PII: S0032-3861(96)00872-5

Polymer Vol. 38 No. 12, pp. 3035–3043, 1997

0032-3861/97/$17.00 + 0.00

Characterization of poly(ethylene terephthalate) and poly(ethylene terephthalate) blends

Bronwyn Fox, Graeme Moad*, Gary van Diepen and Ian Willing
CRC for Polymers, CSIRO Division of Chemicals and Polymers, Private Bag 10, Clayton South MDC, Victoria 3169, Australia

and Wayne D. Cook
CRC for Polymers, Department of Materials Engineering, Monash University, Clayton, Victoria 3168, Australia
(Revised 14 August 1996)

A method for the direct determination of the molecular weight of the poly(ethylene terephthalate) (PET) component in PET/acrylonitrile–butadiene–styrene (ABS) blends by gel permeation chromatography has been developed. This technique has been applied to demonstrate that an observed deterioration in the mechanical properties (e.g. Izod impact strength) of PET/ABS blends on processing can be correlated with a decrease in the molecular weight of the PET component. In the course of this work, various methods for evaluating the molecular weight and chemical microstructure of PET were examined. The use of nuclear magnetic resonance (n.m.r.) spectroscopy as a means of quantitatively identifying end groups and comonomers that are present at the 1–4% level in commercial PET (e.g. diethylene glycol, cyclohexanedimethanol and isophthalic acid) is critically evaluated with reference to the stability of PET and PET end groups in various n.m.r. solvents. New ^{1}H n.m.r. chemical shift assignments for cyclohexanedimethanol units are presented, and the reactivity of hydroxy end groups in trifluoroacetic acid mixtures is examined. © 1997 Elsevier Science Ltd.

(Keywords: PET; ABS; blends; n.m.r.; g.p.c; degradation)

INTRODUCTION

It has been observed that certain mechanical properties of poly(ethylene terephthalate) (PET) and its blends with acrylonitrile–butadiene–styrene (ABS) copolymers (impact strength, tensile properties) are strongly dependent on processing conditions. These effects are discussed in greater detail elsewhere[1]. However, the data shown in *Figure 1* illustrate the problem. There is a dramatic decrease in Izod impact strength of injection-moulded specimens of PET/ABS blends according to the temperature at which the blend is extruded.

It is well known that the mechanical properties of PET are molecular weight dependent[2,3]. It is also established that PET can degrade under conditions typically encountered during processing and that the extent of degradation is dependent on temperature and other processing variables[4–6]. Thus, degradation of the PET component of the PET/ABS blend provides a likely explanation for the data summarized in *Figure 1* and related findings[1].

However, other explanations are possible. These include: changes in the degree of crystallinity of the PET component, degradation of the ABS (possibly by cross-linking of the butadiene rubber component) and/or a dependence of the blend morphology on the processing conditions[1,7]. In order to confirm the mechanism for property deterioration it was important to establish the molecular weight of the PET component of the PET/ABS blends. This would allow an assessment of whether any changes in molecular weight could be correlated with the variation in mechanical properties and allow optimization of processing conditions and blend performance.

Methods used for molecular weight determination of PET include intrinsic viscosity measurement, gel permeation chromatography (g.p.c.)[8] and end group determination (e.g. by i.r.[9,10], n.m.r.[11–13] or chemical analysis[14]). Many of these methods cannot be directly applied to ABS/PET blends without a need for component isolation. Two methods were selected for investigation: g.p.c. and n.m.r. spectroscopy. These techniques were selected because they have the potential to be applied directly to the blend samples with no sample treatment other than dissolution in a solvent. In the course of this work we have also evaluated n.m.r. methods as a means of identifying comonomers and end groups that are present at the 1–4% level in commercial PET.

EXPERIMENTAL

Materials

Details of the commercial PET samples employed in this study are summarized in *Table 1*. The ABS was supplied by Huntsman Australia (acrylonitrile/

---

* To whom correspondence should be addressed

butadiene/styrene = 19/36/45 (weight ratio), $\bar{M}_n$ (of $CHCl_3$ soluble fraction) = 35 000 polystyrene equivalents). The maleic-modified SEBS [poly(styrene-*block*-(ethene-*co*-butene)-*block*-styrene)] compatibilizer (Shell Kraton FG1900X) had an $\bar{M}_n$ of 39 000.

Preparation of PET blends

The ABS/PET blends were prepared from PET (PETV—see *Table 1*), ABS and in a 47.5/47.5/5 ratio with a Brabender PL2000 single-screw extruder. All components were dried before processing. Full details of the processing conditions and mechanical properties of the blends are published elsewhere[1]. The average processing temperature referred to in *Figures 1* and *4* is the average of the three barrel temperatures and the die temperature; the ratio of the zone temperatures was kept constant. Injection moulding was performed with an Engel SE600-125 120 tonne reciprocating screw injection moulder operated at a screw speed of 40 rpm, a barrel temperature of 250°C, a mould temperature of 60°C and a moulding time of 33 s.

N.m.r. spectroscopy

PET samples were cryoground and dried at 120°C under vacuum for 4 h immediately prior to ^1H n.m.r. analysis. N.m.r. spectra were obtained with a Bruker AC250 spectrometer or a Bruker 500DRX spectrometer. A 2/1 mixture of CF_3COOD and $CDCl_3$ was used as the n.m.r. solvent. Chemical shifts are reported in parts per million from tetramethylsilane. For some ^{13}C n.m.r. measurements a mixture of 2% 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) in $CDCl_3$ was used.

