analyses were carried out on polyesters before and after different treatments, such as purification from reaction by-products or heating at 120°C in a phenolic solution. They strongly support the hypothesis of a chain extension mechanism due to specific reactions between phosphite and polymer chain ends. The stability of the new bonds formed appears much lower than that of the polyester backbone. The presence of in-chain phosphorus atoms is investigated to verify the exact chemical reactions occurring in the blends. Phosphorus elemental analyses were therefore performed on different polyesters sampled during the reactive processing with the phosphite.

Polyesters mixed with 2 or 5% phosphite were sampled after different times and immediately analysed. The results obtained by phosphorus elemental analysis are presented in Table 4. It must be noted that the addition of 2 or 5% TPP corresponds to a theoretical phosphorus content increase of respectively 1958 and 4755 ppm. However, due to the experimental procedure, evaporation of phosphorus-containing low molecular weight species can occur during the experiment. This point is confirmed by the decreasing amounts observed for long reaction times.

A proper study of the reaction between phosphite and polyester chain ends requires a preliminary purification of the polymers in order to remove unreacted TPP and any free phosphorus by-products. The purification is achieved by refluxing finely ground powder in acetone. The remaining phosphorus detected is thus assumed to

**Figure 11** Phosphorus content versus mixing time for two PET/PBT (75/25) blends with 2% TPP, after purification of the samples by acetone refluxing**Figure 12** Phosphorus content versus mixing time for two PET/PBT (75/25) blends with 5% TPP, after purification of the samples by acetone refluxing (arrows refer to parallel control by dissolution/precipitation—see text)

be chemically bonded to the polyester backbone. Figures 11 and 12 present the evolution of linked phosphorus content during the polyester mixing in the presence of different amounts of phosphite. An evaluation of the limiting phosphorus content can easily be determined: the number-average molecular weight of the blends immediately before TPP addition is estimated at 17 400. If a phosphorus atom is picked up by each chain end, whatever its chemical nature, 3556 ppm should be found in the polymer. Selective reactions with hydroxyl or carboxyl groups should lead to a phosphorus content of 1996 or 1560 ppm, respectively.

Figure 11 indicates the difficulty of reproducible polyester preparation in the Brabender plastograph. Differences are indeed observed in the phosphorus content between two PET/PBT blends with 2% TPP. On the contrary, a much better reproducibility is obtained with a large phosphite excess (Figure 12).

In order to confirm the extraction efficiency of free phosphorus compounds by refluxing acetone, a comparison has been made with purification by dissolution/precipitation. In parallel with the extraction procedure, two blends containing 5% phosphite (10 and 20 min mixing time—see arrows in Figure 12) were dissolved in a phenol/TCE (3/2) mixture, reprecipitated and washed in methanol before the elemental analysis. For the samples mixed 10 and 20 min, the values measured after acetone refluxing were 1080 and 2010, respectively, while the corresponding values after dissolution/precipitation were 1070 and 1935. The selection of the samples to be purified by the two different ways was conducted on the

Table 5 Linked phosphorus content (ppm) in PET after reaction with various phosphite quantities. The polyester was withdrawn at maximum torque values (0% TPP; 2% TPP 15 min reaction; 5% TPP 8 min reaction), purified by acetone washing and treated as indicated

	0% TPP	2% TPP	5% TPP
Amount of phosphorus added	0	1958	4755
After purification	75	820	1020
Washed by water reflux	75	370	460
Heated in a phenol/TCE solution	64	260	350

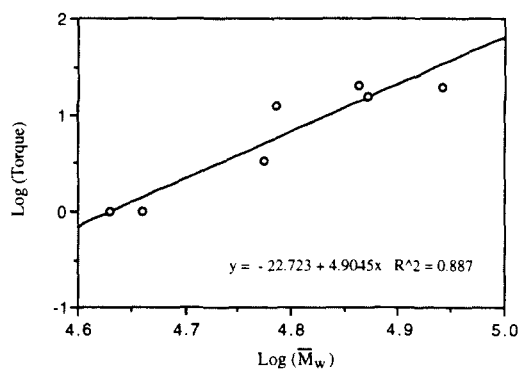


Figure 13 Relationship between the logarithm of the torque and the logarithm of the weight-average molecular weight for different PET/PBT (75/25) blends containing 2 or 5% TPP, withdrawn during the ascending part of the torque curve

basis of the large amount of phosphite added; their efficient purification thereby required the elimination of large quantities of by-products. The comparison, presented in *Figure 12*, is thus conducted on highly selective bases. The perfect agreement between the observed values clearly confirms the equivalence of the two purification procedures.

