

# Reactions induced by triphenyl phosphite addition during melt mixing of poly(ethylene terephthalate)/poly(butylene terephthalate) blends: influence on polyester molecular structure and thermal behaviour

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The influence of triphenyl phosphite addition in molten poly(ethylene terephthalate) or poly(ethylene terephthalate)/poly(butylene terephthalate) blends has been investigated. Torque measurements during polyester processing and corresponding intrinsic viscosity values confirm an expected chain extension. Chromatographic results similarly indicate a molecular-weight increase. The precise nature of this chain extension mechanism is questioned. Chromatographic and calorimetric observations strongly suggest the formation of ester bonds and of bonds including phosphorus atoms. The enhanced reactivity of these new links towards phosphorous by-products or phenolic solvents at high temperature could explain the degradation observed in specific conditions.

(Keywords: poly(ethylene terephthalate); triphenyl phosphite; reactive processing)

## INTRODUCTION

Poly(ethylene terephthalate) (PET) is an industrial polymer produced worldwide on a large scale. Its intrinsic properties have resulted in the development of numerous applications in fibres, films, bottles and reinforced plastics. However, at processing temperatures, thermal, oxidative and hydrolytic degradation occurs, leading to polyester chain scissions<sup>1–6</sup>. These phenomena limit the recycling possibilities and, therefore, processes for increasing the molecular weight are valuable procedures in counteracting such degradation and recovering suitable mechanical properties<sup>7–11</sup>.

Aharoni and coworkers<sup>12</sup> observed that PET intrinsic viscosity increases after reaction with triphenyl phosphite (TPP) in an extruder. The proposed mechanism is a phosphite reaction with hydroxyl end-groups by displacing one phenoxy group of the TPP. Then a slow reaction takes place between the alkyl diphenyl phosphite and the carboxyl chain end. An ester bond is created and the production of diphenyl phosphite (DPP) as a by-product is observed. Aharoni noted that no phosphorus atoms were included in the polyester backbone.

This mechanism can be extended to polymers

including a similar structure and chain ends. For example, an increase of the weight-average molecular weight has been observed in poly(butylene terephthalate) (PBT) by Delimoy after TPP or DPP addition<sup>13</sup>.

Although industrial applications already exist, often in combination with elastomers or polycarbonates<sup>14,15</sup>, few papers are concerned with PET/PBT blends<sup>16,17</sup>. Stein *et al.*<sup>16</sup> observed a single glass transition, which varies with the composition of the blends. Changes in the crystallization behaviour were explained on the basis of this  $T_g$  modification. Miscibility of PET and PBT in the amorphous phase was therefore suggested. X-ray, d.s.c. and i.r. spectra indicated separate crystals for the two components rather than a co-crystallization.

PET/PBT block copolymers, prepared by end-group coupling of preformed oligomers, exhibit a considerably higher crystallization rate than pure PET and corresponding random copolymers of equivalent molecular weight<sup>18,19</sup>. Large differences are also observed with regard to polyester blends: small amounts of PBT have a much larger effect on increasing the crystallization rate in block copolymers than in simple polyester blends<sup>16,18</sup>. PBT blocks crystallize first and provide built-in nucleation sites for the subsequent crystallization of PET. Improved toughness and tear strength, observed in PET/PBT blends, was also attributed to the formation of certain amounts of block or graft copolymers<sup>17</sup>.

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Polyester blends commonly undergo chemical reactions at elevated temperatures in the solid state and in the melt<sup>20</sup>. Alcoholysis, acidolysis or direct ester interchange can occur between constituents<sup>21–23</sup>. As interchange proceeds, blends convert initially to block copolymers and finally to random copolymers. This is confirmed from studies by small-angle neutron scattering (SANS) of blends involving normal PET and deuterium-labelled PET. Results show that ester interchange is rapid in the melt and also takes place slowly in the solid state below  $T_m$  (refs 24 and 25). The ester interchange reaction was also investigated by the transfer of di(oxyethylene)oxy units from an oligoester to the PET chain, free of catalyst. It was concluded that the reaction in the melt is catalysed by the polyester carboxyl end-groups<sup>27,28</sup>.

Interchange reactions occur in both fully and partially miscible blends<sup>20,23,29–32</sup>. As PET and PBT are completely miscible in the molten state, no delay time is expected before the start of the reactions, contrary to what is observed with other blends<sup>13,33</sup>. Direct evidence of the rapid transesterification occurring in PET/PBT blends can be obtained<sup>17</sup> by <sup>13</sup>C n.m.r. via the difference in chemical shifts of the 'quaternary' aromatic carbon<sup>34</sup>.

It is well known that the rate of ester interchange reaction between polyesters and polycarbonates is significantly accelerated by titanium alkoxides<sup>13,23,29,35,36</sup>. On the other hand, the effectiveness of phosphorus compounds, and particularly phosphites, for deactivation of such residual transesterification catalysts has been established<sup>13,29,35</sup> and their use as stabilizers has been studied extensively<sup>37–45</sup>. The phosphonate species resulting from phosphite hydrolysis with moisture or created *in situ* after phosphite reaction with polyester carboxyl chain ends were also found to be effective transesterification suppressors<sup>13,41</sup>.

Therefore, although blending conditions (temperature, duration of mixing, preparation method) have a large influence on the transesterification rate and resultant molecular chain microstructure<sup>40,41,46</sup>, phosphite addition is presumed to reduce the ester interchange reactions. Following the proposed mechanism<sup>12</sup>, a dual mechanism can be distinguished: not only is complexation of the catalyst residue achieved, but also the number of chain ends capable of reacting through alcoholysis or acidolysis processes with the polymer backbone is reduced by direct reaction with the phosphite.

This inhibiting action of the phosphite supports the choice of triphenyl phosphite as additive for PET/PBT blends. Other PET chain extenders indeed exist and some offer advantages as a result of the absence of any by-product formation<sup>9–11</sup>.

The present work is devoted to the study of the influence of phosphite addition on PET/PBT blends. During reactive processing of these systems, only limited modification of the polymer backbone is expected. However, an extension of the described mechanism suggests reactions involving chain ends and block copolymer formation, together with modified crystallization behaviour.

Different techniques have been used to confirm the occurrence of the chain extension reaction, to investigate its mechanism and to highlight its consequences. Such reactive processing between PET/PBT blends and TPP should indeed enable molecular design by allowing a fine

**Table 1** Polyester hydroxyl and carboxyl chain end concentrations and absolute number-average molecular weights, determined by infra-red spectroscopy on polyesters as received, and calculated values for PET/PBT 75/25 (w/w) blends

	PET	PBT	PET/PBT 75/25 (calculated)
[–OH] (eq. g/10 <sup>6</sup> g)	68	26	58
[–COOH] (eq. g/10 <sup>6</sup> g)	38	44	39
$M_n^a$	18 900	28 600	20 600

<sup>a</sup> Assuming only –OH and –COOH end-groups are present

control of the microstructure of the copolymers formed, thus enhancing the possibility of further industrial applications.

