Transesterification in poly(butylene terephthalate)/polyarylate blends

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Triad concentrations obtained by ^{1}H n.m.r. analysis enable the determination of the degree of randomness and average sequence length of poly(butylene terephthalate) (PBT) units for a number of melt processed PBT/polyarylate blends. Transesterification was confirmed by reduced degrees of crystallinity and melting points.

(Keywords: transesterification; polymer blends; n.m.r.)

The understanding and characterization of the trans-reactions which frequently accompany melt processing in polyester blends are of great practical importance. In the course of our studies on the phase behaviour and crystallization of poly(butylene terephthalate) (PBT)/polyarylate (PAr) blends[1,2], we undertook a brief study of the PBT/PAr transesterification reaction using ^{1}H n.m.r. and the resulting change in selected physical properties. The results of these experiments, undertaken at conditions which are typical for melt blending these materials, are summarized in this paper.

The intrinsic viscosity of the PBT (provided by the Hoechst Celanese Corporation) used in this study was found to be 0.84 dl g^{-1} in a 40/60 wt% mixture of 1,1,2,2-tetrachloroethane and phenol at 30°C ($\bar{M}_w$ = 45 000 g mol^{-1}, $\bar{M}_w/\bar{M}_n$ = 1.9)[3]. The PAr used (also from Hoechst Celanese) was based on bisphenol A and isophthalic and terephthalic acids (in the mole ratio of 75/25 isophthalic/terephthalic) and had an intrinsic viscosity of 0.60 dl g^{-1} at 30°C in tetrahydrofuran ($\bar{M}_v \sim$ 36 000 g mol^{-1})[4]. Blends of PBT and PAr have been found to be miscible both in the presence and absence of transesterification[2,5].

A twin screw Brabender Plastigraph was used to prepare all blends. Prior to melt blending, the PBT and PAr were dried at 120°C under $\sim 333 \times 10^2$ Pa and nitrogen sweep for 16 h. All mixtures contained 50/50 wt% PBT/PAr. Additional catalyst in the form of tetrabutyl titanate was added to some of the samples during melt mixing to increase the concentration from 60 ppm (concentration of titanium), the amount originally present, to a total of 270 ppm. The processing conditions of the various samples are given in *Table 1*.

The melt blends were analysed by ^{1}H n.m.r. spectroscopy to obtain information on triad concentrations, which was used to calculate average sequence lengths and degrees of randomness. N.m.r. samples were prepared by dissolving the blends in a 50/50 mixture of deuterated chloroform and deuterated trifluoroacetic acid. Tetramethylsilane was added to the solution as an internal standard. Samples were analysed at field strengths of either 200, 360 or 500 MHz on Bruker nuclear magnetic instruments (models WP-200, WM-360 and AM-500, respectively).

Measurement of melting points, heats of fusion and glass transition temperatures (T_g) of selected samples was accomplished with a Perkin Elmer differential scanning calorimeter (DSC-7). A heating rate of 20°C min^{-1} was used in all cases and the melting endotherm was defined by a baseline constructed from 135°C to a temperature above which no melting was observed. Weight per cent crystallinity was calculated using a perfect crystal heat of fusion[6] for PBT of 34 cal g^{-1}. It should be noted that the calculated degree of crystallinity in the blends was based upon the weight per cent of PBT in the blend. All measured values reported are based on an average of a minimum of two d.s.c. scans. Pure indium was the reference material used to correct temperature values and heats of fusion.

The 200 MHz ^{1}H n.m.r. spectra of PBT and PAr are shown in *Figure 1* along with peak assignments. In the spectrum of PAr, the 'extra' peak in the centre of the 'B' quartet ($\sim$7.3 ppm) is due to chloroform. The 500 MHz ^{1}H n.m.r. spectrum of a 50/50 wt% solution (no melt mixing) of PBT and PAr is shown in *Figure 2*. As would be expected, it is a combination of the spectra of the two individual components. In this figure the partial spectrum of a melt-processed, transesterified blend (i.e. CAT-320-15) is superimposed in the chemical shift region of 8.0–8.5 ppm. This is the spectral region on which we will concentrate our analysis.