Chromatographic experiments undeniably show that heating samples in water or in phenolic solution suppresses the molecular weight increase observed after TPP addition. Different PET/TPP systems, previously purified by acetone refluxing, have been submitted to a water reflux or heated during 15 h in a phenol/TCE (3/2) solution. The phosphorus content evolution is presented in *Table 5*. It clearly appears that the amount of linked phosphorus is largely influenced by these treatments.

DISCUSSION

Polyester processing and corresponding molecular weight values

During the ascending part of the torque curves, excellent agreement is observed between viscometric results, g.p.c. molecular weights and torque measurements.

For polymer melts under sufficiently low shear stress, the viscosity can be considered as Newtonian and a well known relationship exists between melt viscosity (η) and weight-average molecular weight (\bar{M}_w)¹⁰:

$$\log(\eta) = \alpha \log(\bar{M}_w) + k \quad (\text{where } \alpha \cong 3.4) \quad (1)$$

Figures 13 and 14 show the linear correlation between the logarithm of the torque and the logarithm of the molecular weight in our polyester/phosphite system. The data are extracted from different experiments containing various quantities of phosphite. The regressions calculated for PET or PET/PBT blends lead to results lying

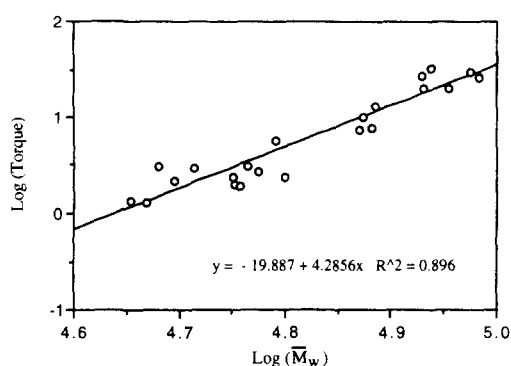


Figure 14 Relationship between the logarithm of the torque and the logarithm of the weight-average molecular weight for different grades of PET, after addition of 2% TPP, withdrawn during the ascending part of the torque curve

reasonably close to each other, despite the fact that the slopes are different from 3.4.

This confirms two important points: in the ascending part of the curve, the torque can actually be considered as an indirect molecular weight measurement. Moreover, the excellent correlation between torque and molecular weight is an indirect but clear indication of the accuracy of the g.p.c. procedure developed and of the reliability of the values obtained on purified polyesters.

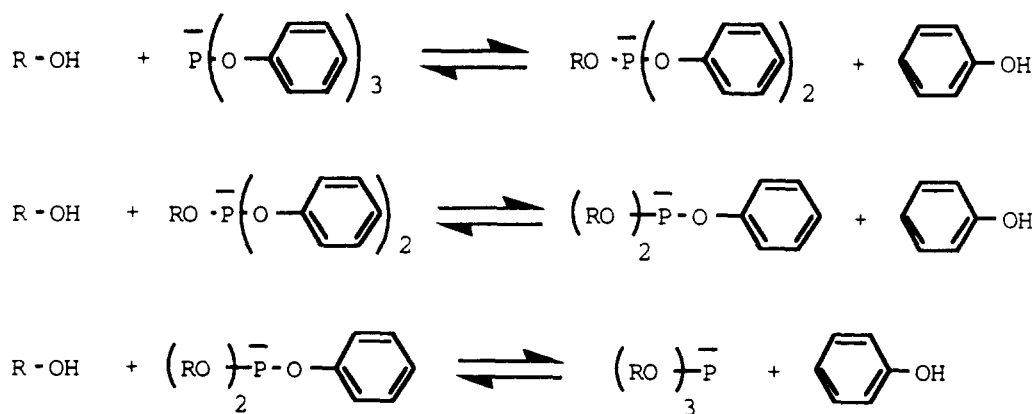
There are at least three reasons why the absolute values of the regression coefficients are not equal to 3.4. First of all, even if the melt can be considered as Newtonian the flow field in the mixer is certainly not monodimensional, and thus, the torque is not directly proportional to the melt viscosity. Another reason is that the molecular weights are deduced from g.p.c. measurements, and thus, are actually not the absolute polyester molecular weights as they are expressed in molecular weight of polystyrene equivalents. Finally, despite the different hydrodynamic volumes of PET, PBT and copolymer, the polyester blends are analysed just as a pure homopolymer. Nevertheless, these three limitations do not reduce the validity of our conclusions.

