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Characterization of copolyester of polyethylene terephthalate and polyoxyethylene terephthalate by ^{1}H NMR and GPC

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SUMMARY

The copolyester of polyethylene terephthalate-polyoxyethylene terephthalate (PET-POET) has been characterized by ^{1}H NMR and GPC(Gel Permeation Chromatography). The ^{1}H NMR method provides a ready determination of the PET/POET mole ratio as well as the number of ethoxylate (EO) units in POET. Factors that may affect the accuracy of the determination are also discussed.

INTRODUCTION

The copolyester of PET-POET has been shown to function as a soil release agent for polyester and polyester blend fabrics (1). It has also been found to improve the stability of lipolytic enzymes in isotropic enzymatic liquid detergent compositions(2). Over the years, it has been studied by both ^{1}H NMR(3) and ^{13}C NMR(4,5). While ^{1}H is more efficient than ^{13}C for characterization purposes, the previous ^{1}H study(3) was hampered by poor resolution. Moreover, in that study, the number of ethoxylates(EO) in POET was not determined directly from the ^{1}H NMR data of PET-POET. Rather, it was derived from the EO number of polyethylene glycol (PEG) starting material. If the starting PEG is not known, as is often the case, the entire quantification becomes problematic. For this reason, it is desirable to re-evaluate the ^{1}H NMR approach.

By obtaining better resolution on a spectrometer of higher magnetic field strength, we show that the PET/POET mole ratio can be readily calculated. Also, the EO number can now be determined directly from the ^{1}H NMR data of PET-POET. We also show that ^{1}H NMR results could be skewed by unreacted PEG whose presence should always be checked by GPC.

EXPERIMENTAL

Materials

All chemicals used in this study were reagent grade. The starting materials included: PEG (m.w. 0.6kD-3.4kD, Union Carbide), ethylene glycol(EG)(Fisher) and dimethyl terephthalate(DMT)(DuPont). Antimony trioxide(Sb_2O_3) and calcium acetate (CaAc)(Aldrich) were used as catalysts to cover the temperature range encountered during the reaction. Phosphorous acid (Aldrich) was used to quench the catalysts. 4,4'-methylene-bis (2,6-di-tertbutyl)phenol(MTBP) (Pfaltz & Bauer) was used as an oxidation inhibitor.

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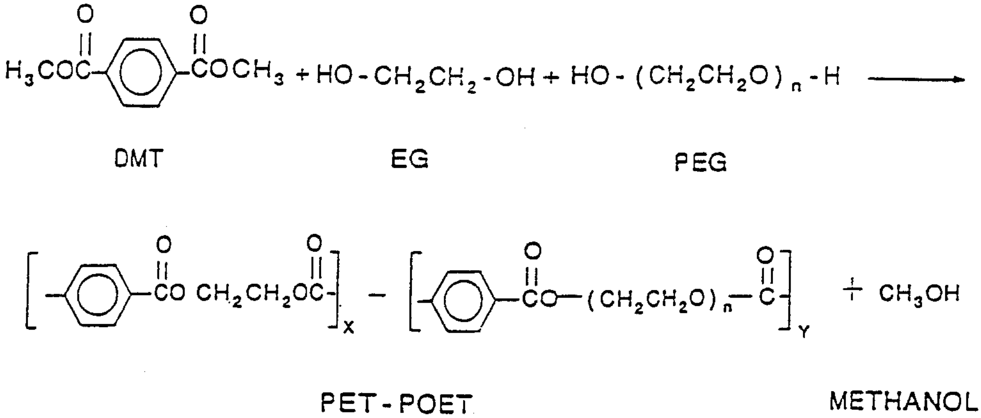
Preparation

Under the influence of the catalysts calcium acetate and antimony trioxide, DMT reacts with EG and PEG via a transesterification mechanism in the temperature range of 210°C to 280°C to form copolyester and liberate methanol (Scheme 1). Since this transesterification reaction is an equilibrium reaction, methanol is removed continuously from the reactor in order to force the reaction to completion.



Scheme 1

Five PET-POET samples of varying composition (Table 1) were prepared with the following general procedure:

Stoichiometric amounts of PEG, EG and DMT were charged to a resin kettle, followed by catalytic amounts of CaAc, Sb_2O_3 and MTBP. The mixture was heated to 210°C for 1.5h. Afterwards, the reaction temperature was raised to 280°C and held there for 2h. At this point, while the mixture was still under continuous heating, a 24.8% solution of phosphorous acid in EG was added to the kettle to quench the catalysts. After 5 min, a stream of nitrogen was passed over the reaction mixture for 2h in order to remove any remaining volatile material.