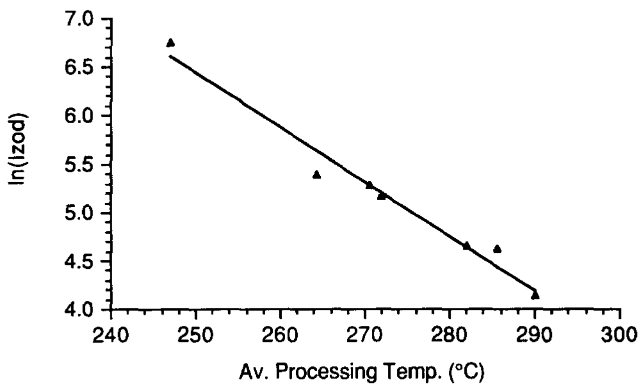


Figure 1 Effect of processing temperature on Izod impact strength (joules per metre) of injection-moulded samples of blends of PET/ABS with compatibilizer (0.475/0.475/0.05). Average processing temperature refers to the average temperature of the four barrel sections of the Brabender single-screw extruder used in preparation of the blends. For details of blend preparation, see the Experimental section

G.p.c.

Molecular weights were determined by g.p.c. using a Waters linear mixed-C and a Polymer Laboratories 5 μ 100 Å column connected in series to a Hewlett Packard HP 1090 Liquid Chromatograph equipped with a diode array u.v. detector and a refractive index detector. The eluent was a mixture of 2% (v/v) HFIP in chloroform. Calibration was performed using a series of polystyrene standards. Mark–Houwink parameters for polystyrene ($K = 1.91 \times 10^{-4}$ ml g^{-1}, $\alpha = 0.731$) and PET ($K = 1.91 \times 10^{-4}$ ml g^{-1}, $\alpha = 0.693$) in 2% (v/v) HFIP/$CHCl_3$ were from the literature[15].

The samples of PET/ABS blends were cryoground at liquid nitrogen temperature and were then dissolved in HFIP and diluted with chloroform to give a final concentration of ~5 mg ml^{-1}. The solutions were filtered through a 2 μm syringe filter before injection. This also removed the small amounts of cross-linked rubber gel present in the ABS/PET blends. Control experiments showed that the PET was not degraded by cryogrinding and that there was no loss or fractionation of the PET during filtration of the blend solutions.

RESULTS AND DISCUSSION

G.p.c. analysis of PET and ABS/PET blends

The analysis of PET and its copolymers by g.p.c. has been complicated by the low solubility of the polymers in solvents appropriate for g.p.c. elution. However, this problem has been resolved by the use of hexafluoroisopropanol (HFIP)/$CHCl_3$ mixtures as the eluting medium[8,15]. PET samples are completely soluble in HFIP/$CHCl_3$ at room temperature and show no detectable degradation over several days. Only small amounts (2% v/v) of HFIP are required for solubility. However, higher proportions of HFIP give more rapid dissolution. It is important that the amount of HFIP in the eluting medium be minimized due to the incompatibility of g.p.c. columns containing cross-linked polystyrene with solvent mixtures containing high proportions of HFIP (and due to the expense and toxicity of HFIP)[8]. In the present work, HFIP/choroform mixtures also have the benefit of relatively good u.v. transparency in the wavelength range of interest (240–350 nm), which permits the use of u.v. detection.

Table 1 Composition and intrinsic viscosity data for commercial PET samples.

				% comonomer[c]		
Sample	Origin	*IV* (dl g^{-1})[a]	$\bar{M}_w$[b]	**3**	**8 + 9**[d]	**10**
PETV	Eastman Kodak, Kodapak PET Thermoplastic copolyester 9921W	0.80	56 800	5.9	1.1	–
PETH	Hoechst T-95, PET copolymer	0.78	54 700	5.4	–	2.2
REPET	ACI (regranulated bottles)	–	–	5.3	1.3	–
CPET	Hoechst T-58, PET homopolymer	0.95	73 000	5.1	–	–

[a] Intrinsic viscosity values taken from data sheets provided by the suppliers
[b] Calculated from the intrinsic viscosity using the following relationship[5]: intrinsic viscosity = 4.68×10^{-4} $(\bar{M}_w)^{0.68}$
[c] Mole per cent of comonomer determined by ^1H n.m.r. analysis (see text). Error in composition is ~10% for **3** and **10**, and ~20% for (**8 + 9**)
[d] The ratio of **8/9** was ~3/7 for both samples

Weisskopf[15] has conducted a detailed study of the molecular weight determination of PET and polystyrene by g.p.c.-light scattering with 2% HFIP in $CHCl_3$ as the eluent, and also reported the Mark–Houwink parameters necessary to perform universal calibration based on polystyrene standards.

In preliminary studies, the molecular weights of four commercial samples of PET were determined by g.p.c. with 2% HFIP in $CHCl_3$ as the eluent (see *Table 2*). These results are consistent, within experimental error, with the values calculated from the intrinsic viscosities provided in the manufacturers' data sheets (*Table 1*). The presence of low molecular weight cyclic oligomers[15–17] is evident in all samples from the small low molecular weight shoulder to the main PET peak. The amount of these oligomers appeared the same for each of the four samples.

PET is characterized by having relatively strong absorption in the u.v. spectrum. The u.v. spectra of PET and ABS in 2% HFIP in $CHCl_3$ are shown in *Figure 2*. Over the wavelength range 240–300 nm, the absorption per unit weight of PET is more than 100 times greater than that of the ABS or the compatibilizer (a maleated styrene/butadiene copolymer—Kraton FG1900X) in which the principal chomophores are isolated phenyl groups. This difference in relative extinction coefficient suggested that the PET component in the PET/ABS blends might be reliably analysed by g.p.c. with u.v. detection even though the PET, the soluble component of the ABS, and the compatibilizer have overlapping molecular weight distributions and would elute together from the g.p.c. column.

