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A ^{13}C n.m.r. study of transesterification in mixtures of poly(ethylene terephthalate) and poly(butylene terephthalate)

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Poly(ethylene terephthalate) and poly(butylene terephthalate) homopolymers and mixtures of these two polymers have been heated in the absence of oxygen at 573 K for 30 min and 476 K for 6 h. The resultant polymers have been analysed using solution viscometry, d.s.c., density determination and ^{13}C n.m.r. Degradation has been observed when the polyesters are heated at 573 K and this is particularly evident for the poly(butylene terephthalate). Assignment of resonances due to homogeneous and heterogeneous dyads and degradation products in the n.m.r spectra have been made using model compounds and a random copolyester which have been synthesized by us. Using these assignments we have calculated sequence length distributions of ethylene and butylene sequences in the materials obtained. On heating at 573 K transesterification of the polyester present in the minority is complete and a single random copolymer is obtained. From the melting point data, it is clear that two copolyesters result when the mixtures are heated at 476 K for 6 h. The values for the number average sequence length suggest that block copolyesters are produced.

(Keywords: poly(ethylene terephthalate); poly(butylene terephthalate); transesterification)

INTRODUCTION

The occurrence of transesterification reactions in polyesters has been known for many years[1]. However, it is only comparatively recently that more detailed descriptions of the kinetics of the reaction and the sequence length distribution in the resulting copolymer have been obtained. In the majority of cases, transesterification has been induced in the melt phases of the polyesters but there have also been indications of such reactions taking place below the melting point of the polyester. Kugler *et al.*[2] used small-angle neutron scattering (SANS) to determine the kinetics of poly(ethylene terephthalate) (PET) transesterification. Subsequently, Benoit *et al.*[3] published revised scattering equations for SANS from transesterifying blends of polyesters which have been used in the study of a main chain liquid crystalline polyester by MacDonald *et al.*[4]. Following this report, the same approach was used by Li *et al.*[5] and Arrighi *et al.*[6] in interpreting their neutron scattering data. Coincident with these scattering studies, Montaudo *et al.*[7,8] have reported the use of fast atom bombardment mass spectrometry and ^{1}H n.m.r. in conjunction with Monte-Carlo modelling to ascertain the mechanism of the transesterification in polyester melts.

Configurational changes in main chain liquid crystal polyesters have been observed to take place below the melting point[9]. Furthermore, McLean[10] observed that different thermal properties (transition temperatures, number of transitions) could be obtained for this same polyester if it was heated below the melting point for finite times. Such reactions in polyesters have been remarked on before by Lenz and Go[11,12] who coined the term 'crystalline induced reorganization' to describe such reactions. In a series of papers[13–16] the formation of non-equilibrium blocky molecules was proposed to be the source of these phenomena, such reactions being promoted by an active ester interchange catalyst. With regard to the use of a catalyst, it should be noted that McLean found that no catalyst was necessary with the polyester she studied.

We report here the use of ^{13}C n.m.r. on mixtures of PET and poly(butylene terephthalate) (PBT) which have been heated above and below the melting points of the two pure polyesters. From the assignments of the n.m.r. data the number average sequence lengths have been obtained and some conclusions made about the nature of the copolymers formed.

EXPERIMENTAL

Polyesters

PET was donated by ICI Films, Wilton, UK. PBT was purchased from Polysciences. Each polymer was dissolved in dichloroacetic acid to form a 4% (w/v) solution which was then poured into a large excess of well stirred methanol to precipitate each polymer. After filtration and washing, each polymer was Soxhlet extracted overnight with dry methanol to remove final traces of dichloroacetic

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*To whom correspondence should be addressed acid. The polymers were then dried under vacuum at 313 K to constant weight.

Molecular weights of PET and PBT were calculated from intrinsic viscosity data. For PET, the intrinsic viscosity was determined using dilute solutions of PET in a 60/40% (w/w) mixture of 1,1,2,2-tetrachloroethane and phenol. These same two components were also used to make dilute solutions of PBT but the solvent composition was 40/60% (w/w) in this case.

Polyester blend preparation and transesterification

Solutions of PET and PBT were prepared in dichloroacetic acid such that the total concentration of polymer was ~4% (w/v) polymer. The homopolymer solutions were mixed in proportions such that the range of PET:PBT ratios covered was between 25:75 and 90:10. Each of these solutions (including those of the homopolymers) was precipitated into methanol, the polymer mixture obtained was filtered off and Soxhlet extracted for 48 h before drying to constant weight under vacuum. Approximately 0.5 g of each finely ground mixture was placed in a Carius tube which was then repeatedly evacuated and purged with dry nitrogen before being finally evacuated and sealed off. Each Carius tube was placed in a steel sheath and then placed in an oven. Two transesterification conditions were used: a low temperature treatment wherein the samples were maintained at 476 K for 6 h, and a high temperature treatment with samples being held at 573 K for 30 min. After heat treatment each specimen was allowed to cool before the Carius tubes were opened. The polymer in each tube was removed and re-ground to provide a fine powder which was stored over silica gel.