Gouinlock *et al.*[7], in a ^{1}H n.m.r. study of bisphenol A–neopentyl glycol–terephthalic acid copolyesters and model compounds, assigned chemical shifts to the

Table 1 Melt processing conditions (50/50 PBT/PAr)

Sample	Conditions
290-5	290°C, 5 min
290-20	290°C, 20 min
300-5	300°C, 5 min
CAT-320-15	320°C, 15 min, catalyst added
ND-260-20	260°C, 20 min, polymers not dried
CAT-ND-290-12	290°C, 12 min, catalyst added, polymers not dried

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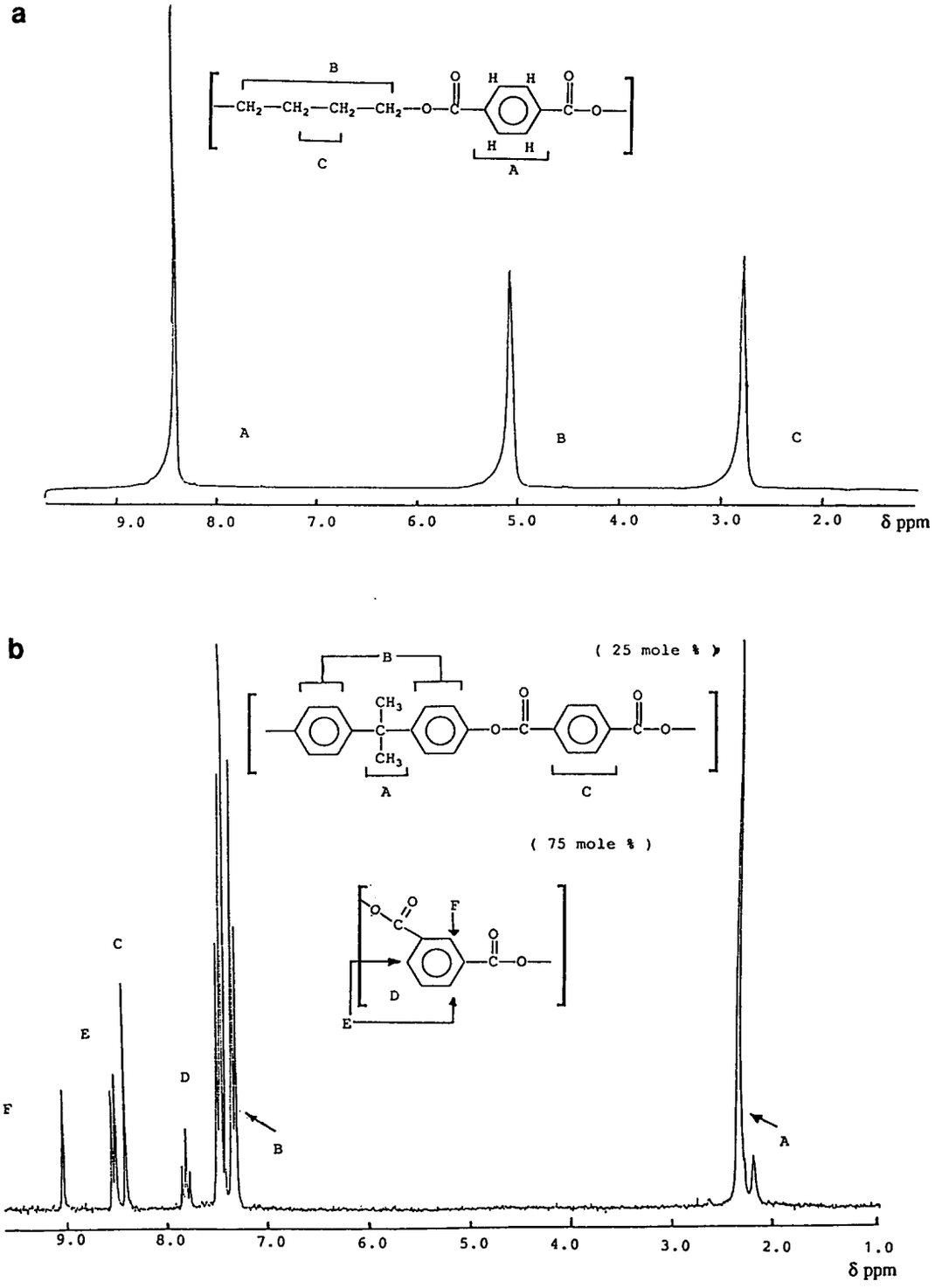