## EXPERIMENTAL CONDITIONS AND MATERIALS

### Materials

Poly(ethylene terephthalate) (PET) was B73L supplied by ICI. Poly(butylene terephthalate) (PBT) was Celanese 2000 supplied by Hoechst Celanese. Concentrations of chain ends were measured by infra-red spectroscopy and absolute number-average molecular weights were calculated. Both are displayed in *Table 1*. Values for PET/PBT 75/25 blends are extrapolated from measurements conducted on pure polyesters.

Triphenyl phosphite (Janssen, 99+%) and Phenol (Janssen, 99%) were used as received. 1,1,2,2-Tetrachloroethane (TCE) (Aldrich, 99%) and *m*-cresol (Merck, P.S.) were distilled before use.

### Processing conditions

The research was conducted on PET/PBT 75/25 (w/w) blends. Different quantities of triphenyl phosphite (TPP) were added to the polyester blends: 0, 1, 2 or 5% TPP. Phosphite concentrations are always reported in amount of additive per weight of base polymer. By considering the polyester number-average molecular weights (deduced from infra-red measurements) immediately before phosphite addition, it appears that 1.78 wt% TPP amounts to one TPP molecule per polyester chain. By taking into account the possible evaporation of some phosphite during mixing, a stoichiometric reaction has been assumed to occur using 2% TPP. The influence of a lower addition or an excess was observed with 1% and 5% phosphite, respectively.

PET and PBT, previously dried overnight at 120°C under vacuum, were kneaded in a Brabender Plastograph equipped with an electrically heated mixing device WEH50. The mixing speed used was 30 rotations per minute. 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.

In all experiments, the polymers were mixed for 5 min in order to get a homogeneous polyester melt before adding the triphenyl phosphite. The zero time corresponds to the withdrawal of a reference sample of the homogeneous melt, followed by the introduction of TPP into the mixer. Other samples were withdrawn after different mixing times ranging from 1 to 20 min. These samples were finely ground in a crushing mill from IKA.

The polyester purification from phosphite reaction by-products was carried out by extraction with acetone for 72 h in a Soxhlet-type apparatus and drying afterwards overnight at 120°C under vacuum.

#### Infra-red spectroscopy

Films were prepared by compression moulding of dried, purified polyesters at 275°C between Teflon<sup>®</sup>-coated aluminium sheets sandwiched between thick stainless-steel plates. Water quenching resulted in 100 µm thick transparent films. The infra-red spectra of these were recorded in a 580B dispersive Perkin-Elmer spectrometer, controlled by a 3600 Data Station micro-processor. Software from Perkin-Elmer (PE580) is used for data collection, storage and analysis.

The method used to measure hydroxyl and carboxyl end-group concentrations in PET/PBT blends was developed by Bricmont<sup>47</sup>. The wavelengths of the absorption bands corresponding to end-group vibrations were previously determined by Ward<sup>48,49</sup>, Zichy<sup>50</sup> and Kosky<sup>51</sup>. For PET/PBT blends, the absorbance values corresponding to hydroxyl and carboxyl chain ends were measured at 3550 and 3270 cm<sup>-1</sup>, respectively. Calibration was realized by using standard values obtained as described by Zichy for PET and Kosky for PBT. Hydroxyl and carboxyl end-group concentrations were computed from absorbance values. Providing no other end-groups exist, the total concentration [X] of hydroxyl and carboxyl end-groups (expressed in equivalents/10<sup>6</sup>g polymer) is related to the number-average molecular weight ( $\bar{M}_n$ ) by:

$$\bar{M}_n = \frac{2 \times 10^6}{[X]} \quad (1)$$

Films were dried for 15 min inside the spectrometer before analysis. Processing differences during film preparation mostly explain variation in the data obtained. For example, accuracy for the end-group concentration values is estimated to 10% and maximal variations observed for  $\bar{M}_n$  values are limited to a 10% range. In order to improve the reproducibility, on each point, several measurements were conducted and only the average value was considered.

#### Viscometry

Intrinsic viscosity was measured with a modified Ubbelohde viscometer in a thermostatic bath regulated at 25°C. The solvent used was a phenol/TCE 60/40 (w/w) mixture. The polyester (0.2 g) was dissolved in 50 ml solution at a temperature not exceeding 40°C. Between each dilution, the solution was properly homogenized by bubbling air and waiting a few minutes before the next measurement. Since polyester blends were analysed, no Mark-Houwink coefficients are available. Intrinsic viscosity values, whose precision range is estimated to a few per cent, are therefore used for comparisons.

#### Gel permeation chromatography

Gel permeation chromatography was performed by using a Waters 150C high-temperature chromatograph with a refractive index detector. Two Shodex columns from Showa Denko (ref. AT-80M/S) were used in series. *m*-Cresol at 115°C was initially used as eluent and the flow rate was 0.8 ml min<sup>-1</sup>. Polyesters were dissolved by

heating for 20 min at 160°C in *m*-cresol. Other samples were also dissolved in a 60/40 (w/w) phenol/TCE mixture at room temperature.

The chromatographic conditions were modified during the course of this work. Therefore, a third Ultrastyrigel column (500 Å from Waters) was added in series. The temperature of the apparatus was decreased to 70°C and the flow rate was 0.4 ml min<sup>-1</sup>. All samples were dissolved in phenol/TCE 60/40 at room temperature, in the latter experiments.

Polyester samples for g.p.c. analysis were purified from reaction by-products and dried before dissolution. The concentrations were 8–10 mg of polymer dissolved in 2 ml of solvent. Approximately 120 µl were injected. 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 2700 to 2 700 000 g mol<sup>-1</sup>. These were dissolved in *m*-cresol. Molecular-weight values are therefore expressed in polystyrene equivalents (PS g mol<sup>-1</sup>). The precision inherent to chromatographic measurements is better than 10%. In order to prevent any modification of the system, the polyester blends were analysed with a calibration curve deduced from polystyrene samples injected immediately before. Polystyrene calibrations were then repeated regularly.

#### Differential scanning calorimetry

Differential scanning calorimetry experiments were carried out under nitrogen in a Perkin-Elmer DSC-7 thermal analyser, coupled with a PE7500 computer. The size of the samples varied between 5 and 10 mg. The d.s.c. instrument was calibrated with metal standards (indium and lead).

Samples were melted and crystallized with a controlled scanning rate of 10°C min<sup>-1</sup>. The sample was held at 280°C for 1 min and then the temperature of crystallization upon cooling ( $T_{cc}$ ) was measured at the top of the peak.

## RESULTS

#### Brabender processing

During polymer processing in the Brabender Plastograph, the torques recorded throughout the experiment are representative of melt viscosity in the system. Typical polyester torque vs. time curves during mixing with various triphenyl phosphite amounts are presented in *Figures 1* and *2*. By comparison with pure polyester behaviour, a very large increase in torque is observed after triphenyl phosphite addition. The torque gains more than one order of magnitude. Similar behaviour was observed for PET and polyester blends.