Table 2 Molecular weights of commercial PET samples determined by g.p.c.[a]

Sample[b]	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$[c]
PETV	25 300	65 000	2.56	56 800
PETH	23 500	60 100	2.55	54 700
REPET	21 200	50 800	2.40	-
CPET	26 300	70 700	2.69	73 000

[a] Molecular weights obtained by universal calibration and polystyrene standards

[b] For sample descriptions see *Table 1*

[c] Estimated from intrinsic viscosity (see *Table 1*)

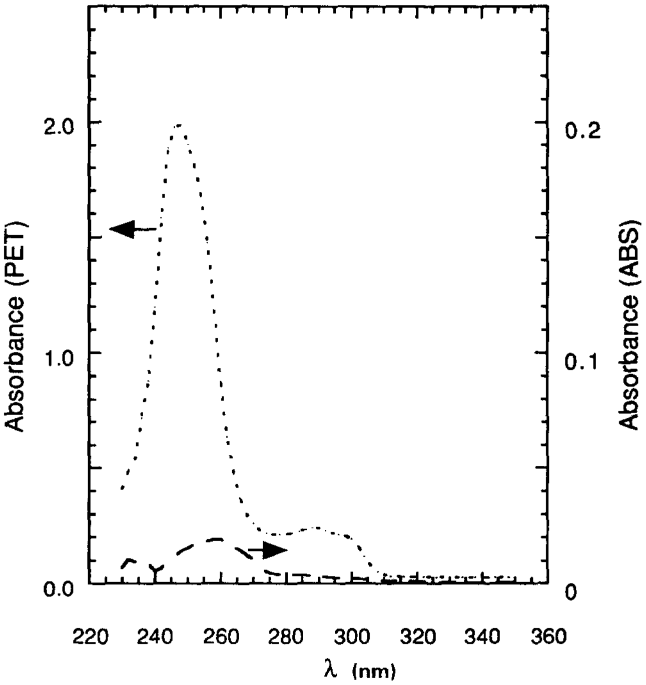


Figure 2 U.v. spectra for solutions of 0.0226 mg ml^{-1} of ABS (——) (10 × expansion) and 0.0222 mg ml^{-1} of PET (-----) in a mixture of HFIP (2%) and chloroform

The cryground PET/ABS blends were found to be largely soluble in HFIP. A small amount of cross-linked rubber particles was readily removed by filtration through a 0.2 μm filter. Control experiments established that the PET component was entirely soluble and that there was no fractionation of PET in this process.

The diode array detector also provided complete u.v. spectra of the eluted sample as a function of molecular weight. The u.v. spectra were found to be the same across the entire molecular weight range and identical to that of pure PET. This observation demonstrates that there is no significant contribution to the chromatogram from the other blend components.

Structure property correlation for PET/ABS blends

The molecular weight distributions of pure PET (all references to PET in this section relate to PETV unless otherwise indicated) and the PET component of the ABS/PET blends processed under several different conditions are shown in *Figure 3*. Each of the processing stages (preblending of PET with compatibilizer, ABS/PET blend preparation and injection moulding) was

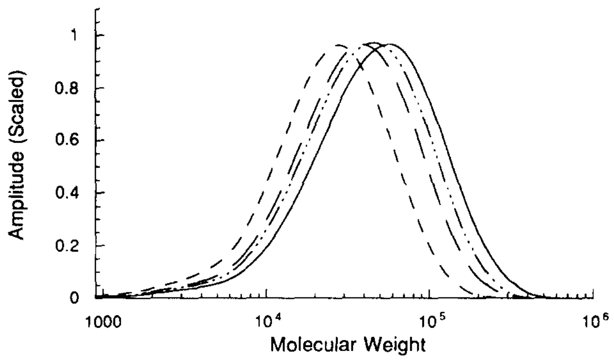


Figure 3 Molecular weight distributions for PET samples (from right to left): (i) PETV (as received), (ii) after blending with compatibilizer (291°C), (iii) 1/1 blend with ABS processed at low temperature (247°C), and (iv) 1/1 blend with ABS processed at high temperature (282°C). For details of blend preparation, see the Experimental section

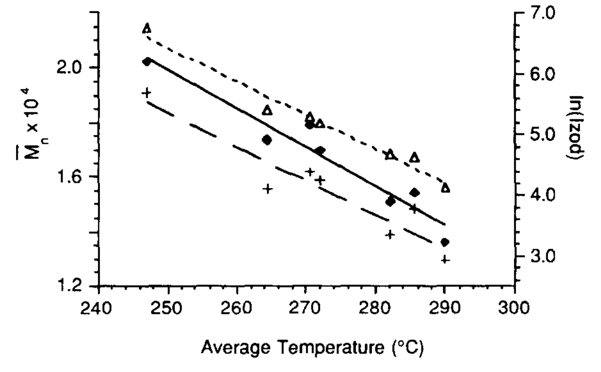


Figure 4 Correlation of the impact properties and molecular weight of the PET component of ABS/PET blends with the average processing temperature. The data are for the blends described in *Figure 1*. -----, ln(Izod); ——, $\bar{M}_n$ for extruded pellets; – – –, $\bar{M}_n$ for injection-moulded parts

found to give some reduction in the molecular weight of the PET component. Molecular weights obtained for injection-moulded samples (used for Izod impact testing) were also consistently ~2000 units lower than for the blends as initially prepared (see *Figure 4*)

A strong correlation between impact strength and molecular weight is clear from the data presented in *Figure 4*. Both the molecular weight and ln(Izod) appear to decrease linearly with an increase the temperature used in the blend preparation step. Further work is required to establish the mechanism of PET degradation. It is noteworthy that there is no increase in polydispersity or in the proportion of oligomeric components of the samples on processing.

As significantly greater degradation is observed for the blends than for the PET alone processed under similar conditions, it appears possible[1] that degradation is catalysed by some component in the ABS. The possibility that degradation of PET during processing might be due to trace amounts of water in blend components was investigated. However, while greater degradation was observed when the blend components were inadequately dried, more rigorous drying did not further ameliorate the extent of degradation observed. A similar effect attributed to ABS contaminants on bisphenol-A polycarbonate (PC) stability and blend properties has been observed in studies on PC/ABS blends[18].

Additional studies were performed of ABS/PET blends containing another commercial PET. This polymer was of similar molecular weight but differed from PETV in its chemical microstructure (it contained isophthalate comonomer—see below). The processing conditions used to form the PET/ABS blend and the observed molecular weight change were similar to those for the best PETV blend. However, the impact properties for this sample corresponded to those of the poorest of the PETV blends. The result indicates that the molecular weight of the PET component is not the only factor influencing impact properties and there may be a need to establish the chemical microstructure of the PET used in blending applications. Further studies to establish the origin of this effect are warranted. It is known that the nature and amount of comonomer(s) present in PET influences the degree of crystallinity[19].