For samples mixed during times longer than those corresponding to the maximum of the torque, the observed correlation between torque and molecular weight values does not apply any more. This discrepancy is easily explained by the observations realized in the Brabender mixer: the observed behaviour of the polyester melts, resembling 'rubbery' materials, prevents the use of the torque values as a correct representation of the polymer viscosity.

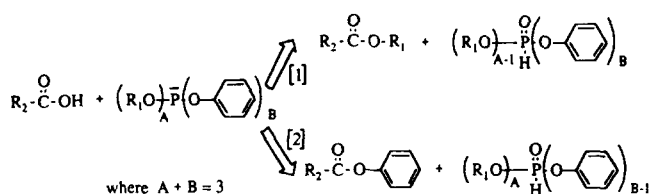
Polyester reactions with phosphite and molecular weight evolution

The large modifications caused by the phosphite addition at 280°C obviously indicate the occurrence of a reaction between TPP and polyesters. The reactivity of the hydroxyl and carboxyl polymer endgroups towards phosphite has already been analysed by an investigation on model molecules⁹. The results can be summarized as follows.

On the one hand, the reaction of TPP with hydroxyl groups results in a phenyl substitution with production of phenol. The phosphorus atom remains in its reactive (P_{III}) state. We have shown that the presence of three phenoxy functions allows the phosphite to undergo a



Scheme 1 Reaction mechanisms between phosphite and alcohol (R = alkyl group)

Scheme 2 Reaction mechanisms between phosphite and acid (R₁ = alkyl; R₂ = aryl)

multisubstitution process (Scheme 1), the equilibrium being displaced by phenol elimination.

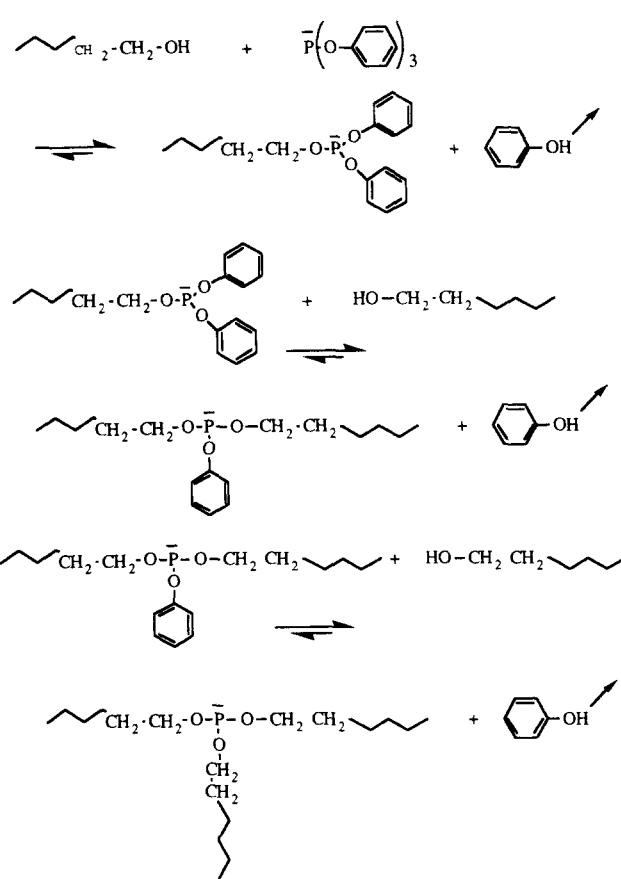
On the other hand, the reaction between carboxyl groups and phosphite (the latter being substituted or not) leads to ester bond formation and phosphonate release (Scheme 2). On model compounds, the reaction pathway [1] has been shown to be favoured.

A scheme can therefore be proposed for the reactions occurring between phosphite and polyesters. After exchange with polyester hydroxyl chain ends, the phosphite is linked to the backbone. In the case of multiple reactions, the phosphorus atom becomes a binding point between different polymer chains. Thus, a molecular weight increase and finally a branching point can occur (Scheme 3).