Melting points and densities

Melting points and densities of the heat treated blends and the pure homopolymers were obtained using a Perkin–Elmer DSC-7 and a heating rate of 10 K min^{-1}. Densities of each blend and of the homopolymers were obtained using a density gradient column prepared from a mixture of aqueous zinc chloride and distilled water which had been calibrated using glass floats.

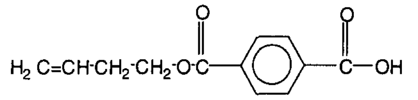
Synthesis of random copolymer and low molecular weight model compounds

A random copolymer of PET and PBT was prepared using apparatus developed by Gümther and Zachmann[17] for the preparation of deutero PET. Dimethyl terephthalate (6.3 g), ethylene glycol (2.98 g), and butane diol (2.88 g) together with triphenyl phosphate (3×10^{-5} g), manganese acetate (6.2×10^{-4} g) and antimony trioxide (2.7×10^{-5} g) were placed in a dry reaction tube in an argon atmosphere. The reaction tube was immersed in an oil bath and fitted with a cold finger condenser and stirrer. Stirring was started whilst argon was passed through the reaction tube, and the tube raised to a temperature of 463 K at a rate of 6 K min^{-1}. On reaching this temperature it was maintained for 30 min after which time the temperature was raised to 473 K at 1 K min^{-1}. After 45 min at 473 K, the temperature was then increased to 513 K at 4 K min^{-1}, held there for 15 min before being increased to 533 K at 2 K min^{-1} where it was held for 40 min. At this stage the argon flow was ceased and the reaction tube connected to a vacuum pump. The temperature of the reaction tube was raised to 543 K at 1 K min^{-1} and the pressure in the tube slowly reduced to 0.05 torr (1 torr = 1.33×10^2 Pa) over a period of 1 h. After a further 2 h, the reaction tube was removed from the oil bath and allowed to cool. On cooling to ambient temperature, the reaction tube was broken open to remove the random copolymer which was dissolved in dichloroacetic acid and reprecipitated in methanol. The random copolymer was Soxhlet extracted and dried in the same way as the PET and PBT homopolymers.

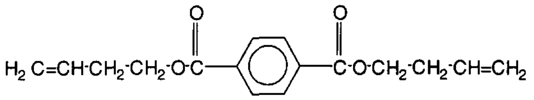
Model compound synthesis

Model compounds, 1,4-benzene dicarboxylic acid mono-3-butenyl ester (I) and 1,4-benzene dicarboxylic acid di-3-butenyl ester (II) were prepared. Terephthaloyl chloride (0.09 mol) was dissolved in 1,4-dioxane (150 ml) to which was added triethylamine (0.18 mol). This solution was placed in a flask fitted with a condenser and a stirrer. The flask and contents were purged with nitrogen and a continuous flow of nitrogen maintained whilst 3-buten-1-ol (0.14 mol) was added dropwise. The reaction mixture was stirred for a further 18 h before the reaction was terminated by addition of water. A mixture of mono- and diester was obtained which were separated on a silica gel column using methylene chloride as eluting solvent.

Elemental analyses were made on the two purified esters: monoester: C 65.63%, H 5.60%, O 28.77% (theoretical C 65.45%, H 5.45%, O 29.1%); diester: C 70.35%, H 6.82%, O 22.83% (theoretical C 70.07%, H 6.57%, O 23.36%). I.r. spectra of both compounds had absorption bands at 731 cm^{-1} (aromatic C–H vibration), 1720 cm^{-1} (carbonyl absorption), 3000 cm^{-1} (aliphatic C–H), 3078 cm^{-1} (aromatic C–H stretch). Only the monoester showed a broad peak in the region of 2500–3000 cm^{-1}, characteristic of the O–H stretching frequency.



I



II

N.m.r.