N.m.r. analysis of PET

Numerous studies have shown n.m.r. spectroscopy to be an invaluable tool in the analysis of polymers[20–22]. The technique has advantages over most other analytical methods in that it allows simultaneous determination of

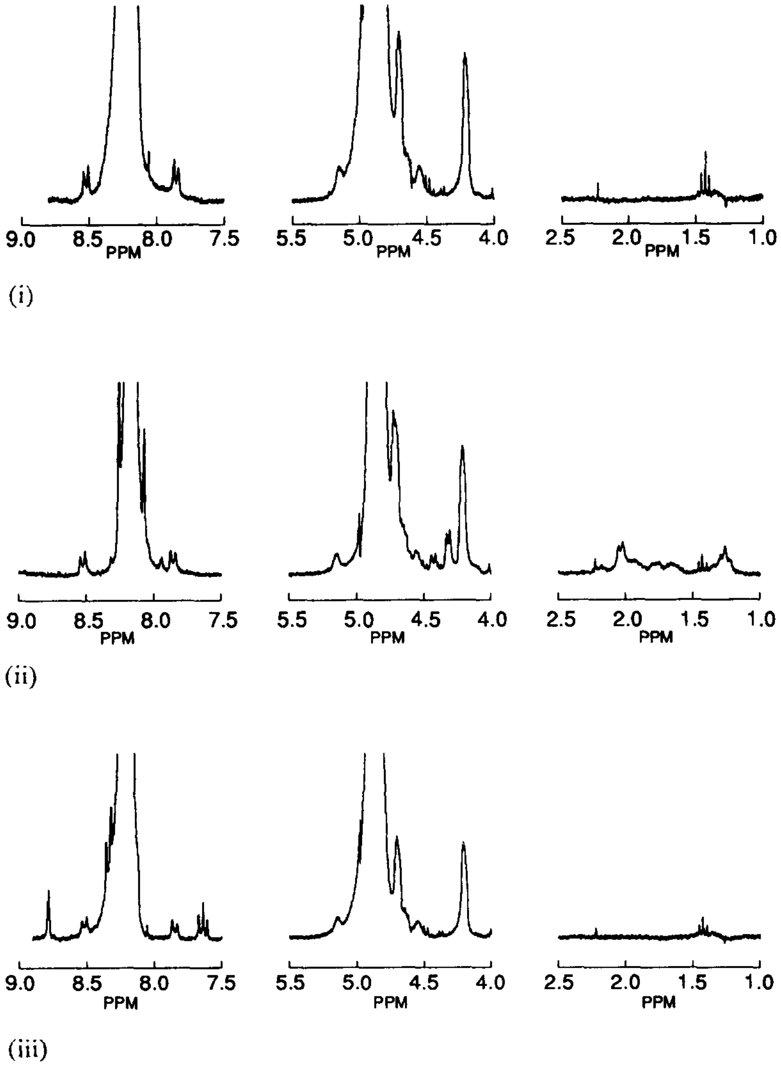


Figure 5 250 MHz ^{1}H n.m.r. spectra ($CF_3COOD/CDCl_3$, 50 × expansion) of (i) PETV, (ii) CPET and (iii) PETH. For sample descriptions, see *Table 1*. A small triplet at δ 1.4 is due to a $CDCl_3$ impurity

the detailed chemical microstructure of the polymer and the determination of polymer end groups (which can allow calculation of the molecular weight). Information is obtained on the types as well as number of end groups that are present in the polymer sample[20,23]. Of the studies that have appeared on the n.m.r. of PET and its copolymers[11–13,24–28], relatively few have dealt with analysis of the polymer end groups. Most of these have dealt only with samples of very low molecular weight.

As with g.p.c., n.m.r. studies of PET were for a long time impeded by the limited solubility of the polymer in common n.m.r. solvents. With the use of single solvents, for example, dimethyl sulfoxide-d_6[12,13] or 1,1,2,2-tetrachloroethylene-d_2[29], high molecular weight PET is only soluble at high temperatures, and high probe temperatures >120°C are required. Under these conditions, even trace amounts of water cause PET degradation. The use of mixtures containing fluorinated solvents, for example $CF_3COOD/CDCl_3$[26,28] or HFIP/$CDCl_3$ (see below), is advantageous since they allow room temperature spectra.

Four commercial PET samples were examined in the present work (see *Table 1*). In data sheets provided with the materials, one material (CPET) was designated as a PET homopolymer, while the two others (PETV and PETH) were designated PET copolymers and are intended for use in bottle manufacture. The fourth material was a recycled PET derived by granulating used PET bottles (REPET). As appears common in commercial practice, little information on the chemical composition of the various PET grades was provided in the data sheets. In particular, the nature of the comonomer(s) in PETV and PETH was not specified.

In the ^1H n.m.r. spectrum of the CPET 'homopolymer' obtained in $CF_3COOD/CDCl_3$ (see *Figure 5(i)*) the most obvious features are singlets at δ 8.2 arising from the four equivalent methylene protons of the PET repeat unit. Small singlets at δ 4.2 and 4.7 indicate the presence of diethylene glycol units **3** and can be assigned to the $CO_2CH_2C\mathit{H}_2OC\mathit{H}_2CH_2O_2C$ and the $CO_2C\mathit{H}_2CH_2OCH_2C\mathit{H}_2O_2C$ protons respectively[12,25]. Since the end groups **1** are readily esterified and shifted downfield (see below), the concentration of diethylene glycol comonomer **3** can be reliably determined (see *Table 1*).