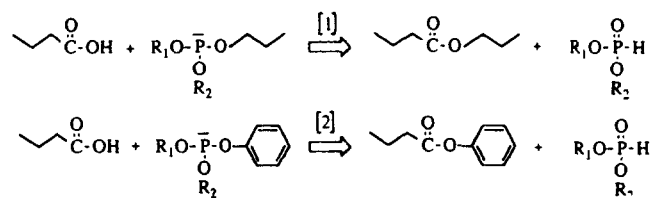
If a carboxyl endgroup reacts with a phenoxy group of a phosphite molecule, phenyl ester is created at the polymer chain end (Scheme 4, pathway [2]). On the other hand, if the exchange occurs on a previously substituted site, it creates a new ester bond as a link between two polyester molecules. A molecular weight increase can thus be observed (Scheme 4, pathway [1]).

The large torque, viscosity and molecular weight increases observed after phosphite addition on polyesters fully confirm the chain-extension mechanisms. In the proposed scheme, different ways lead to a molecular weight increase: reactions between phosphite and successive hydroxyl chain ends causes the appearance of links containing phosphorus atoms. In parallel, a first phosphite reaction with an hydroxyl group, followed by carboxyl chain end attack, creates a new ester bond, as proposed by Aharoni *et al.*¹. The results from chromatographic experiments allow a demonstration of the creation of both links.

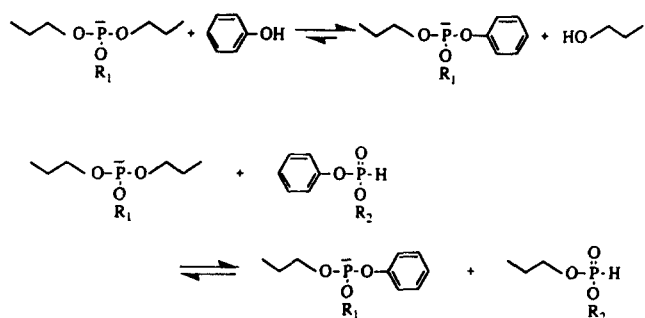
Links containing phosphorus atoms. The effective polyester molecular weight after reaction with phosphite is obtained on samples purified by acetone refluxing. The chromatographic analysis of non-purified samples



Scheme 3 Reaction mechanisms between polyester hydroxyl chain ends and phosphite

Scheme 4 Reaction mechanisms between polyester carboxyl chain ends and phosphite (R₁ and R₂ = phenyl groups or polyester chains)

clearly show that the presence of phosphite by-products in the polymer, combined with heat exposure, causes a molecular weight decrease. With similar conditions, no degradation is observed on the ester bonds of pure polymers. The presence of links containing phosphorus atoms in polyester/TPP systems can explain the discrepancy between the values of initial and purified samples.



Scheme 5 Equilibrium displacement caused by the presence of phenolic solvent or phosphite by-products, resulting in phosphorus link substitutions and subsequent molecular weight decrease (R_1 and R_2 = phenyl groups or polyester chains)

Such links offer an intrinsically good stability during the chromatographic procedure (including polyester drying) and they contribute to the molecular weight increase observed on polyesters after TPP addition. However, the presence of TPP by-products and an activation by heat exposure during 16 h at 120°C (for drying) lead to the observed chain scissions. The creation of phosphorus bonds between polyester chains is realized by successive substitutions between phenoxy groups of the phosphite and different hydroxyl chain ends. The reaction temperature (280°C) favours the phenol elimination and displaces the equilibrium in the desired way. Nevertheless, some phenol or phosphonates arise from the TPP reaction and are trapped in the polymers. They can undergo subsequently similar substitutions with the phosphorus atoms joining the polyester chains, causing thereby the chain scissions and the molecular weight decrease observed (*Scheme 5*).

In the same way, the presence of phosphorus links between polyester chains after reaction with phosphite allows explanation of the polyester molecular weight decrease after heating in phenolic solution. A reaction between phosphite and polyesters induces in the latter an increased sensitivity to phenol/TCE or *m*-cresol. No degradation is observed on the polyester backbone. The phosphite by-products, efficiently eliminated by the acetone refluxing, cannot be considered any more as responsible for the molecular weight decrease. Thus, only the creation of a different bond, promoted by the phosphite addition, can explain the observed differences.