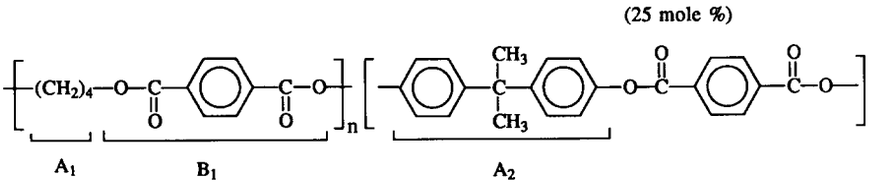
Figure 1 200 MHz ^{1}H n.m.r. spectra of (a) PBT and (b) PAr

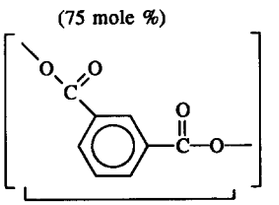
terephthalate protons. A singlet is observed in both cases where the terephthalate unit is symmetrically substituted with either aliphatic (neopentyl) or aromatic (bisphenol A) units at $\delta = 8.06$ and 8.28 ppm, respectively. When the terephthalate protons exist within an unsymmetrical diester sequence (e.g. aliphatic–terephthalic–aromatic) the *para*-disubstituted benzene ring is expected to give rise to a four spin spectrum of the AA'BB' type[8]. The resulting spectrum is complicated but under ordinary resolution resembles two distorted doublets as was observed by Gouinlock *et al.*[7].

The *para* substitution of a benzene ring by aliphatic and/or aromatic units is directly analogous to transesterified mixtures of PBT and PAr in which the aromatic group is bisphenol A and the aliphatic group is $-(CH_2)_4-$. In *Figure 2* the portion of the transesterified spectrum clearly shows the two singlets and quartet which confirm this analogy. By measuring the relative areas of the terephthalate resonance peaks, the fraction of terephthalate groups of each manner of substitution can be determined. This triad concentration information can then be used in a statistical analysis to calculate the degree of randomness and average sequence length[9,10].

Table 2 Results from n.m.r. experiments

Sample	$f(A_1B_1A_1)$	$f(A_2B_1A_2)$	$f(A_iB_1A_j)_{i\neq j}$	B_{B_1}	X
Initial	0.87	0.13	0	0	109
290-5	0.81	0.14	0.06	0.12	30
290-20	0.81	0.11	0.09	0.19	19
300-5	0.81	0.12	0.07	0.14	26
CAT-320-15	0.74	0.11	0.15	0.32	11
ND-260-20	0.80	0.13	0.07	0.14	25
CAT-ND-290-12	0.80	0.13	0.08	0.16	22





Scheme 1

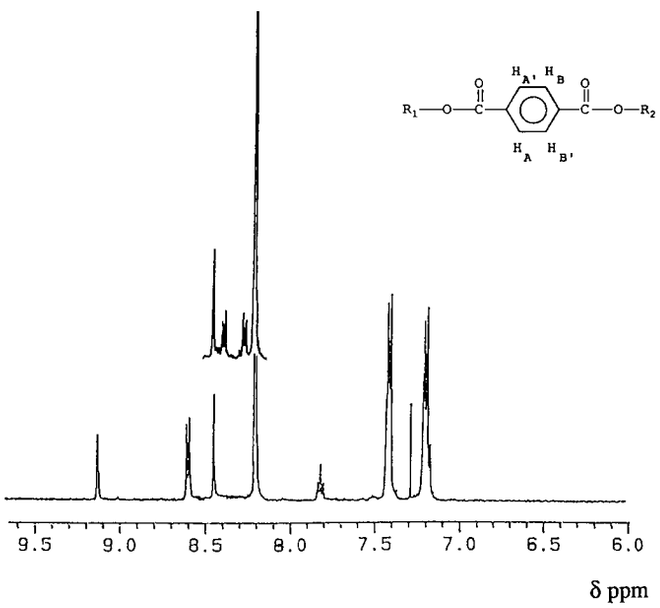


Figure 2 Partial 500 MHz ^{1}H n.m.r. spectra of 50/50 wt% mixture of PBT and PAr (δ = 6.0–9.5 ppm) and transesterified melt processed blend (δ = 8.0–8.5 ppm)

For the sake of clarity we can assign letters to all chemical groups present in the blends. For example, a PBT molecule is represented by a string of A_1B_1 repeating units and a PAr molecule is represented by a string of A_2B_2 repeating units interspersed with 25 mol% A_2B_1 units (see *Scheme 1*).