The spectrum of PETV copolymer (*Figure 5(ii)*) also displays the above-mentioned signals due to diethylene glycol units **3**. It has additional signals in the regions δ 1.3–2.2 and δ 4.3–4.4 which appear characteristic of 1,4-cyclohexanedimethanol comonomer (**8** and **9**)[30]. The doublet at δ 4.43 is due to the axial methylene substituent, whereas the more intense doublet at δ 4.32 arises from the equatorial methylene substituent. The chemical shifts are consistent with the n.m.r. spectra of other 1,4-disubstituted cyclohexane derivatives which exist in a chair conformation[31]. The signals (at δ 4.43 and 4.32) have previously been assigned incorrectly to the *cis* and *trans* isomers rather than to the axial and equatorial substituents[30]. This interpretation gives an incorrect quantification of the isomer ratio. Since the *cis* isomer **8** has one equatorial and one axial methylene substituent, whereas the *trans* isomer **9** has two equatorial methylene substituents, the ratio of *cis* and *trans* isomers can be calculated from the measured peak intensities spectrum as follows:

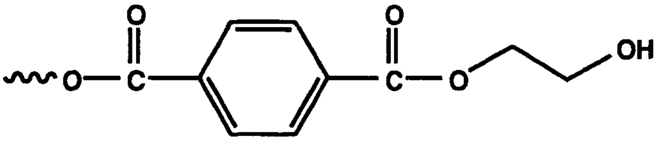
$$\frac{cis}{trans} = \frac{2 \times \text{equatorial}}{\text{axial} + \text{equatorial}}$$

The 30/70 mixture of *cis* and *trans* isomers **8** and **9** found is similar to the isomer distribution in commercial cyclohexanedimethanol[19].

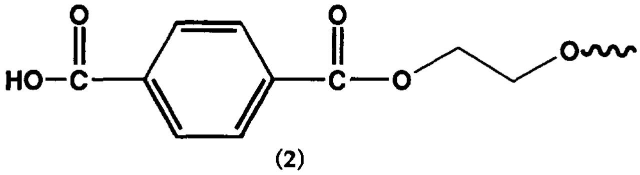
The connectivity of the methine protons α to the methylene groups was established by decoupling experiments. The equatorial methine proton gives rise to a broad signal at δ 2.21 while the axial methine proton gives rise to a signal at δ 1.93. Other signals at δ 2.04, 1.76, 1.65 and 1.26 are attributed to the cyclohexane ring methylene protons.

The spectrum of PETH copolymer (*Figure 5(iii)*) has additional signals in the aromatic region (at δ 8.78, 8.35, 8.32 and 7.64) characteristic of an isophthalate ring **10**. The ^1H n.m.r. chemical shifts are similar to those reported for the ethyleneglycol isophthalate homopolymer[32].

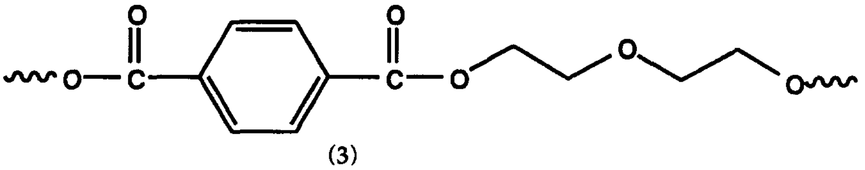
^1H n.m.r. spectra can thus be used to determine quantitatively the composition of commercial PET (see *Table 1*). Such analysis is of particular importance in the case of recycled PET where the exact origin of the material and comonomer level will often be uncertain. Effects of the type and level of comonomer on the properties of PET products have not been widely reported. The ^1H n.m.r. spectrum of the recycled PET (REPET) sample used in the present study appears identical to that of the PETV, and this is consistent with



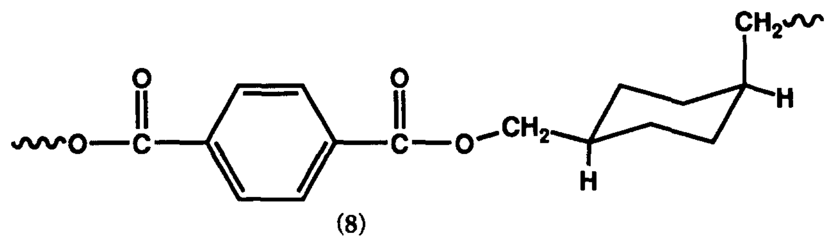
(1)



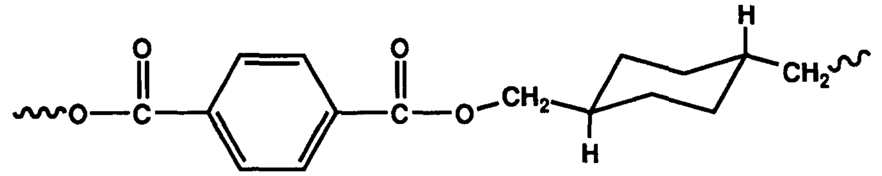
(2)



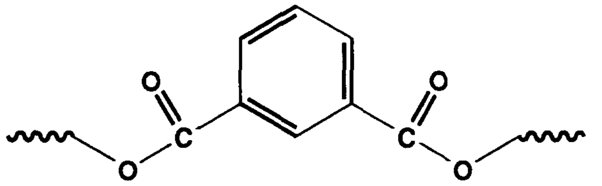
(3)



(8)



(9)



(10)

its origin being from reclaimed bottles of PETV or a similar copolymer.

N.m.r. end-group determination of PET

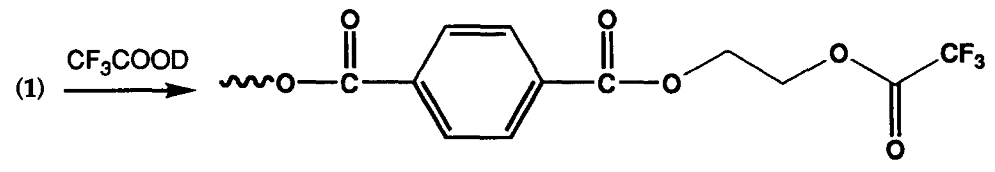
Several groups have reported on the use of ^{1}H n.m.r. spectroscopy for end group determination. Shit and Maiti[13] studied the ^{1}H n.m.r. spectra of very low molecular weight PET in dimethyl sulfoxide-d_6, and were able to assign and quantify signals due to the alcohol end groups **1** and derivatized acid end groups. Pétiaud *et al.*[12] provided a more detailed analysis of oligo(PET) by both ^{1}H and ^{13}C n.m.r. spectra in dimethyl sulfoxide-d_6 at 140°C and provided assignments for both the aliphatic (**1**) and aromatic end groups (**2**).