Phenol or *m*-cresol used as solvent does not induce any problem in the temperature range used for the chromatographic measurements (20–50°C). Heating at 120°C enhances the reactivity and leads to substitutions with the phosphorus atoms linked to the polymer chains (*Scheme 5*). The chromatographic results show that the degradation is rapidly realized in these conditions and can be assumed as complete: all the links created by reaction with phosphite are more reactive than ester bonds and are assumed to be broken by heating in phenolic solution.

The behaviour of the polyesters in the presence of boiling water not only confirms the presence of more reactive bonds in the polymer after reaction with phosphite, but also, more precisely, strongly supports the presence of phosphorus atoms linked to the polymer chains. The stability of pure polymer molecular weights (*Table 3*) shows clearly that the experimental conditions used do not induce any polyester hydrolysis. On the



Scheme 6 Phosphite sensitivity to hydrolysis and subsequent molecular weight decrease (R_1 and R_2 = phenyl groups or polyester chains)

other hand, the observed degradation of polyester including phosphite involves both new bonds and initial polymer backbone.

Phosphites are well known to be highly water-sensitive (*Scheme 6*)^{11–14}. Moreover, preliminary experiments have demonstrated that prolonged TPP reflux in boiling water leads to the formation of a mixture of phosphorous and phosphoric acids with phenol production. Consequently, the scission of phosphorus bonds in the polyester by boiling water results in the formation of different acids. The large degradation observed can thus be explained by the acidification of the water medium, catalysing hydrolysis of the ester bonds.

The torque oscillations and the ‘rubbery’ behaviour of polyester melts observed after long reaction times can also be considered as a confirmation of the tendency to branching, due to the phosphorus bond creation between multiple hydroxyl chain ends.

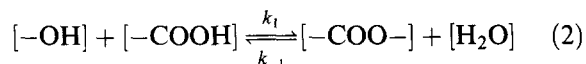
In conclusion, these observations confirm the presence of new bonds between polyester chains. Created by reaction with TPP, these new links most likely include phosphorus atoms and present a reduced stability: their scission occurs after heating of polymers in the presence of water, phenolic solvent or phosphite by-products.

Ester bonds. In order to throw light on the role of phosphite on the creation of new ester bonds between different polymer chains, advantage has been taken of the lower stability of the phosphorus containing links: these have been selectively broken by heating the polyesters in a phenol/TCE (3/2) mixture. Consequently, the molecular weights presented in *Figures 8–10* relate to the presence of only ester bonds in the polymer backbones. This molecular weight evolution during mixing, concerning PET or PET/PBT blends, confirms the phosphite action, already observed by Delimoy on PBT⁴.

In these figures, a polymer molecular weight increase (reduced but real) can still be observed immediately after the phosphite addition. This obviously confirms that the chemical reactions induced by the phosphite addition promotes the formation of new ester bonds between polyester chain ends, as proposed by Aharoni *et al.*¹. It has to be concluded that the creation of two different links in polyesters after phosphite addition is occurring, as suggested by preliminary chromatographic results⁷. The extension to polymers of the reaction mechanisms deduced from the model compound studies (*Schemes 3 and 4*) is, therefore, also confirmed.

Polyesters (PET or PET/PBT blends) show a maximum molecular weight 10–20 min after the phosphite addition. *Figures 8–10* clearly show that the subsequent decrease cannot simply be attributed to the scission of phosphorus links, but that the number of ester bonds is also significantly reduced. This molecular weight decrease can be explained by condensation/hydrolysis mechanisms occurring in polycondensates. In polyesters for example, the final molecular weight is determined by an equilibrium between chain ends, ester groups and

remaining water concentrations:



An equilibrium constant can be written as

$$K = \frac{[-\text{COO}-][\text{H}_2\text{O}]}{[-\text{OH}][-\text{COOH}]} = \frac{k_1}{k_{-1}} \quad (3)$$

where K is the condensation equilibrium constant, k_1 is the condensation kinetic constant, and k_{-1} is the hydrolysis kinetic constant.

The equilibrium constant for polyesterification is typically¹⁵ not larger than 1–10. Consequently, the condensation and hydrolysis kinetic constants are of the same order of magnitude. Different papers dealing with PET polycondensation studies by using model molecules report K values in the range 1–5 and an order of magnitude of 10^{-3} ($\text{l}^2 \text{mol}^{-2} \text{min}^{-1}$) for k_1 ^{16–18}.