Samples of each homopolymer, the random copolymer and the heat treated blends were dissolved in deutero trifluoroacetic acid (dTFA) such that polymer concentrations were in the range 5–25% (w/v). In this concentration range no significant shifts in peak positions were noted. All spectra were obtained on a Varian VXR 400-S operating at 100.58 MHz for ^{13}C and at ambient temperature. Spectra were acquired using 60° pulses under conditions of continuous decoupling and with relatively short repetition times of 1.5–3 s. Because of this, all the peak intensities in the spectra may not necessarily be in quantitative ratios. However, signals arising from similar environments within each polymer molecule, e.g. ester groups, should all have similar T_1 and nuclear Overhauser effect characteristics and the peak areas

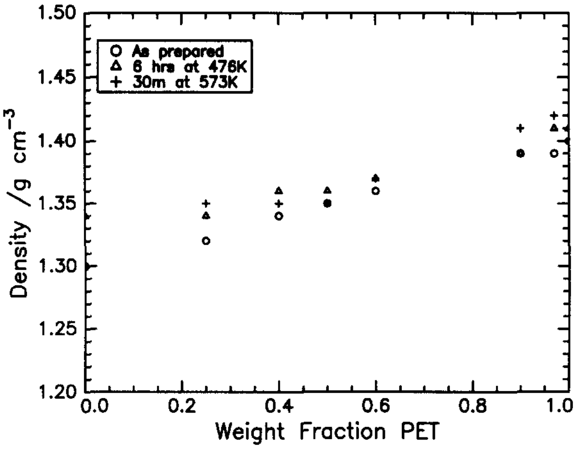


Figure 1 Density of PET–PBT mixtures as a function of composition

within such groups of signals should all be in quantitative ratios. All spectra were referenced to the higher frequency resonance of the two central lines of the CF_3 quartet of the solvent. This resonance was taken as +118.02 ppm from tetramethylsilane.

RESULTS

Characterization

Using the Kuhn–Mark–Houwink coefficients available in the literature for PET[18] and PBT[19] in the mixed solvents specified, the viscosity average molecular weight calculated from the intrinsic viscosity was 32 900 g mol^{-1} for PET and 31 000 g mol^{-1} for PBT. We were concerned about the possibility of thermal degradation in the polyesters especially at the higher temperature of 573 K. Separate t.g.a. of the PET and PBT homopolymers showed that significant (i.e. $>5\%$ of initial weight) thermal degradation did not take place until the temperature was in excess of 620 K when either polymer was heated at 10 K min^{-1} in a nitrogen atmosphere. Nonetheless, each homopolymer was heated at 573 K for 30 min under the same conditions used for the transesterification of the polyester mixtures. After this treatment the viscometric molecular weight of the polymer was redetermined. There was negligible change in the molecular weight of the PET, however the molecular weight of PBT had fallen to 14 000 g mol^{-1}, less than half of the initial starting molecular weight.

The densities of the blends before and after the heat treatments are plotted in *Figure 1*. All the data fall on about the same straight line suggesting that homopolymers and blends adopt the same crystalline unit cell and show little change in unit cell parameters either before or after heat treatment. Furthermore, the proportions of amorphous and crystalline polymer seems to stay the same. The density of PBT has increased after heat treatment, especially when the temperature of 573 K is used. However, since the crystalline density of PBT is 1.396 g cm^{-3}, the observed increase may result from an effective annealing due to the finite cooling rate on removal of the sample from the transesterification oven[20].

Table 1 records the melting points found by d.s.c. on the pure copolymers and the blends before and after each heat treatment. For the PET and PBT homopolymers there is evidence of degradation taking place on heating at the higher temperature of 573 K, this degradation being particularly apparent in the PBT where the melting point has dropped by ~50 K after this heat treatment. For the PET–PBT mixtures, only a single melting point was recorded after heating at 573 K, indicating that a single species is present. Heating the polymers at 476 K for 6 h produces no change in the melting temperature of the PET and only a small reduction of that for PBT. In the heat treated mixtures of the two polymers, two melting points are noted which are lower than those observed in the as-prepared mixtures. Thus we conclude that these lower melting points are symptomatic of the formation of copolymers as a result of transesterification reactions and that the mixtures after heat treatment at 476 K contain two distinct species whose compositions differ from pure PET and pure PBT.

N.m.r. spectra

The n.m.r. spectra recorded for PET and PBT homopolymers and a 50:50 mix of the two polyesters are shown in *Figure 2* and the assignment of the peaks in the spectra of the two homopolymers is given in *Table 2*. As expected, the spectrum of the 50:50 mixture is a superposition of the spectra for the homopolymers. From *Table 2* we note that chemical shifts of the aromatic quaternary and the carbonyl carbon atoms are sensitive to the nature of the alkyl group in close proximity to the phenylene ring. All of the peaks noted in *Table 2* are