In 1981, Kricheldorf *et al.*[26] reported that the use of $CF_3COOD/CDCl_3$ mixtures as a solvent enabled n.m.r. analysis of PET and copolymers to be performed simply and at room temperature. More recently, Pinkus and Harihan[11,24] reported 'a convenient method' for determination of the aliphatic end groups (**1**) based on analysis of the ^{1}H n.m.r. of PET in $CF_3COOD/CDCl_3$ at room temperature. All signals in the region δ 4.1–4.6 were attributed to end groups **1**. Application of the technique[11] to estimate the molecular weights of commercial PET samples gives an apparent $\bar{M}_n$ of ~4000. This value is substantially lower than that expected on the basis of the known intrinsic viscosities (see *Table 1*)[5] and is inconsistent with g.p.c. data. The discrepancy can be attributed to overlap of the signals at δ 4.65 and 4.16 due to the methylene protons of the end groups (**1**) with those of the methylene protons of diethylene glycol units **3** that are present in the backbone of the polymer (see *Figure 5(ii)*). Small amounts of diethylene glycol comonomer are present in all commercial PET samples as an unavoidable by-product of the synthesis[33,34].

The signals due to end groups **1** and diethylene glycol units **3** can be partially resolved with the use of higher-field (500 MHz) n.m.r. However, a further problem is that the presence of small amounts of trifluoroacetic anhydride in $CF_3COOD/CDCl_3$ mixtures results in esterification of the PET end groups **1** (see *Scheme 1*)[26]. This causes the signals due to the end group methylenes to shift downfield to coalesce with the signals due to the methylenes of the main $-O-CH_2-CH_2-O-$ repeat unit at δ 4.95 (see *Figure 5*).

We conclude that end group analysis by ^{1}H n.m.r. with $CF_3COOD/CDCl_3$ as the solvent is not a reliable method for the direct determination of the molecular weight of PET.

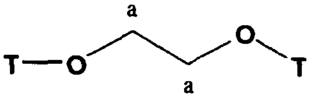
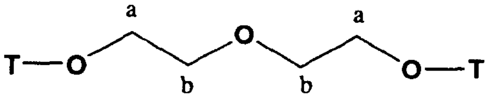
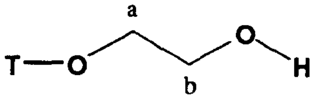
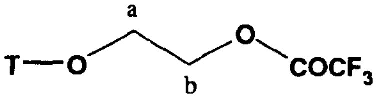
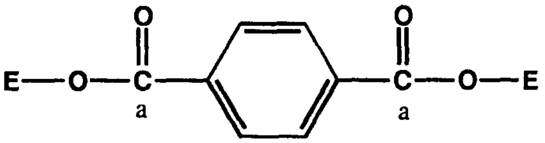
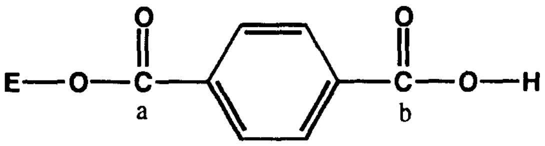
The use of ^{13}C n.m.r. studies of PET for end group determination offers greater potential. In the initial work, the $CF_3COOD/CDCl_3$ solvent mixture was employed. While the methylene carbons of end groups **1** and diethylene glycol **3** have discrete ^{13}C n.m.r. chemical shifts, signals due to the acid end group **2** are not resolved from those of the carbonyl of the PET repeat unit (see *Table 3*).



(4)

Scheme 1

Table 3 ^{13}C n.m.r. chemical shifts of comonomers and end groups in PET derivatives[a]

	Chemical shift (ppm) in solvent					
	$CF_3COOD/CDCl_3$		HFIP/$CDCl_3$		DMSO-d_6[12]	
Structure[b]	a	b	a	b	a	b
	64.5	–	63.3	–	61.4	
	69.6	65.2	–	–	66.7	62.5
	67.4	61.3	66.6	60.9	65.1	57.6
	65.7	63.6	–	–	–	–
	166.7	–	167.7	–	163.4	–
	166.7	–	167.7	168.1	163.6	164.6

[a] Chemical shifts rounded to nearest 0.1 ppm

[b] T = terephthalate unit; E = ethylene glycol unit

The end groups that have been esterified by trifluoroacetic acid (**4**) also give discrete signals in the ^{13}C n.m.r. spectrum. This finding allowed control experiments to be carried out to estimate the rate of esterification of the PET hydroxyl end groups **1** in $CF_3COOD/CDCl_3$ at ambient temperature (~22°C). Thus, ^{13}C n.m.r. spectra of low molecular weight PET ($\bar{M}_n \sim 3000$) dissolved in $CF_3COOD/CDCl_3$ (2/1) containing a small amount of D_2O (to ensure the complete absence of anhydride) showed that the degree of esterification was ~10% after 2 h (*Figure 6(i)*) and >70% after 30 h (*Figure 6(ii)*). These spectra clearly show the disappearance of the signals from the hydroxyl end group **1** (*Figure 6(i)*, signals a and b) and the appearance of the signals due to the new trifluoroacetate end groups **4** (*Figure 6(i)*, signals e and f) whilst the signals from the diethylene glycol comonomer **3** (*Figure 6(i)*, signals c and d) remain of the same intensity.