Water or humid atmosphere can hydrolyse the ester groups to $-\text{OH}$ and $-\text{COOH}$, the latter being able to catalyse further hydrolysis^{17,19,20}. In order to prevent the molecular weight decrease during processing, PET and PBT must be carefully dried preliminarily to decrease the moisture content to less than 30 ppm¹⁹. This hydrolysis action can explain the differences in molecular weights and endgroup contents⁷ observed between initial polyester pellets and samples withdrawn just before TPP addition (i.e. at $t = 0$).

After this initial molecular weight decrease during polymer melting, PET kneading in the Brabender plastograph does not induce any additional molecular weight decrease (Figure 8). This indicates that, under the processing conditions used, the possible subsequent re-equilibration by hydrolysis does not contribute to significant molecular weight modification. It also indicates that thermal degradation by pyrolysis can be neglected and that the nitrogen atmosphere during kneading is assumed to minimize any thermo-oxidative process^{19,21–27}.

However, polyester re-equilibrium is assumed to be the cause of ester link scissions (and hence of molecular weight decrease) observed in polyesters 10–20 min after phosphite addition. Indeed, by considering that the ester concentration is virtually constant and that the water concentration is fixed by the processing conditions, a simplified version of the equilibrium constant, equation (3), can be written as

$$K' = [\text{OH}][\text{COOH}] \quad (4)$$

This means that, in polyesters, the critical parameter is the product of the alcohol concentration by the acid concentration. The post-condensation will occur when this product is higher than K' and the hydrolysis would run in the opposite situation.

The chemical reactions occurring between polymer chain ends and phosphite during melt processing reduce the hydroxyl and carboxyl endgroup concentrations. The large amounts of phosphite used (2–5%) can explain a large equilibrium displacement and, therefore, the occurrence of an hydrolysis reaction. The decreases of polymer torque, viscosity and molecular weight, observed 10–20 min after the TPP addition, appear when re-equilibration rules over the chain-extension mechanism induced by the phosphite. The lowest molecular weights, obtained for degraded samples after

long time reactions, confirm the hydrolysis action, especially important for large phosphite quantities.

Such a reorganization, occurring on pure polymers or promoted by a reaction with an external component during melt processing, has also been observed on polyamides. Polyamide 6 exhibits an hydrolysis rate of the same order of magnitude as observed for PET model molecules: 10^{-3} ($\text{l}^2 \text{mol}^{-2} \text{min}^{-1}$)²⁸. However, the polyamide equilibrium constant is estimated in the range 100–1000^{15,28,29}, two orders of magnitude higher than for polyesters. The polyamide synthesis is, therefore, less complicated from an equilibrium viewpoint.

De Roover²⁹ has observed that initial poly(*m*-xylylene adipamide) with different amine and acid chain end concentrations, kneaded in a Brabender plastograph under similar conditions, undergoes re-equilibrium by condensation or hydrolysis. The equilibrium is reached after 35 min and similar viscosity results are obtained for all samples. Maréchal³⁰ studied the end-capping of molten polyamide 6. He observed that the strong reduction of amine chain ends after anhydride reaction on polyamide is followed by a molecular weight decrease: an hydrolysis reaction occurs in order to recover the equilibrium chain end concentrations. These observations of similar reorganization processes, carried out on polyamides, support the proposed explanation for the polyester molecular weight decrease.

Polyester phosphorus content

A direct confirmation of the presence of phosphorus atoms in the bonds created during polyester/phosphite reactive processing is most successfully realized by phosphorus elemental analysis.

The values obtained from blend analyses (Table 4) confirm that the phosphorus elemental analyses are reliable: when 5% TPP is added to the blends, 4750 ppm of phosphorus are indeed measured. Moreover, it is also observed that the total quantity of phosphorus in the polyesters decreases with time. This effect is attributed to the evaporation of some TPP or by-products during mixing at 280°C. Analysis of blends withdrawn just before TPP addition clearly reveals that pure polyesters already contain phosphorus compounds. The quantities found for PET and PET/PBT (75/25) blends range from 65 to 75 ppm. Such additives are often used in industrial compositions. They are included during the polymer synthesis for different purposes: heat or radiation stabilizers, yellowing inhibitors, antioxidants, antifoaming or catalyst deactivating agents, etc.^{2,3,5,6,13,31–36}.