Table 1 Melting point data for PET–PBT mixtures before and after heat treatment

	T_m (K)		
PET–PBT (%, w/w)	As prepared	Heated at 476 K for 6 h	Heated at 573 K for 30 min
100:0	530.1 ± 0.1	530.0 ± 0.2	523.0 ± 0.2
90:10	529.8 ± 0.1	534.4 ± 0.2	508.2 ± 0.3
60:40	529.0 ± 0.2	503.0 ± 0.3	
	498.7 ± 0.2	476.1 ± 0.3	467.7 ± 0.4
50:50	528.3 ± 0.2	494.6 ± 0.3	
	495.4 ± 0.2	475.6 ± 0.3	436.5 ± 0.4
40:60	526.6 ± 0.2	523.6 ± 0.3	
	498.3 ± 0.2	486.9 ± 0.3	458.3 ± 0.4
25:75	524.6 ± 0.2	479.5 ± 0.3	
	496.3 ± 0.2	471.5 ± 0.3	438.1 ± 0.4
0:100	504.3 ± 0.1	492.7 + 0.2	455.3 ± 0.2

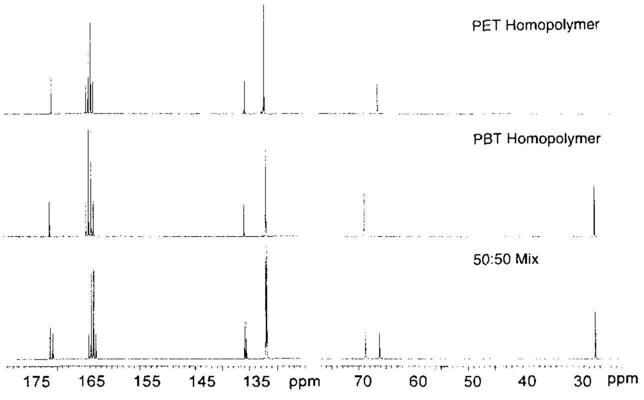
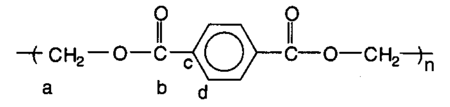


Figure 2 ^{13}C n.m.r. spectra of PET and PBT homopolymers and a 50:50 mixture of the two. The resonances centred at 164 ppm are due to solvent

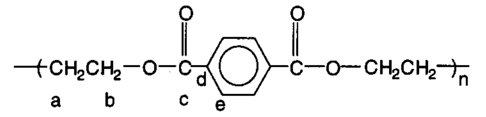
observed in the spectrum of the 50:50 random copolymer shown in *Figure 3* plus additional peaks. In *Table 3* the chemical shift assignments to the quaternary aromatic and carbonyl carbon atoms in the random copolymer are associated with the environment of the atoms, i.e. whether an ethylene glycol or butane diol alkyl residue is neighbouring the aromatic ring. The chemical shifts reported in *Table 3* are marginally greater than those given by Newmark[21] in his ^{13}C n.m.r. study of random copolyesters obtained from dimethyl terephthalate, ethylene glycol and butane diol. The chemical shifts due to the quaternary carbon and carbonyl carbon atoms are diagnostics of their environment and are sufficient to characterize and quantify changes in chain structure (particularly sequence lengths) due to transesterification.

Table 2 Peak assignments in ^{13}C n.m.r. spectra of PET and PBT

PET



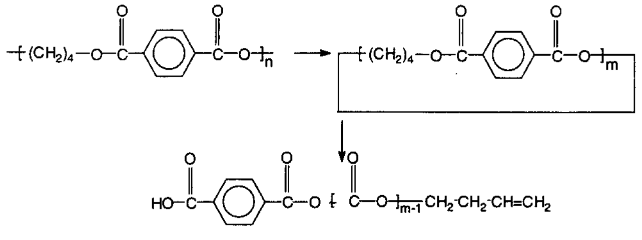
PBT



PET[a]		PBT	
Carbon atom	Peak position (ppm)	Carbon atom	Peak position (ppm)
a	66.26	a	26.87
b	170.87	b	68.82
c	135.62	c	171.36
d	132.15	d	135.92
		e	131.98