Some differences were observed depending on TPP concentration. When stoichiometric amounts of phosphite were added, the top of the curve was observed after 15–20 min of mixing. As larger quantities of the phosphite were added, so the increase in torque was more rapid. With a large phosphite excess (5%) the torque curve maximum occurred earlier (in approximately 10 min), but the observed maximum value was then lower.

After the maximum torque value is attained, a decrease is observed at longer mixing times. However, when high torque values are reached, instabilities and

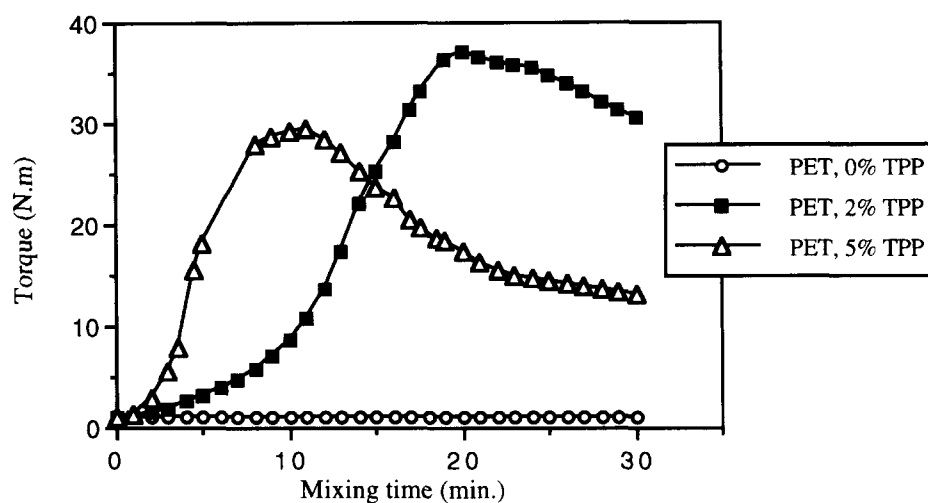


Figure 1 Torque versus mixing time for PET with addition of 0%, 2% or 5% TPP

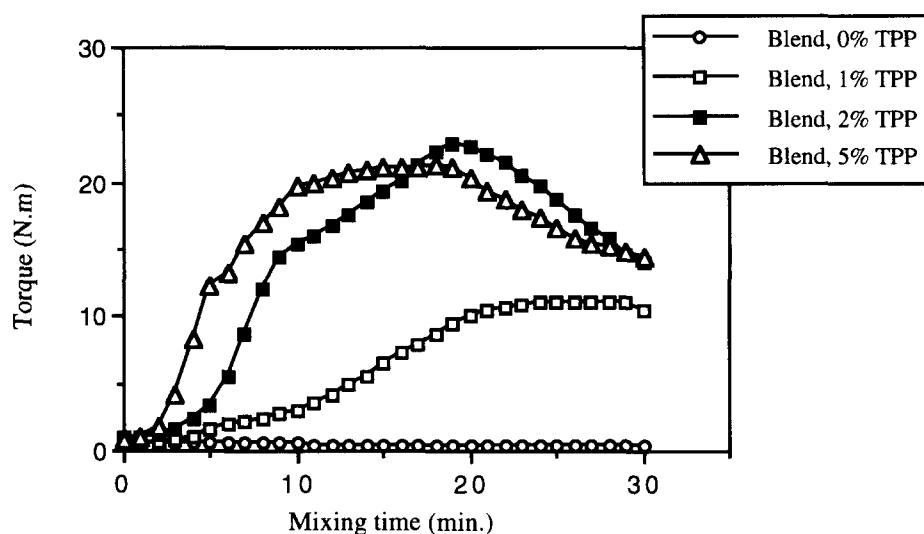


Figure 2 Torque versus mixing time for PET/PBT 75/25 blends with addition of 0%, 1%, 2% or 5% TPP

large oscillations are also observed and average values must be calculated. The polyester melt progressively adopts an elastic behaviour, suggesting the possibility of branching. Therefore, it becomes meaningless still to consider the torque measurements as purely indicative of viscous flow for that part of the curves.

Some processing parameters exert a large influence on the exact torque values and any modification leads to less quantitative reproducibility. For example, a fine control of the processing temperature appears absolutely necessary. An accurate measurement of the TPP quantity appears also critical, especially for stoichiometric amounts. Finally, the delay time between the introduction of polyester pellets into the Brabender and the phosphite addition also plays an important role on the torque value, most probably by modifying the initial chain end concentrations by polyester hydrolysis for example. However, in this work, despite minor variations, large differences in the absolute values are not observed and similar curve shapes are always obtained.

#### Intrinsic viscosity

The intrinsic viscosity of polyester blend samples

taken during mixing after addition of different phosphite quantities is represented on Figure 3. The intrinsic viscosity of pure PET/PBT blends is stable throughout mixing. On the other hand, an increase is observed if TPP is added, the increase being related to the level of phosphite addition. For stoichiometric phosphite amounts, a maximum is observed and then intrinsic viscosity values reduce at longer mixing times.

Different experiments were carried out in order to check the stability of the new bonds created after phosphite addition. On the one hand, neither washing of the blends by refluxing in acetone for 72 h nor heating in air for 20 min at 160°C modify the intrinsic viscosity. On the other hand, these polyester blends were modified after heating in a phenol/TCE solution (Table 2). For example, the intrinsic viscosity of a reacted blend ( $1.43 \text{ dl g}^{-1}$ ) reduces to  $1.21 \text{ dl g}^{-1}$  after 30 min heating at 140°C in phenol/TCE solution. A subsequent heating for 4 h at 110°C in solution causes a drop to  $0.92 \text{ dl g}^{-1}$ . On the other hand, pure PET or PBT heated for 30 min at 140°C in phenol/TCE 60/40 solution do not show any intrinsic viscosity decrease.