Sample purification is an efficient way to obtain meaningful results concerning the chemical reactions induced by the phosphite. All the performed measurements unambiguously demonstrate the presence of phosphorus atoms chemically bonded to the polyester chain. The detected quantities are not insignificant and, on the contrary, represent a large proportion of the added phosphite. For example, after an initial addition of 2% TPP (1958 ppm), 600–900 ppm of phosphorus are found to be linked to the polymer after 10 min processing (Figure 11). Such observations are in opposition with the results of Aharoni *et al.*¹: they claim that TPP addition to PET during processing does not lead to any phosphorus incorporation into the backbone.

This large discrepancy between our results and the literature cannot be attributed to the different procedures used for the samples purification. Two selected samples,

Table 6 Molar ratio between the added TPP and the amount of hydroxyl, carboxyl and total chain ends in the PET/PBT (75/25) blends, measured immediately before phosphite addition, i.e. at $t = 0$

	TPP/[–OH]	TPP/[–COOH]	TPP/([–OH]+[–COOH])
2% TPP	1.01	1.29	0.57
5% TPP	2.52	3.22	1.41

presented in *Figure 12*, were indeed separately purified in two different ways. Despite the large initial phosphite addition (5% TPP), the same amounts of chemically bonded phosphorus were found by both methods. Dissolving and reprecipitating the polymer constitutes the most accurate way to achieve a complete purification from all residual chemicals. The perfect agreement of the results justifies the efficiency of the acetone reflux method.

Other indications point also in the same direction: the chromatographic measurements show the stabilizing effect of the acetone reflux on the molecular weight of the blends. Furthermore, the values obtained by elemental analysis are entirely consistent, and the purification appears totally efficient. An obvious confirmation is obtained in *Figure 11*: the pure blend already contains 70 ppm of phosphorus. Only 1 min after a 2% TPP addition, the reaction is certainly limited to a small extent and large quantities of residual chemicals are therefore still present. However, an acetone reflux conducted on that sample only reveals a low linked phosphorus amount (93 ppm), thus confirming its efficiency.

Figure 11 points to differences observed concerning the phosphorus content between two PET/PBT blends with 2% TPP. An explanation lies in the molar ratio between the added phosphite and the polymer chain ends (*Table 6*). A 2% phosphite quantity is too low to induce a reaction with every reactive chain end. Thus, small differences in the blending conditions (temperature, mixing time prior to addition, accuracy of the phosphite amount) lead to a large variation in the extent of reaction and, therefore, in the linked phosphorus content. As expected, a much better reproducibility is obtained with a large phosphite excess (*Figure 12*).

At the beginning of the reaction, the rate of phosphorus incorporation in the polyester chain is not strongly modified by the addition of larger phosphite quantities. Therefore, the number and reactivity of the polymer chain ends seems to represent the rate-limiting factor during the first moments of the reaction, rather than the phosphite amount. However, at longer times, the reaction extent is controlled by the phosphite quantity. *Figure 11* shows that the phosphorus incorporation in the polymer is limited by the initial 1958 ppm amount. On the other hand, the use of a large excess induces a regular phosphorus content increase, even when serious reductions are observed in the polymer torque and molecular weight (*Figure 12*).

The understanding of the reactions occurring between model compounds⁹ and their extension to polymers (*Schemes 3* and *4*) shows that the incorporation of phosphorus atoms in the polyester chain can only be attributed to the presence of hydroxyl groups. The reaction between acid and phosphite indeed leads to ester formation and phosphonate release, but no link including phosphorus is created. The theoretical maximum

quantity of linked phosphorus atoms can therefore be calculated on the basis of the initial polyester hydroxyl end-groups' concentration. However, after a large phosphite addition, this value is largely exceeded and the phosphorus content increases as long as phosphite is available in the system. In these conditions, a continuous appearance of hydroxyl groups is required. This point agrees completely with the suggested mechanism concerning polyester reorganization during processing. Chain end consumption by reactions with phosphite induces a large displacement of the condensation equilibrium. The observed torque and molecular weight decreases are consequences of the backbone scissions by hydrolysis. Simultaneously, the creation of hydroxyl groups allows a fixation of additional phosphorus quantities to the polyesters, as measured.

The relationships between the covalent phosphorus linkage in the polymer chain and the torque and molecular weight increases after phosphite addition were also investigated. Chromatographic results undeniably show that different treatments, ineffective on pure polymers, are very sufficient in breaking the new bonds created in the polyester/phosphite systems. The results presented in *Table 3* clearly demonstrate that destroying the new bonds accompanies a significant drop in the phosphorus content together with chain scission. The creation of a phosphorus link between chains, due to the reaction with TPP, is thereby directly proved as one major cause of the molecular weight increase.