To further substantiate the mechanism, an investigation of the esterification of ethylene glycol in $CF_3COOD/CDCl_3$ (2/1) was performed (refer to *Scheme 2*). The two equivalent carbons of ethylene glycol (**5**) give rise to a singlet (*Figure 7(i)*, signal a). Signals (*Figure 7(i)*, signals b and c) which arise from the inequivalent carbons of the monoesterified species **6** can already be observed in the spectrum recorded half an hour after the sample was prepared. A smaller peak (*Figure 7(i)*, signal d) is due a small amount of the diesterified species (**7**) (*Figure 7(i)*, signal d) is also present. The spectrum of the same sample was recorded 2 days later (*Figure 7(ii)*). In this spectrum the signals due to ethylene glycol **5** (*Figure 7(ii)*, signal a) have disappeared altogether. The

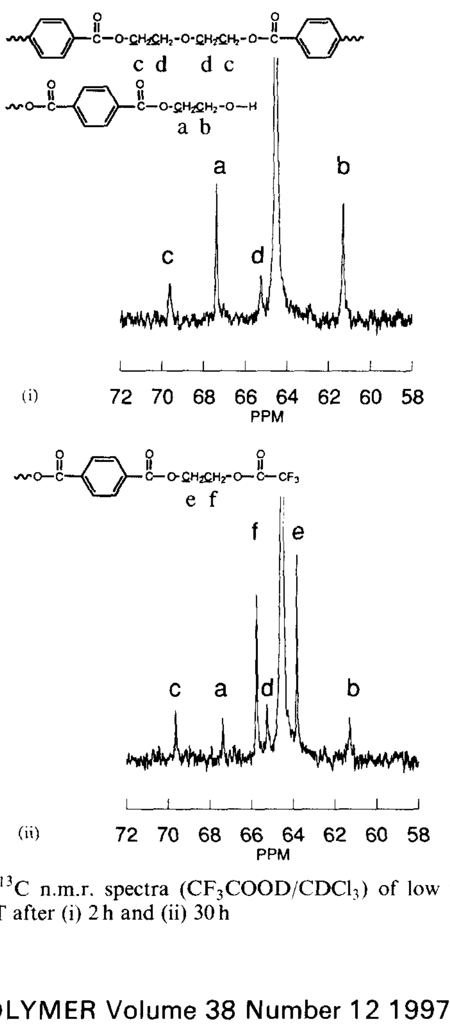
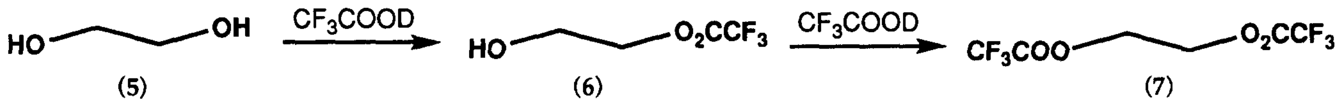


Figure 6 ^{13}C n.m.r. spectra ($CF_3COOD/CDCl_3$) of low molecular weight PET after (i) 2 h and (ii) 30 h



Scheme 2

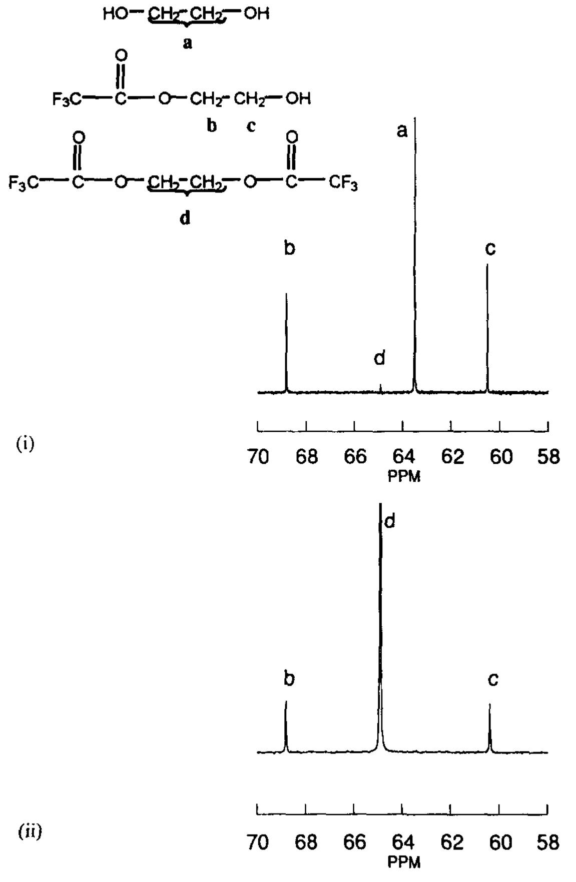


Figure 7 ^{13}C n.m.r. spectra ($CF_3COOD/CDCl_3$) of ethylene glycol after (i) 30 min and (ii) 72 h

diesterified product **7** (*Figure 7(ii)*, signal d) is the dominant species.

The use of HFIP/$CDCl_3$ mixtures as a solvent for ^{13}C n.m.r. analysis avoids the problems found with the use of $CF_3COOD/CDCl_3$ solvent. HFIP with $CDCl_3$ is a good solvent mixture for PET and has been successfully used for g.p.c. analysis of PET (see below). Chemical shifts with HFIP/$CDCl_3$ are similar to those seen with $CF_3COOD/CDCl_3$. Note that this solvent mixture is not suitable for ^1H n.m.r. studies because the signal due to the HFIP methine proton overlaps those for PET methylene protons. A quantitative ^{13}C n.m.r. experiment was performed on a low molecular weight PET sample ($\bar{M}_n \sim 3000$). Signals due to the alcohol (**1**) and acid (**2**) end groups signals were observed (see *Table 3* for chemical shifts).

The end groups in high molecular weight (commercial) PET samples can also be determined by ^{13}C n.m.r. spectroscopy. However, long acquisition times (>20 h with 500 MHz n.m.r.) are required to obtain a spectrum with a signal-to-noise ratio suitable for quantitative determination. Although this renders the technique impractical for routine molecular weight determination (given the availability of the g.p.c. method—see previous section), the method provides a reliable way of ascertaining the concentrations of acid and hydroxy chain ends.