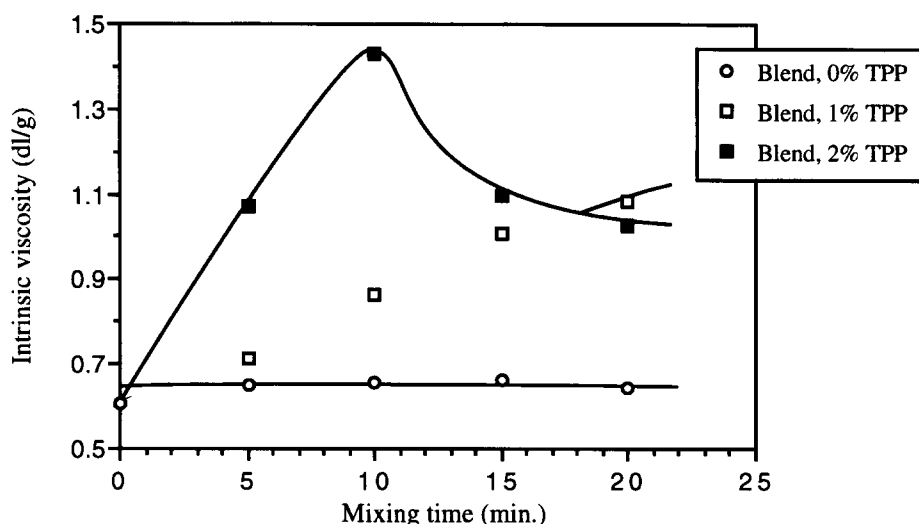


Figure 3 Intrinsic viscosity versus mixing time for PET/PBT 75/25 blends with addition of 0%, 1% or 2% TPP

Table 2 Intrinsic viscosity values of PET/PBT 75/25 plus 2% TPP, measured in phenol/TCE 60/40 at 25°C, after different heating conditions in this solvent

Blend + 2% TPP	Intrinsic viscosity (dl g <sup>-1</sup> )
At room temperature	1.43
After 30 min at 140°C	1.21
After 30 min at 140°C and 4 h at 110°C	0.92

the polyester end-group concentrations after TPP addition is less efficient. Although no interference due to TPP itself is observed at the considered wavelengths, interactions between phosphite and polyesters lead to new bond creation and by-product formation, resulting in spectral modifications that interfere with the chain end measurements.

For example, according to the proposed mechanisms,

Table 3 Polyester hydroxyl and carboxyl chain end concentrations (expressed in eq. g/10<sup>6</sup> g) and absolute number-average molecular weights, measured by infra-red analysis, just before TPP addition. The numbers in parentheses represent the values obtained on polymers as received

	PET	PBT	PET/PBT 75/25	
			Calculated	Measured
[–OH]	71 (68)	33 (26)	61 (58)	67
[–COOH]	45 (38)	42 (44)	44 (39)	56
$\bar{M}_n$	17 300 (18 900)	26 500 (28 600)	18 900 (20 600)	16 100

#### Infra-red analysis

Complementary to titration methods<sup>52,53</sup> and the tritium exchange technique<sup>54</sup>, infra-red spectroscopy can contribute to the determination of hydroxyl ( $N_{OH}$ ) and carboxyl ( $N_{COOH}$ ) end-group concentrations in PET<sup>48–50</sup>, and has already been used to deduce the reaction mechanism in PET/phosphite systems<sup>12</sup>. An extension of this method of chain end determination by infra-red spectroscopy was developed in our laboratory in order to study the behaviour of PET/PBT blends<sup>47</sup>. Absolute number-average molecular weight was deduced from the total end-group concentration.

The infra-red measurements of end-group concentrations and  $\bar{M}_n$  values for polyesters withdrawn just before triphenyl phosphite addition, i.e. after several minutes at 275–280°C, are shown in Table 3. By comparison with virgin polyesters, it is observed that the 5 min processing, necessary to get correct melting and mixing, involves some modifications: both chain end concentrations increase, thus leading to a  $\bar{M}_n$  reduction.

The determination of polyester hydroxyl or carboxyl chain end concentrations is realized by very precise absorbance measurements at 3550 and 3270 cm<sup>-1</sup>, respectively. However, infra-red analysis to determine

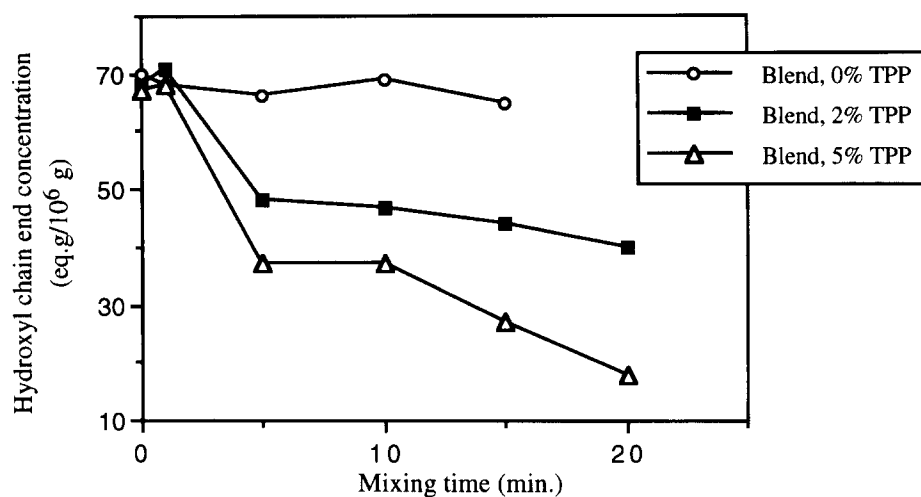
phenol appears as a by-product of the phosphite/polyester reaction. It shows a large absorbance near 3300 cm<sup>-1</sup> due to the stretching of the hydrogen-bonded hydroxyl bonds<sup>55</sup>. Measurements at these wavelengths, especially concerning carboxyl end-groups, are therefore strongly affected.

Efficient by-product elimination is therefore essential prior to any accurate infra-red measurement; this was normally achieved by acetone extraction. No modification due to acetone extraction appears on pure polyesters but an important reduction of  $N_{OH}$  and  $N_{COOH}$  values is observed for polyesters reacted with phosphite, as a result of the elimination of by-products absorbing at the wavelengths concerned.

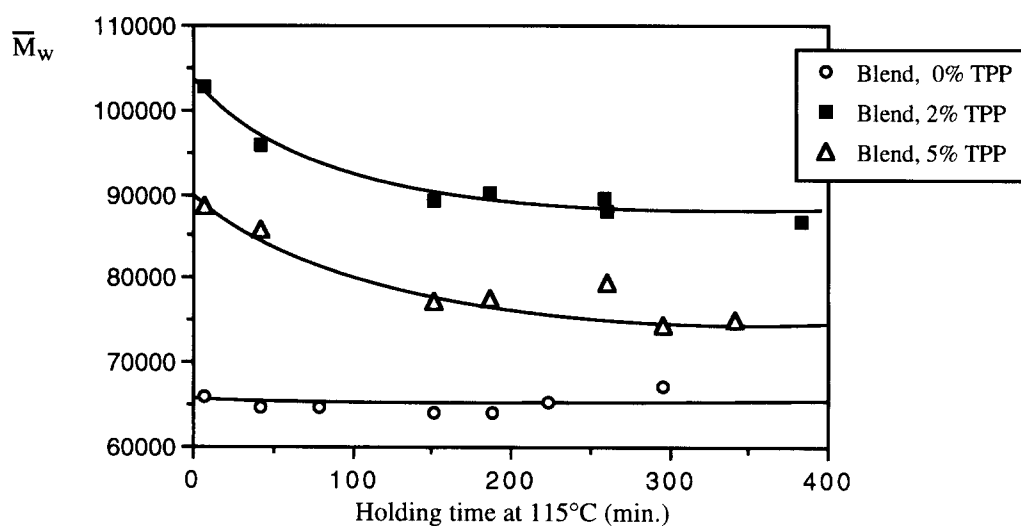
Unfortunately, reliable carboxyl chain end measurements cannot be obtained, even after elimination of the phosphite by-products. However, it is worth noting the significant drop of hydroxyl end-groups observed after phosphite addition. Hydroxyl chain end measurement on PET/PBT blends are shown in Figure 4.