[a] Impurity peaks are also evident at 66.92 and 71.28 ppm

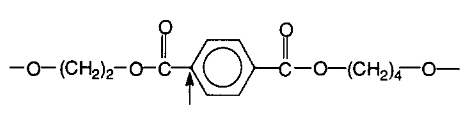
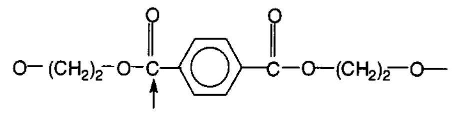
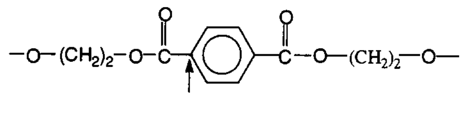
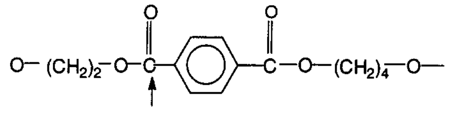
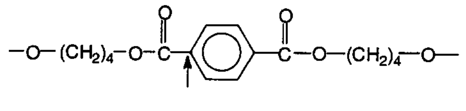
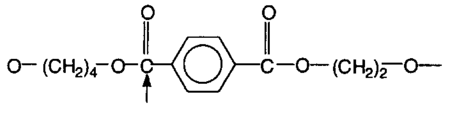
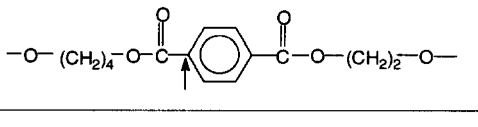
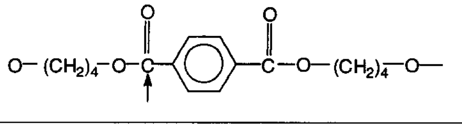
Before attempting to quantify the sequence length distributions, we consider the possible interference with such calculations which may arise from degradation products, particularly from PBT since this has been shown to undergo a significant reduction in molecular weight at 573 K. Montaudo[8] suggests that thermal degradation proceeds via cyclic oligomers which react further producing linear oligomers with vinylic and acid end groups:



^{13}C n.m.r. spectra for PET and PBT homopolymers which have been heated at 573 K for 30 min are shown in *Figure 4*. For the PBT additional peaks (relative to the non-heat treated PBT) are observed in the alkyl, vinyl, aryl and ester/acid regions of the spectrum. Although additional peaks are observed in the spectrum of the heat treated PET, none of these are in the vinyl region. A listing of the chemical shifts of the additional peaks in the spectra of these heat treated polyesters is given in *Table 4*. No additional peaks were observed in the spectra of the two homopolymers which had been heat treated at 476 K for 6 h.

Attribution of the additional peaks due to PBT degradation products was made using the ^{13}C n.m.r. spectra of the two model compounds synthesized, 1,4-benzene dicarboxylic acid mono-3-butenyl ester and

Table 3 ^{13}C n.m.r. chemical shifts assigned to the random copolymer of PET and PBT

Quaternary aromatic carbons		Carbonyl carbon atoms	
Chemical shift (ppm)	Environment	Chemical shift (ppm)	Environment
135.37		170.89	
135.62		170.99	
135.91		171.25	
136.16		171.36	

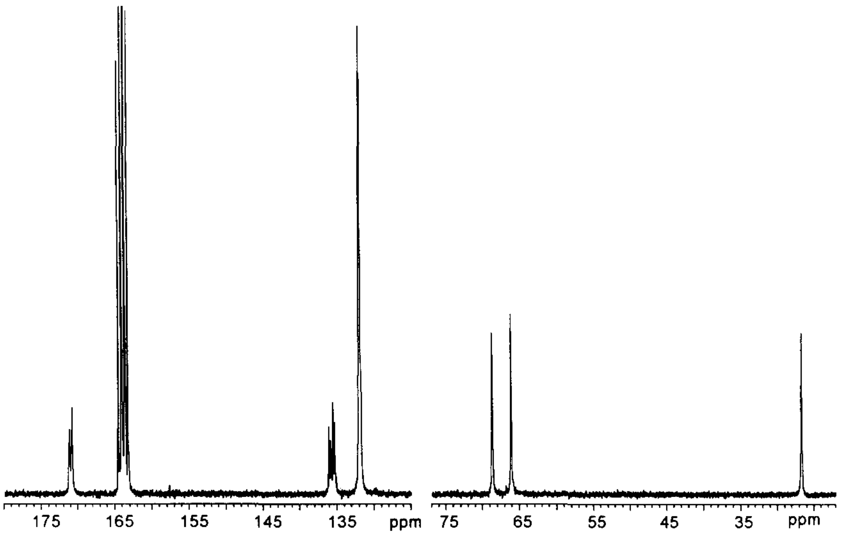


Figure 3 ^{13}C n.m.r. spectrum of the copolymer of ethylene and butylene terephthalate