The mole fraction of triads of type $A_iB_1A_k$ relative to the concentration of B_1 [$f(A_iB_1A_k)$] can be obtained directly from the integrated intensities of the appropriate n.m.r. peaks (*Table 2*). The degree of randomness (B_{B_1}), which is indicative of how the A units are distributed around B_1, can be written as[9]:

$$B_{B_1} = f_{A_iB_1A_k}\left(\sum_{i=1}^{2}\frac{1}{f_{A_i}}\right)(i \neq k) \qquad (1)$$

where f_{A_i} is the mole fraction of A_i units relative to the total A concentration. B_{B_1} can assume values between 0 and 2. $B_{B_1} = 0$ corresponds to the case where no or very little transesterification has occurred while $B_{B_1} = 1$ indicates that transesterification has progressed to such a point that a copolymer is produced which has a random distribution of A_1 and A_2 units around B_1. Values of B_{B_1} between 1 and 2 indicate a tendency for A_1 and A_2 to alternate around B_1.

Finally, the average sequence length of A_1B_1 (butylene terephthalate) sequences (X) can be written as[9]:

$$X = \frac{1}{P_{A_1B_1A_2}} = \frac{\sum_{k=1}^{2} f_{A_1B_1A_k}}{f_{A_1B_1A_2}} \qquad (2)$$

where $P_{A_1B_1A_2}$ is the probability of finding an A_2 unit following an A_1B_1 group. The relevant triad mole fractions, degree of randomness and average sequence lengths of A_1B_1 units are tabulated in *Table 2* for each of the blends and the starting material.

The initial material (i.e. the physical blend prior to melt processing) has a theoretical degree of randomness equal to zero and a calculated, average sequence length of butylene terephthalate A_1B_1 units of 109 (derived from

Table 3 Melt processed 50/50 PBT/PAr blends

Sample	T_g (°C)	T_m (°C)	Crystallinity (wt%)[a]
PBT	42	226	41
PAr	187	–	–
290-5	109	210	29
290-20	108	208	39
300-5	112	210	39
CAT-320-15	86	199	20
ND-260-20	108	215	33
CAT-ND-290-12	101	214	32

[a]All samples except PAr precrystallized at 175°C prior to analysis. Calculation based on weight of PBT in the blend

$\bar{M}_n = 24\,000$ for PBT). The values for the degree of randomness calculated for the majority of the melt blends are in the range 0.12–0.19, while the average sequence length generally falls between 19 and 30. This indicates that the polymers in these blends have transesterified to the point of forming copolymers with blocks which are an average of 19 to 30 butylene terephthalate units in length. One of the melt blends (CAT-320-15) has a significantly different value for B_{B_1} (i.e. 0.32) outside the range of error of most of the other blends. It should be noted that error in measurement of the n.m.r. peak areas results in the following uncertainties in the variables: approximately ± 0.01 in $f(A_iB_1A_k)$, ± 0.03 in B_{B_1} and ± 4 in X. The results for CAT-320-15 are reasonable considering that this specimen was exposed to the most severe combination of processing conditions, i.e. 320°C for 15 min with added catalyst.

The T_g, melting point and weight per cent crystallinity for each of the blends as well as for PBT and PAr are presented in *Table 3*. All specimens, except for CAT-320-15, show a single T_g near 110°C, a melting temperature (T_m) depression (relative to PBT) of 10–15°C and perhaps some reduction in the degree of crystallinity (although in many cases the per cent crystallinity is within experimental error of pure PBT). Some of the reduction in the PBT crystallinity probably also arises from kinetic effects in the 50/50 mixtures. A T_m depression is expected simply on the basis of the miscibility of the two polymers but on similar 50/50 blends that were prepared using a solution precipitation procedure (no detectable transesterification), a depression of ~3°C was noted, considerably less than that for the melt processed blends[11]. The implication is that the significant reduction of T_m for the melt processed materials is dominated by the reduction in average PBT sequence length. The reduction in T_m observed here is similar to that noted for segmented block copolymers consisting of PBT hard segments and poly(tetramethylene oxide) soft segments of comparable butylene terephthalate sequence lengths[12].

Results from the n.m.r. experiments show clearly that sample CAT-320-15 has a significantly higher degree of randomness and this is consistent with the properties shown in *Table 3*. The degree of crystallinity has been reduced by ~50% from that of PBT, an appreciable amount even when considering the error inherent in heat of fusion measurements. This decrease is also consistent with the lower T_g for this blend since, as the crystallinity decreases, more PBT will be present in the amorphous phase and there will be fewer restrictions on amorphous phase mobility.

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