#### Gel permeation chromatography

The evolution of polyester molecular weight can be followed by g.p.c. analysis, enabling changes occurring



**Figure 4** Hydroxyl chain end concentration (expressed in eq. g/10<sup>6</sup> g) versus mixing time, for PET/PBT 75/25 blends, as measured by infra-red analysis on samples containing 0, 2 or 5% TPP



**Figure 5** Weight-average molecular weight versus holding time at 115°C in a phenol/TCE 60/40 solution for PET/PBT 75/25 samples with addition of 0%, 2% or 5% phosphite, respectively

in the molten state between polyesters and phosphite to be followed. In the initial chromatographic procedure, polyesters were dissolved for 20 min at 160°C in *m*-cresol and the analysis was carried out at 115°C in the same solvent. However, reproducible data were not obtained under these conditions for blends reacted with phosphite, and no systematic molecular-weight evolution during mixing was obtained. Even for pure polyesters, degradation caused by the dissolution procedure was observed.

Changes in the procedure were therefore introduced and samples were dissolved at room temperature in a phenol/TCE 60/40 mixture and then analysed in *m*-cresol at 115°C or 70°C. The possibility of polyester degradation during analysis was investigated. The weight-average molecular weight ( $\bar{M}_w$ ) evolution of blends with various phosphite concentrations versus holding time in a phenol/TCE solution at 115°C or 70°C is presented in Figures 5 and 6, respectively. The polyester samples used in these analyses at the two temperatures were withdrawn from different experiments, however.

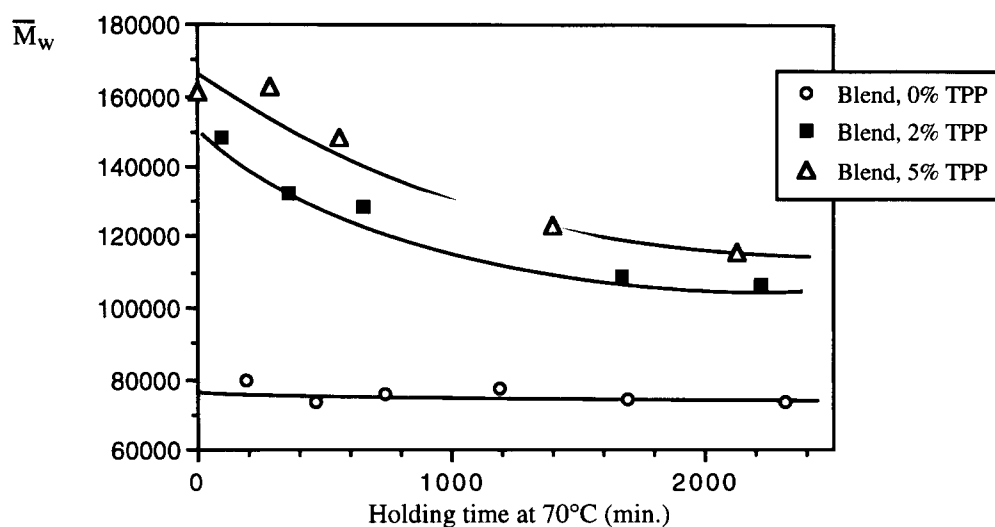
Marked changes are observed in the molecular-weight evolution of polyester blends depending on the presence

of phosphite. On the one hand, molecular weights of pure polyester blends are stable for times up to 5 h at 115°C and 38 h at 70°C. On the other hand, the  $\bar{M}_w$  values of polyester blends containing 2% or 5% TPP are influenced by the sample holding time at high temperature in phenol/TCE solution. Initially, a large decrease is observed, followed by, at longer times, stabilization at values higher than those corresponding to pure polyester blends. The behaviour is similar at the two temperatures used (115°C and 70°C) and only the timescales are different: the higher the holding temperature, the faster the  $\bar{M}_w$  decrease.

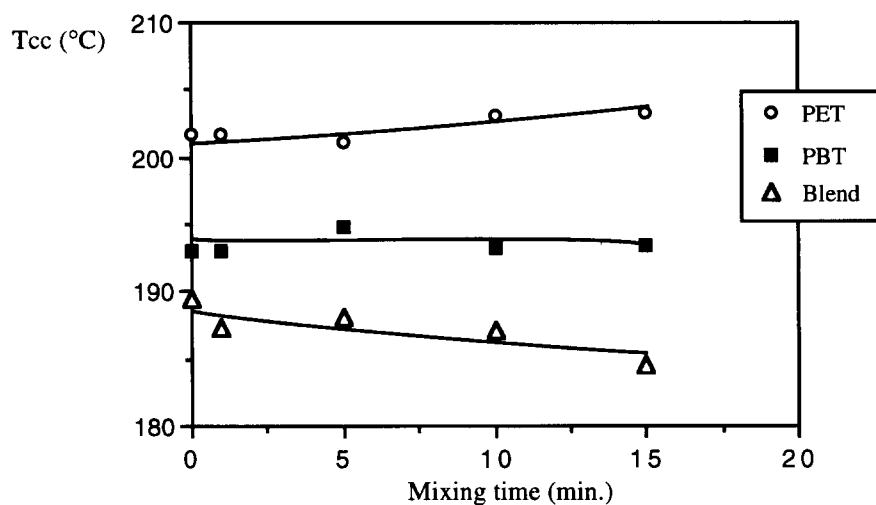
Before the decrease, it should be noted that the correspondence between molecular weights and Brabender torque measurements is qualitatively confirmed with samples withdrawn at higher torque values corresponding to higher molecular weight.

#### Differential scanning calorimetry

The use of crystallization temperature upon cooling ( $T_{cc}$ ) for the evaluation of crystallization rates has been reported elsewhere<sup>56</sup>. For different systems, higher  $T_{cc}$



**Figure 6** Weight-average molecular weight versus holding time at 70°C in a phenol/TCE 60/40 solution for PET/PBT 75/25 samples with addition of 0%, 2% or 5% phosphite, respectively



**Figure 7** Crystallization temperature upon cooling versus mixing time, measured on PET, PBT and PET/PBT 75/25 blend, without phosphite addition

values correspond to faster rates of crystallization. In this work, we used  $T_{cc}$  to investigate the modifications of polyester crystallization behaviour after phosphite addition. PET constitutes the major part (75% by weight) of the blends analysed.

In pure PET/PBT blends realized without phosphite, lower  $T_{cc}$  values are obtained, compared to both initial components (Figure 7). These values do not change significantly with mixing time.