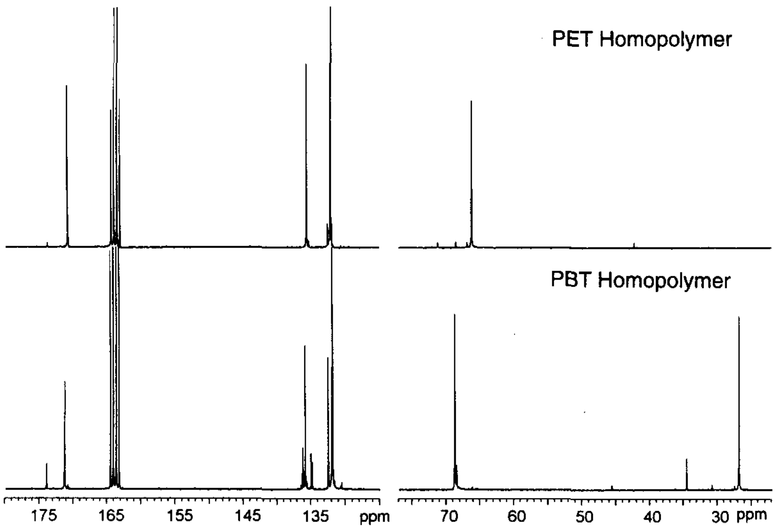


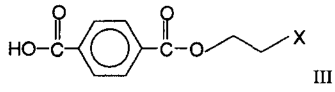
Figure 4 ^{13}C n.m.r. spectra of PET and PBT homopolymers after heating at 573 K for 30 min

Table 4 Chemical shifts of additional peaks in ^{13}C n.m.r. spectra of PET and PBT heated at 573 K for 30 min

Polymer	Chemical shift (ppm)
PET	42.31
	68.57
	132.00
	132.56
	135.27
	135.74
	170.94
	173.83
PBT	34.53
	68.51
	119.24
	131.87
	132.54
	134.85
	135.05
	136.27
	171.39
	173.97

1,4-benzene dicarboxylic acid di-3-butenyl ester. *Table 5* lists the chemical shift assignments of the various carbon atoms in these two compounds. Comparing *Table 5* with the PBT part of *Table 4*, it is clear that all the additional peaks in the partially degraded PBT are evident in the assignments made for the model compounds. Consequently the occurrence of vinyl and acid moieties due to degradation of PBT is confirmed and this supports the formation of cyclic species as a mechanism for the degradation of PBT.

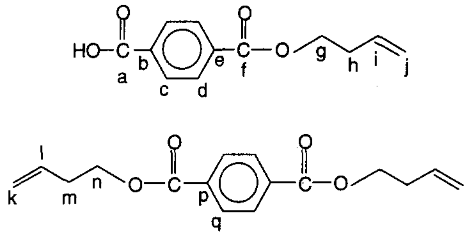
For PET degradation, the absence of vinyl end groups and the appearance of additional resonances in the alkyl region indicates that the same mechanism cannot prevail. Additionally, the spectrum of the PET heat treated at 573 K suggests the presence of inequivalent CH_2 groups and phenylene rings substituted as in III below in the resulting polymer:



III

The nature of the end group X is unknown. Although the presence of resonances due to degradation products after heat treatment at 573 K for 30 min is a complicating factor in the interpretation of the spectra of the transesterified mixtures, they are easily detectable for both PET and PBT and consequently do not obscure the identification of those resonances due to transesterification. In some cases peak overlap makes the evaluation of peak areas more difficult and we remark on this where necessary.

Table 5 Chemical shift assignments of 1,4-benzene dicarboxylic acid mono-3-butenyl ester and 1,4-benzene dicarboxylic acid di-3-butenyl ester



Carbon atom	Chemical shift (ppm)
h, m	34.52
n	68.34
g	68.57
j, k	119.20
q	131.86
d	132.29[a]
c	133.02[a]
e	134.81
i, l	134.89
p	135.90
b	136.42
f	171.06
o	171.18
a	173.80

[a]These two assignments may be interchangeable

In discussing the n.m.r. spectra we will use the terms homogeneous and heterogeneous dyads to describe sequences where a phenylene ring is flanked by the same or different alkyl chain residues, respectively. Denoting a PBT residue by subscript B and a PET residue by subscript E, then the number average sequence lengths and weight fraction composition are given by[22]:

$$\bar{n}_E = \frac{N_{EE} + (N_{EB}/2)}{(N_{EB}/2)} \tag{1}$$

$$\bar{n}_B = \frac{N_{BB} + (N_{EB}/2)}{(N_{EB}/2)} \tag{2}$$

$$w_B = \frac{N_{BB} + (N_{EB}/2)}{N_{EE} + N_{BB} + N_{EB}} \tag{3}$$

where $\bar{n}_i$ is the number average length of an i sequence, w_B is the mole fraction of PBT in the copolymer, N_{ii} is the number of homogeneous dyad sequence runs of type ii and N_{ij} is the number of heterogeneous dyad sequence runs of either type (N_{ij} or N_{ji}). The values of N_{ii} and N_{ij} are directly proportional to the area under the spectral peaks associated with the particular dyad sequence concerned. Values of $\bar{n}_E$ and $\bar{n}_B$ should lie between 1 and infinity. A value of 1 corresponds to a strictly alternating copolymer and a value of infinity pertains to a homopolymer. When we consider a mixture of PET and PBT, the number average sequence length of the minority component is the factor to consider. A value of $\bar{n}_i = 2$ indicates that the minority component is randomly distributed over all molecules in the mixture. Equations (1)–(3) have been applied to the spectra obtained and values of $\bar{n}_E$, $\bar{n}_B$ and w_B are given in *Table 6*. Both quaternary aromatic and carbonyl carbon atom resonances have been used and the values of $\bar{n}_B$ and $\bar{n}_E$ are reasonably consistent with each other. This confirms our assumption expressed earlier that resonances within a given region can be treated quantitatively. Using the homogeneous

Table 6 Sequence lengths and composition of random copolymer and heat treated PET–PBT mixtures

	Peaks analysed	Mole fraction PBT	$\bar{n}_B$	$\bar{n}_E$
Random copolymer	Q–Ar	0.429	1.8	2.4
	C = O	0.430	1.7	2.3
PET–PBT mixtures heated at 573 K for 30 min				
90:10	Q–Ar	0.066	2.2	30.7
	C = O	0.057	1.8	30.1
60:40	Q–Ar	0.215	1.8	6.6
	C = O	0.209	1.8	6.9
50:50	Q–Ar	0.474	2.9	3.2
	C = O	0.485	3.7	3.9
40:60	Q–Ar	0.574	8.0	5.9
	C = O	0.547	8.0	6.6
25:75	Q–Ar	0.695	4.8	2.1
	C = O	0.665	4.3	2.2
PET–PBT mixtures heated at 476 K for 6 h				
50:50	Q–Ar	0.505	14.0	13.6
	C = O	0.485	9.6	10.2
40:60	Q–Ar	0.569	7.2	5.5
	C = O	0.557	6.0	4.8
25:75	Q–Ar	0.767	16.1	4.9
	C = O	0.759	13.3	4.2

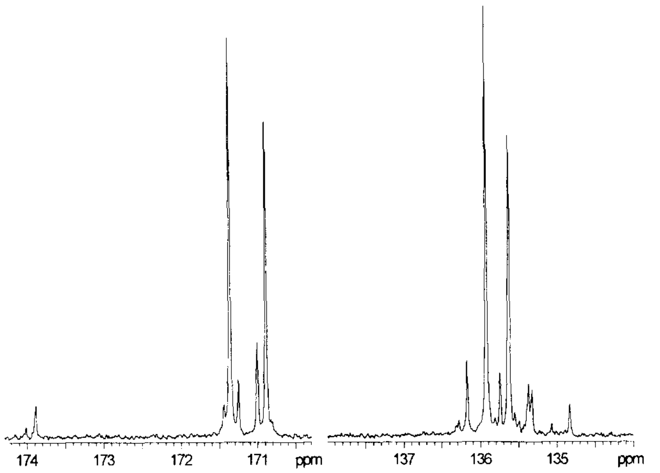


Figure 5 ^{13}C n.m.r. spectrum of the C = O and quaternary aromatic carbon atoms of the 40:60 PET–PBT mixture after heating at 573 K for 30 min

and heterogeneous dyad assignments discussed earlier, the copolymer synthesized by us does indeed appear to be truly random. The values of the number average sequence length of PBT and PET units ($\bar{n}_B$ and $\bar{n}_E$, respectively), given in *Table 6* are very close to the value of 2 expected for a random copolymer. Moreover the PBT content of the copolymer calculated from the spectral data is in agreement with the amounts of butane diol used in the synthesis.