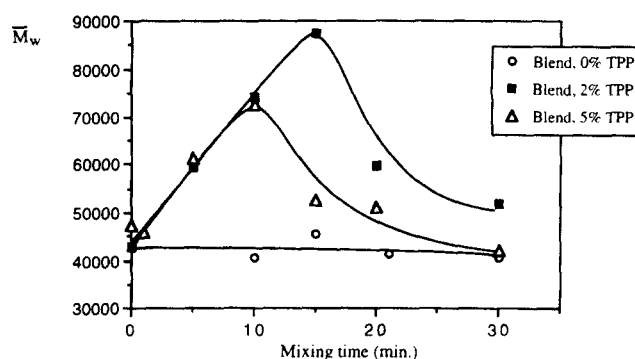
CONCLUSIONS

A detailed chromatographic investigation has been carried out concerning the consequences of TPP addition to polyesters in the molten state. The molecular weight evolution (*Figure 15*) perfectly corresponds to torque and viscosity observations. It fully confirms the occurrence of high temperature reactions between polyesters and phosphite.

The reaction mechanisms deduced from model compound studies⁹ are successfully applied to polymers. The formation of bonds of different types is verified. This modifies the conclusions of Aharoni *et al.*¹.

Phosphite reactions with hydroxyl chain ends lead to the incorporation of significant phosphorus quantities into the polyester backbone. This explains both molecular weight and torque increases.

The weakness of the bonds including phosphorus

**Figure 15** Weight-average molecular weight versus mixing time for PET/PBT (75/25) blends with addition of 0, 2 or 5% TPP, purified by acetone washing

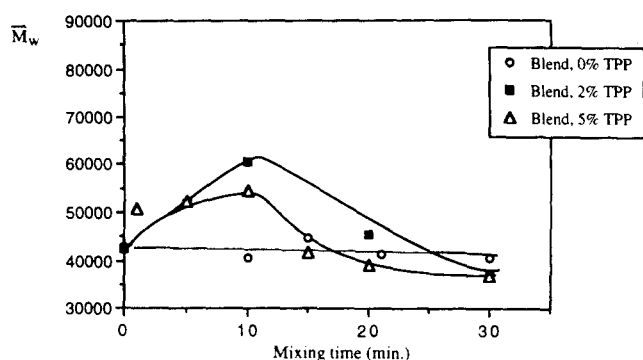


Figure 16 Weight-average molecular weight versus mixing time for PET/PBT (75/25) blends with addition of 0, 2 or 5% TPP, purified by acetone washing, after heating at 120°C in a phenol/TCE (3/2) solution

requires great care with respect to any treatment prior to analysis. In association with the high PET solvent resistance, this point makes the dissolution operations particularly critical. A molecular weight decrease is actually observed when the modified polyesters are heated in the presence of phosphite by-products, phenolic solvent or water (Figure 16). Elemental analysis has shown that this degradation is obtained, together with an important phosphorus content reduction. Exchange reactions between these new bonds and water, phenol or *m*-cresol are assumed to break the phosphorus bond in the chain and to reduce the molecular weight. These observations can explain several differences between our results and the literature, especially concerning the incorporation of phosphorus atoms into the polymer chain.

The addition of TPP induces also the creation of new ester bonds. Actually, the subsequent carboxyl chain end attack secures the stability of the intermediate phosphorus link by turning it into an ester bond (no longer containing P). However, the molecular weight increase observed could perhaps be considered as too small to constitute definitive evidence of the 'catalytic' effect of the phosphite addition on the direct esterification between chain ends.

The decrease of hydroxyl and carboxyl groups by reaction with phosphite leads to a large out-of-equilibrium displacement. With this driving force, hydrolysis progressively occurs to balance the chain-building reaction by recreating the consumed chain ends. The molecular weight decrease after 10–20 min mixing is thus fully explained by the hydrolytic reaction that causes the random scission of ester bonds in the polymer backbone.

As a conclusion, it is difficult to prove unquestionably the formation of new ester bonds when they are already part of the backbone and, moreover, when a reorganization by hydrolysis occurs! In order to prove definitively the complete phosphite action, this point requires confirmation by another method and will be the subject of a following paper.

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