For blends containing phosphite, d.s.c. measurements are not reproducible. First, different  $T_{cc}$  values are observed when two measurements are successively performed on the same sample (Table 4). Moreover, further d.s.c. analyses of blends held for 3 months at room temperature in air shows that no changes occur for pure polyesters but a large  $T_{cc}$  increase is observed for polyester that had been reacted with phosphite (Table 5). Also, predrying of blends containing TPP for 16 h at 100°C results in a large modification of the  $T_{cc}$  values (Table 6).

When the polyester blends are purified by acetone extraction, the d.s.c. behaviour is very different and

successive d.s.c. analyses show similar  $T_{cc}$  values (Table 7). With those, neither holding for 5 months at room temperature in a desiccator nor drying for 16 h at 100°C significantly changes the observed crystallization rate values (Table 8).

Purification by acetone refluxing therefore appears to be an appropriate way to prevent the samples from undergoing further modifications. The changes in polyester/phosphite systems during Brabender mixing are thus preferably studied by measurements on polyesters after elimination of the reaction by-products (Figure 8). After extraction, both PET and PET/PBT blends, containing 2% phosphite, show a  $T_{cc}$  reduction with increasing mixing times.

In order to study the correlation between the polyester chain extension induced by phosphite addition (observed by Brabender torque and intrinsic viscosity measurements) and the crystallization rate modifications, experiments were carried out to confirm the relationship between  $\bar{M}_w$  and  $T_{cc}$  values. The chromatographic experiments (described above) highlighted the different molecular weights obtained for PET/PBT blends after

**Table 4** Crystallization temperature upon cooling measured on PET/PBT 75/25 blends containing 2% or 5% TPP, withdrawn after 10 or 20 min mixing time and analysed twice ((1) and (2) correspond to the first and second runs)

	Mixing time (min)	$T_{cc}$ (°C)	
		(1)	(2)
2% TPP	10	170.7	160.6
5% TPP	20	172.6	160.6

**Table 5** Crystallization temperature upon cooling measured on polyesters with different phosphite quantities, withdrawn after 5 or 10 min mixing time, immediately analysed (1) or held for 3 months at room temperature in the open air before a second analysis (2)

	Mixing time (min)	$T_{cc}$ (°C)	
		(1)	(2)
PET + 0% TPP	5	201.2	200.8
	10	203.1	204.2
PET + 2% TPP	5	171.0	204.0
PET + 5% TPP	5	182.3	206.8
PET/PBT + 0% TPP	5	188.0	181.4
	10	187.2	180.0
PET/PBT + 2% TPP	5	149.9	179.0
PET/PBT + 5% TPP	10	172.6	181.8

**Table 6** Crystallization temperature upon cooling measured on PET/PBT 75/25 blends containing 2% TPP, withdrawn after different mixing times and immediately analysed (1) or held for 16 h at 100°C before analysis (2)

Mixing time (min)	$T_{cc}$ (°C)	
	(1)	(2)
1	160.0	201.4
5	151.8	196.6
10	154.2	201.8
15	150.1	197.9

**Table 7** Crystallization temperature upon cooling measured on purified PET/PBT 75/25 blends with different phosphite quantities, withdrawn after 10 or 15 min mixing time and analysed twice ((1) and (2) correspond to the first and second runs)

	Mixing time (min)	$T_{cc}$ (°C)	
		(1)	(2)
0% TPP	10	191.6	187.2
2% TPP	10	174.2	175.1
5% TPP	15	160.2	158.2

**Table 8** Crystallization temperature upon cooling measured on purified PET/PBT 75/25 blends with different phosphite quantities, withdrawn after 15 min mixing time and immediately analysed (1), held at room temperature in a desiccator for 5 months (2) or held at room temperature in a desiccator for 6 months and heated for 16 h at 100°C before analysis (3)

	$T_{cc}$ (°C)		
	(1)	(2)	(3)
0% TPP	184.6	185.3	185.4
2% TPP	170.0	171.1	166.4
		169.4	166.6
5% TPP	170.0	171.4	167.8
		171.1	170.6

reaction with various TPP concentrations. Holding the polyester/phosphite samples at 115°C in phenol/TCE solution also caused a  $\bar{M}_w$  drop (Figure 5). Some blends treated in this way were analysed by d.s.c. The measured  $T_{cc}$  values, obtained with a good reproducibility, are represented in Table 9. In Figure 9,  $T_{cc}$  values correlate well with the molecular weight. Clearly in polyester/phosphite systems the polymer chain length influences the crystallization behaviour: lowest  $T_{cc}$  values were found on samples presenting highest  $\bar{M}_w$ .

## DISCUSSION

### Polyester evolution during processing

Figures 1 and 2 show that TPP addition to PET or PET/PBT melt blends induces a very large increase of Brabender torque values, corresponding to the polymer melt viscosity increases. Pure polyesters and their blends show a stable behaviour during all the processing time. The addition of phosphite can therefore undeniably be considered as the only reason for the large modifications of the melt viscosity observed. This behaviour is different from that observed with polyester/polycarbonate blends, where a torque increase during processing was assigned to be caused by transesterification reactions<sup>57</sup>.

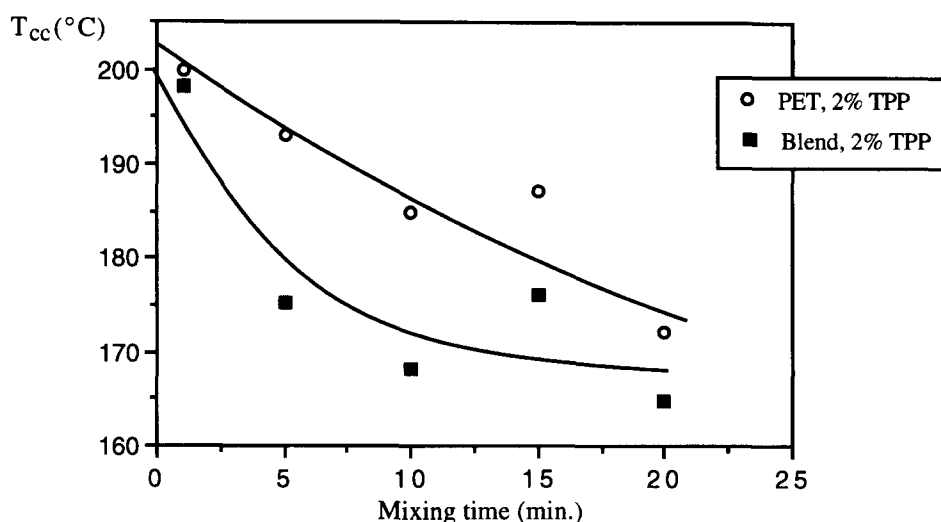
Maximum values of the Brabender torque and their rate of attainment are largely dependent on the phosphite quantities. The torque maximum occurs earlier for polyesters containing larger phosphite amounts. A stoichiometric TPP addition (2%) gives the highest torque values. Intrinsic viscosity measurements (Figure 3) perfectly corroborate torque observations: the viscosity increase constitutes also a sign of polyester chain build-up by phosphite reaction. These experiments confirm the few results described in the literature<sup>58</sup>. In these, large torque increases after aromatic phosphite addition were observed for PET and PET/polyester elastomer blends. For large phosphite amounts, lower values of the torque maximum after shorter mixing times were also measured. Superior impact strength was attributed to grafting reactions induced by the phosphite. However, no explanation for those observations was offered.