Considering first of all the PET–PBT mixtures which have been heat treated at 573 K for 30 min. An example of the spectra obtained is shown in *Figure 5* for the 40:60 mixture and we show the carbonyl and quaternary aromatic carbon atom regions of the spectrum only. Both regions contain a considerable number of peaks many of which can be attributed to: (1) sites with identical glycol residues each side of the phenylene ring; (2) sites with differing glycol residues flanking the phenylene ring; (3) thermal degradation products of the type modelled by the two low molecular weight compounds previously described. However, not all of the observed peaks could be accounted for in these ways. The small number of peaks not due to any of these three sources (e.g. those at 171.44, 135.75 and 135.33 ppm) are probably due to the occurrence of sequences such as an ethylene glycol residue attached to a phenylene ring (via a carbonyl group) with a degradation fragment of PBT on the other side of the ring, e.g. a vinyl chain end. Nonetheless, sufficient number of peaks could be assigned to analyse the spectra fully. Where the signal to noise ratio was sufficiently large, spectral deconvolution was used to obtain peak areas for peaks attributable to the quaternary aromatic and carbonyl carbon atoms set out in *Table 3*. From the results in *Table 6* it is immediately apparent that the amount of PBT in the blend has been considerably reduced. This reduction is particularly evident for the 60:40 mixture where analysis of the n.m.r. spectrum suggests that the mixture only contains ~21% PBT. We can suggest no reason why this mixture should be more prone to PBT degradation than the others. The reduction in PBT content of all the blends is consistent with the proposed degradation of PBT based on the observation of a reduction in the molecular weight of pure PBT noted above and the identification of resonances due to vinyl end groups in the spectra. In attempting to obtain $\bar{n}_B$ and $\bar{n}_E$ from peak area analysis of heterogeneous and homogeneous dyads, we have not taken this degradation of PBT into account. Consequently the values of $\bar{n}_B$ and $\bar{n}_E$ may be subject to systematic errors in terms of their *absolute* values but comparison of these values with each other allows meaningful conclusions to be made. Melting point data tell us that only one polymeric species is present and as we compare values of $\bar{n}_B$ and $\bar{n}_E$ for the different compositions, attention should be focused on the number average sequence length of the minority component in the mixture. Hence for the 90:10 and 60:40 mixtures, $\bar{n}_B \simeq 2$, which suggests that the original PBT homopolymer has become completely dispersed over all molecules in the system. Copolymers are formed with the PBT units distributed randomly along the molecule. Similarly for the 25:75 PET/PBT mixture, now $\bar{n}_E$ is ~2, indicating that transesterification of the PET is complete and the PET units are randomly distributed in the resultant copolymer molecules. For the 50:50 composition the values of $\bar{n}_B$ and $\bar{n}_E$ are such that small blocks of PET and PBT are formed. This is also true for the 40:60 mixture, but the PBT blocks are somewhat longer since there is a greater probability of transesterification of a PBT molecule with another PBT molecule by virtue of the higher PBT content in the original mixture. All these data are consistent with the formation of random copolymers when the mixtures are heated at 573 K. This view is also consistent with the observation from SANS that the *apparent* molecular weight of deutero PET in a mixture with PBT decreases rapidly on heating at this temperature.

For the blends heated at 476 K we could not obtain peak areas for the 90:10 and 60:40 mixtures with confidence, due to resonances which could not be deconvoluted from those of the dyads of interest. We have therefore confined our comments to the 50:50; 40:60 and 25:75 mixtures. The values obtained for the PBT content from the n.m.r. spectra show that no degradation of the polymer had taken place during heating, however, it is evident from the melting point data that there are two species present in the mixture. The values of $\bar{n}_B$ and $\bar{n}_E$ do not indicate anything about the distribution of PBT and PET units between these two species, all they provide is the *average* sequence length over all molecules in the mixture. Although, as anticipated, the value for $\bar{n}_E$ decreases as the overall content of PET decreases, the value for a random distribution ($\bar{n}_E = 2$) is not obtained even in the 25:75 mixture. These values suggest that the copolymers formed have a 'blocky' organization and in the 50:50 mixture both PBT and PET sequences have the same average number of sequences at ~10–12. Even in the 40:60 mixture where a longer block of PBT sequences would be expected, both sequences have the same number average value of ~6. It is only for the lowest PET content mixture that considerably longer PBT blocks are observed in the heat treated mixture.

CONCLUSIONS

Heating PET and PBT homopolymers at 573 K produces degradation of the polyesters, particularly for the PBT. Identification of degradation products in the ^{13}C n.m.r. spectrum of PBT using model compounds provides support for the reaction mechanism proposed by Montaudo, i.e. degradation is preceded by the formation of cyclic species. In the case of PET, this mechanism does not appear to be followed since the presence of vinyl end groups was not observed and we have been unable to identify the nature of the end group.

Using a random PET/PBT copolyester we have identified resonances due to heterogeneous dyads. These assignments have been used to determine the number average sequence lengths of butylene and ethylene sequences in the PET/PBT mixtures on heating. After heating at 573 K, a single random copolyester species is obtained. By contrast, heating at 476 K results in the retention of two distinct polymer species as indicated by the melting point data. However, both these species appear to be block copolyesters, i.e. a finite extent of transesterification has taken place.

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