CONCLUSIONS

The most effective method for determination of PET molecular weight is by g.p.c. with HFIP/$CHCl_3$ as the eluent. We have shown that this method may be adapted to analyse the PET component of PET/ABS blends though the use of u.v. detection. Diminished mechanical properties for PET/ABS blends are correlated with degradation of the PET component. Some degradation of the PET occurs during each processing stage. The extent of degradation increases with an increase in the processing temperature.

^1H n.m.r. spectroscopy is useful for determining the presence of comonomers (i.e. cyclohexanedimethanol and diethylene glycol units) in the polymer backbone. However, ^1H n.m.r. end group analysis was found to be unreliable for molecular weight determination both due to overlap signals from the end groups **1** with those due to diethylene glycol comonomer units **3**. The end groups **1** undergo rapid esterification when CF_3COOH mixtures are used as the n.m.r. solvent. The rate of esterification has been determined by ^{13}C n.m.r. studies of low molecular weight PET samples. For quantitative identification of both acid and alcohol end groups of PET by ^{13}C n.m.r. spectroscopy, a mixture of HFIP and $CDCl_3$ is recommended as the n.m.r. solvent. The use of this solvent allows ambient temperature n.m.r. studies, and it does not degrade or react with the polymer.

ACKNOWLEDGEMENTS

The authors would like to thank Prof. Robert Shanks and Ruxandra Rosu for providing the low molecular weight PET samples used as models in signal assignment. We are grateful to Tie Zhang for the impact test results. We would also like to thank Lawry McCarthy (CSIRO) and John Ride (Huntsman, Australia) for helpful discussion.

REFERENCES

1. Cook, W. D., Moad, G., Fox, B., Van Diepen, G., Zhang, T., Cser, F. and McCarthy, L., *J. Appl. Polym. Sci.*, 196, **10**, 1709.
2. Tate, S., Watanabe, Y. and Chiba, A., *Polymer*, 1993, **34**, 4974.
3. Stearne, J. M. and Ward, I. M., *J. Mater. Sci.*, 1969, **4**, 1088.
4. Andrassy, M. and Mencer, H. J., *Polym. Degrad. Stab.*, 1993, **41**, 77.
5. Jabarin, S. A. and Lofgren, E. A., *Polym. Eng. Sci.*, 1984, **24**, 1056.
6. Mantina, F. P. L. and Vinci, M., *Polym. Degrad. Stab.*, 1994, **45**, 121.
7. Cook, W. D., Zhang, T., Moad, G., Van Diepen, G., Cser, F., Fox, B. and O'Shea, M., *J. Appl. Polym. Sci.*, 1996, **10**, 1699.
8. Wang, P. J., *Chromatogr. Sci. Ser.*, 1995, **69**, 161.
9. Ward, I. M., *Trans. Faraday Soc.*, 1957, **3**, 1406.
10. Patterson, D. and Ward, I. M., *Trans. Faraday Soc.*, 1957, **3**, 291.
11. Pinkus, A. G. and Harihan, R., *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 1993, **34**, 861.

12. Pétiaud, R., Waton, H. and Pham, Q.-T., *Polymer*, 1992, **33**, 3155.
13. Shit, S. C. and Maiti, S., *Eur. Polym. J.*, 1986, **22**, 1001.
14. Garmon, R. G., *Methods Polym. Eval.*, 1975, **4**, 31.
15. Weisskopf, K., *J. Polym. Sci., Polym. Chem., Part A*, 1988, **26**, 1919.
16. Choun, Y. K. and Ha, W. S., *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17**, 2103.
17. Overton, J. R. and Browning, H. L., Jr., *Org. Coat. Appl. Polym. Sci. Proc.*, 1983, **48**, 940.
18. Lee, M. S., Kao, H. C., Chiang, C. C. and Su, D. T., *Advances in Polymer Blends and Alloys Technology*. 1989, 25.
19. Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G. and Kroschwitz, J. I., *Encyclopedia of Polymer Science and Engineering*. 2 edn, Wiley, Chichester, 1985, p. 222.
20. Moad, G., *Annu. Rep. NMR Spectrosc.*, 1994, **29**, 287.
21. Ibbett, R. N., (ed.), *NMR Spectroscopy of Polymers*. Blackie, London, 1993.
22. Tonelli, A. E., *NMR Spectroscopy and Polymer Microstructure*, VCH, New York, 1989.
23. Bevington, J. C., Ebdon, J. R. and Huckerby, T. N., in *NMR Spectroscopy of Polymers*. Blackie, London, 1993, Vol. 51.
24. Pinkus, A. G. and Harihan, R., *Polym. Bull.*, 1993, **30**, 91.
25. Halacheva, N. and Novakov, P., *Polymer* 1995, **36**, 867.
26. Kricheldorf, H. R., Dröescher, M. and Hull, W. E., *Polym. Bull.*, 1981, **4**, 547.
27. Khorshahi, F., Lin, S., Jensen, A. and Kwoh, D., *Polym. Bull. (Berlin)* 1992, **28**, 451.
28. Backson, S. C. E., Kenwright, A. M. and Richards, R. W., *Polymer* 1995, **36**, 1991.
29. Bunn, A., *NMR Basic Principles and Progress*. Springer-Verlag, Berlin, 1993, Vol. 29, p. 127.
30. Yoshie, N., Inoue, Y., Yoo, H. Y. and Okui, N., *Polymer*, 1994, **35**, 1931.
31. Pretsch, E., Clerc, T., Seibl, J. and Simon, W., *Tables of Spectral Data for Structure Determination of Organic Compounds. ^{13}C NMR, ^{1}H NMR, IR, MS, UV/VIS*. Springer-Verlag, Berlin, 1989, p. H195.
32. Pham, Q.-T., Pétiaud, R., Waton, H. and Llauro, M.-F., *Proton and Carbon NMR Spectra of Polymers*. Wiley, Chichester 1984, Vol. 3, p. 508.
33. Hovenkamp, S. G. and Munting, J. P., *J. Polym. Sci., Part A1*, 1970, **8**, 679.
34. Jabarin, S. A. and Patkar, M., *ANTEC '91*, 1991, 1955.