A torque decrease was also observed for long mixing times. Such a phenomenon was also mentioned by Aharoni<sup>12</sup>, depending on the processing temperature. This can be assigned to polyester degradation when the chain scission rate becomes faster than the chain extension rate due to phosphite. A more detailed investigation of this decrease requires a better understanding of the phosphite/polyester reactivity. The ratio between the polyester chain end concentration and the phosphite amounts should therefore be taken into account. Moreover, observed torque oscillations and polyester elastic behaviour after extended reaction times have not been explained so far and need further investigations.

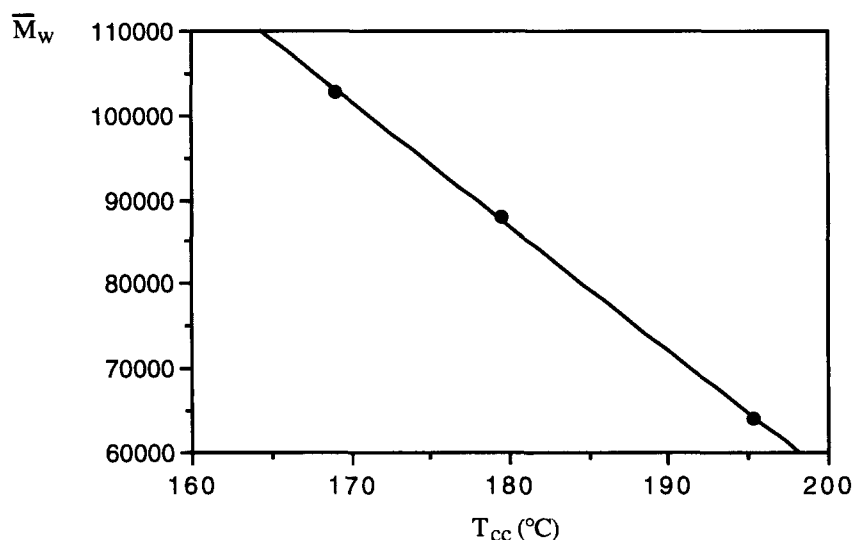
### Chromatographic analyses—polyester evolution in solution

Following the proposed mechanism<sup>12</sup>, phosphite addition induces a polyester molecular weight increase. The literature mentions only Brabender torque and intrinsic viscosity measurements, however. No report was found concerning direct molecular-weight





**Figure 8** Crystallization temperature upon cooling versus mixing time, measured on PET or PET/PBT 75/25 blend after reaction with 2% TPP and purification by acetone refluxing



**Figure 9** Crystallization temperature upon cooling versus weight-average molecular weight for PET/PBT 75/25 blends with addition of 0% or 2% TPP (Samples from Table 9)

**Table 9** Crystallization temperature upon cooling measured on purified PET/PBT 75/25 blends with 0% or 2% phosphite, withdrawn after 15 min mixing time, held in a phenol/TCE 60/40 solution in various conditions, precipitated and washed in distilled acetone and analysed by d.s.c.

	T <sub>cc</sub> (°C)
0% TPP 4 h at 115°C	195.1
	195.5
2% TPP 4 h at 115°C	178.5
	180.5
2% TPP at 25°C	168.9
	169.4

determinations of polyester/phosphite systems. A study by gel permeation chromatography has therefore been undertaken in order to provide data on the extent of reaction.

The initial viscometric study highlighted the degradation observed in polyester/phosphite system at high

temperature in solution. Intrinsic viscosity decreases are indeed observed on polyester blends containing phosphite after holding at 140°C or 110°C in a phenol/TCE solution (Table 2). On the contrary, a similar treatment applied to pure PET or PBT does not induce any appreciable modification. It is deduced from such observations that these conditions do not modify the ester bonds of the initial polymer and the degradation observed can only occur on new bonds created by phosphite in the molten state. The formation of different links, with different behaviour in phenol/TCE of *m*-cresol solutions, is therefore strongly suggested.

In order to study properly the molecular-weight modifications resulting from phosphite addition and to highlight the appearance of different linkages, a procedure has been developed to avoid degradation. Use of solvents such as *m*-cresol or phenol/TCE for polyester chromatography is debated elsewhere<sup>59</sup>. In this work, polyesters are therefore dissolved at room temperature in phenol/TCE in order to avoid uncertainty related to ester

bond stability at high temperature in solution. Reliable information can thus be realized by following the polyester molecular weights as a function of the holding time at 115°C or 70°C in solution (Figures 5 and 6).

Samples free of phosphite show stable molecular-weight values, even after 5 h at 115°C or 38 h at 70°C. This clearly proves that these conditions do not modify the ester linkages and therefore are suitable for polyester analysis. On the contrary, when TPP is present, the holding time at high temperature in solution undeniably has a large influence on the polyester molecular weight. Since analysis conditions do not modify ester bonds, the large molecular-weight decrease observed strongly suggests again the creation of other links during polyester/phosphite reactions. A reduced stability with regard to phenol/TCE or *m*-cresol at high temperature should result in their progressive scission and the subsequent chain length reduction observed.

The creation of a different link in polyesters after phosphite addition was not predicted following the conclusions of Aharoni and coworkers<sup>12</sup>. The reactivity of this new bond, combined with the high solvent resistance of the polyesters, can explain why it has not been observed. Strict dissolution and analysis conditions, much more rigorous than those required for pure polyesters, are essential to highlight its presence. Aharoni did not mention the use of such demanding conditions. The presence of a phosphorus atom in this more reactive link, in contrast to Aharoni's conclusions, appears plausible *a priori*, however. The observation of such a new link constitutes a totally new result and further investigations are necessary to confirm its presence and to determine its nature.

Moreover, the creation of new ester bonds after polyester reaction with phosphite, as proposed by Aharoni, is not denied by our experiments. Polyesters held at high temperature in solution show an initial molecular-weight decrease, followed by a stabilization (Figures 5 and 6). Therefore, it is assumed that, after sufficient times, all reactive links have been broken and the remaining bonds in the polymers are not affected by the analysis conditions. However, this stabilization occurs at molecular-weight values that are significantly higher than those corresponding to starting materials (polyesters without phosphite). This strongly suggests the creation of a stable bond during molten-state reactions. This bond might most probably be assumed to be a new ester (–COO–) bond.

In brief, sample dissolution at room temperature in phenol/TCE and analysis at 115°C or 70°C in *m*-cresol, despite the efficiency for pure polyesters, proved to be inadequate for molecular-weight determination of polyester/phosphite systems. This procedure causes a rapid degradation of the bonds created by TPP in the molten state. Measurements are largely dependent on sample holding time at high temperature in solution and the occurrence of degradation prevents the determination of exact molecular-weight values. A new procedure, working close to room temperature with phenol/TCE eluent, was therefore developed, thus avoiding any degradation<sup>59</sup>. Investigations can therefore be carried out in order to confirm fully the new hypothesis about the creation of two links with a different nature. This extended study is more detailed elsewhere<sup>60</sup>.

#### Infra-red analysis

The reliability and the accuracy of the method used is demonstrated by the measurements conducted on pure polyesters. The observed differences between base polyesters and those mixed for 5 min at 275°C (Table 3) are an obvious manifestation of the degradation occurring during PET and PBT processing. The simultaneous hydroxyl and carboxyl end-group increase confirms the occurrence of hydrolysis rather than pyrolysis at initial processing times.

The problems met with polyesters reacted with phosphite show the high sensitivity of infra-red measurements to the presence of such additives in the polyesters. Even after by-product elimination, accurate carboxyl chain end values could not be obtained. Since the efficiency of the purification method was clearly demonstrated by elemental phosphorus analyses<sup>60</sup>, hypotheses of by-product re-creation during film formation or attribution of the infra-red disturbances to new bonds formed in polyester chains are therefore proposed.

With these limitations, the only significant deduction from our infra-red measurements conducted on polyester/phosphite systems is the large hydroxyl chain end decrease after phosphite addition (Figure 4). This supports the idea of a fast reaction between hydroxyl groups and phosphite and confirms the previous observations realized by Aharoni *et al.*<sup>12</sup>. The exact procedure followed by these authors was not mentioned, however.

#### Differential scanning calorimetry

Stein *et al.*<sup>16</sup> found PET and PBT compatible in the amorphous phase. A single glass transition is observed in the blend and this varies with composition. Furthermore, the crystallization rates are primarily affected by the degree of supercooling of each component and by the influence of blending on the glass transition temperature. Therefore, no reliable conclusion could be deduced from the change in  $T_{cc}$  values between PET/PBT blends and pure homopolyesters (Figure 7). The difference between melting temperature and crystallization temperature upon cooling ( $T_m - T_{cc}$ ) should preferably be measured for a reliable comparison of polymer crystallinity<sup>61</sup>.

Molecular-weight modifications obviously influence the polymer crystallization rate<sup>62</sup>. A higher molecular weight leads to reduced chain mobility and therefore to a lower crystallization rate. The dependence of PET crystal growth rate on number-average molecular weight has been described by Van Antwerpen<sup>63</sup> and Dekoninck<sup>64</sup>. Therefore, since Brabender torque, intrinsic viscosity and preliminary chromatographic measurements have confirmed the chain extension induced by the phosphite addition, the regular  $T_{cc}$  decrease observed on polyester/phosphite systems with increasing mixing time (Figure 8) can be related to a molecular-weight modification (Figure 9).

It is difficult to analyse precisely the evolution of the crystallization behaviour due to block copolymer formation. Block copolymers are indeed expected to increase the crystallization rate, but this effect is largely balanced by the simultaneous chain extension. Samples of similar molecular weights are therefore necessary in order to separate the effects of PET/PBT block

copolymer creation from the influence of chain length increase.

Many different factors can influence the calorimetric observations. A detailed crystallization rate study requires therefore a better understanding of the reactions induced by phosphite. This point is fully confirmed by the huge influence of polyester purification methodology on the crystallization measurements. Reproducible values are only obtained after elimination of the reaction by-products (non-reacted TPP, DPP, phenol, . . .). One can only speculate concerning the large differences measured on polyesters analysed without purification. Not only chemical modifications, but also physical effects can affect the crystallization rate of the system.  $T_{cc}$  decreases observed between two successive analyses could correspond to a further molecular-weight increase caused by an extended phosphite reaction during the heating scans (Table 4).

Various hypotheses can be formulated concerning the possibilities of by-product action. For example, g.p.c. results suggest the creation of phosphorus-containing, reactive bonds. The observed crystallization modifications could result from the increased sensitivity of such links to by-products during holding at room temperature in air or for 16 h at 100°C under vacuum. The substantial molecular-weight reduction resulting from the scission of such bonds could therefore explain the large increase of  $T_{cc}$  values (Tables 5 and 6). However, only speculative hypotheses are possible without further investigations.

Finally, it is concluded that a detailed and valuable crystallization study requires further progress in the investigation of these systems. First, an appropriate g.p.c. procedure is necessary to determine accurately the polyester molecular weights after phosphite reaction. Only comparisons between different samples of similar molecular weights will allow the determination of the influence of block copolymer formation on the crystallization rate. Similarly, a more detailed investigation of the precise reactions induced by the phosphite in the molten state is essential to determine the nature of the bonds created in the polymer chain and their possible enhanced reactivity. The hypotheses concerning links including phosphorus atoms must be verified and the by-product action must be understood and controlled.

## CONCLUSION

The influence of triphenyl phosphite addition in molten PET or PET/PBT blends on molecular structure and thermal behaviour has been investigated. Torque measurements during polyester processing and the corresponding intrinsic viscosity values confirm the expected chain extension. Moreover, preliminary chromatographic results indicate a molecular-weight increase. Accurate  $\bar{M}_n$  determinations could not be realized by i.r. analyses of chain ends, owing to absorbance modifications in the polyester spectra, induced by the phosphite addition. Also, no effects of block copolymer formation on blend crystallization were observed by d.s.c., the influence of block copolymers being largely balanced by the chain extension. Only comparisons between samples of similar molecular weights would highlight the occurrence of an increased crystallization rate.

The precise nature of this chain extension mechanism is questioned. Chromatographic and calorimetric obser-

vations strongly suggest the formation of new and different linkages during the reactions between phosphite and polyesters in the molten state. In addition to ester bond creation, the formation of other links, including phosphorus atoms, is proposed. The enhanced reactivity of these new links towards phosphite by-products or phenolic solvents at high temperature could explain the unexpected modifications observed in the polymers.

A better comprehension of the mechanisms involved is therefore necessary in order to control the consequences of phosphite addition. A study has indeed been carried out with model molecules representative of the hydroxyl and carboxyl polyester chain ends to determine the precise reactions induced by the presence of phosphite<sup>65</sup>. A chromatographic procedure appropriate for polyester/phosphite systems is simultaneously developed<sup>59</sup>. The influence of phosphite addition on the ester-interchange reaction in PET/PBT blends has also been studied by n.m.r.<sup>66</sup>. Further detailed investigations can therefore be conducted on polymers and confirmation about the creation of two links with a different nature during polyester reaction with phosphite will be specially researched<sup>60</sup>.

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