TABLE 1 Starting materials in mmoles

SAMPLE	PEG M.W.	PEG	EG	DMT	CaAc	Sb_2O_3	MTBP
1	600	466.67	720.96	666.49	1.28	0.18	0.69
2	1,450	310.34	479.03	446.90	0.85	0.15	0.46
3	3,350	142.09	216.13	200.00	0.39	0.53	0.21
4	3,350	125.37	1,080.65	1,000.00	1.91	0.26	0.10
5	3,350	41.79	720.96	666.49	1.28	0.18	0.69

Characterization

For ^{1}H NMR analysis, samples were prepared at 5% concentration in deuterated chloroform in 5 mm tubes. Their spectra were collected on a Varian XL-300 NMR spectrometer at ambient temperature with chemical shifts reported relative to tetramethylsilane. Acquisition parameters were: sweep width 4000 Hz, acquisition time 3.7s, 30° flip angle corresponding to 7uS. 200 transients were collected for each spectrum.

GPC experiments were performed on a Waters GPC instrument, model 745B, equipped with a Waters model 410 refractive index detector. Three Ultrastyrogel columns were used in sequence: 10^4A, 10^3A, and 10^2A. All samples were prepared as 0.2 wt% solutions in chloroform, followed by filtration through 0.45um Millex filter. The elution rate was 1 mL/min. Columns were maintained at 31.5°C.

RESULTS AND DISCUSSIONS

^{1}H NMR frequency assignments

The chemical shifts of major resonances in the five PET-POET samples are identical. However, the line intensities vary, depending on the amounts of the starting materials. For this reason, Sample 1 (Table 1) will be used as an example for the discussion on frequency assignments(Fig. 1).

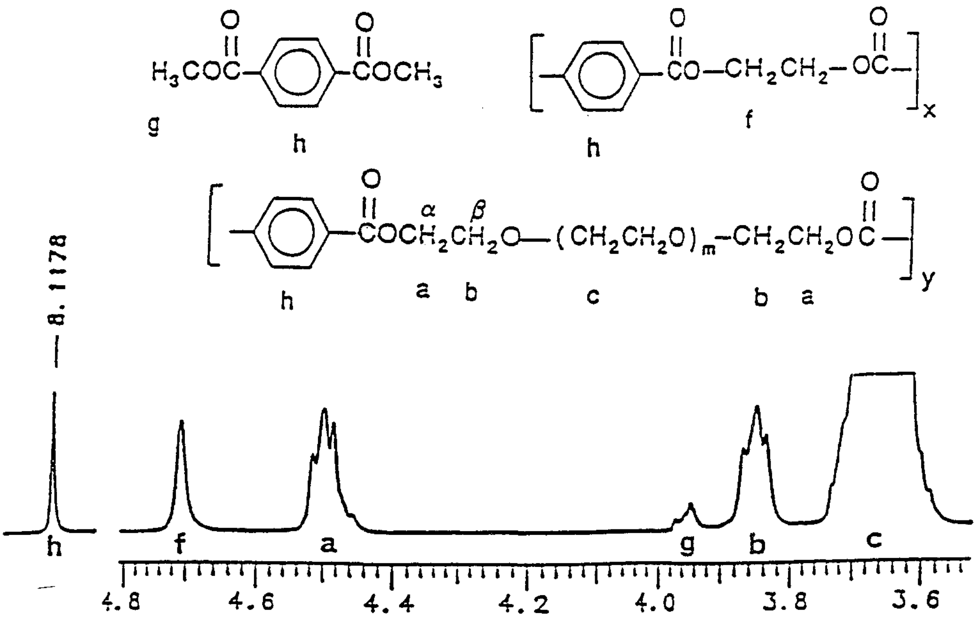


Fig.1 300 MHz ^{1}H NMR spectrum of PET-POET Sample 1

The aromatic protons(h) are equivalent and one resonance in the aromatic region is therefore expected for the copolyester.

This may be assigned to the resonance at 8.12 ppm. Because the four methylene protons(f) of PET are equivalent, a singlet is expected and may be assigned to the resonance at 4.71 ppm. The α(a) and β(b) methylene protons of POET, due to their proximities to the carboxyl group, should have different chemical shifts from the methylene protons in the bulk of the EO chain(c, i.e. within the m units of EO). Thus the triplets at 4.50 and 3.85 ppm are respectively assigned to the α and β methylene protons. The intense resonance at 3.68 ppm is due to the bulk methylene protons(c) in the EO chain in POET and/ or in unreacted PEG. The resonance at 3.95 ppm is due to the methoxy protons(g) of unreacted DMT.

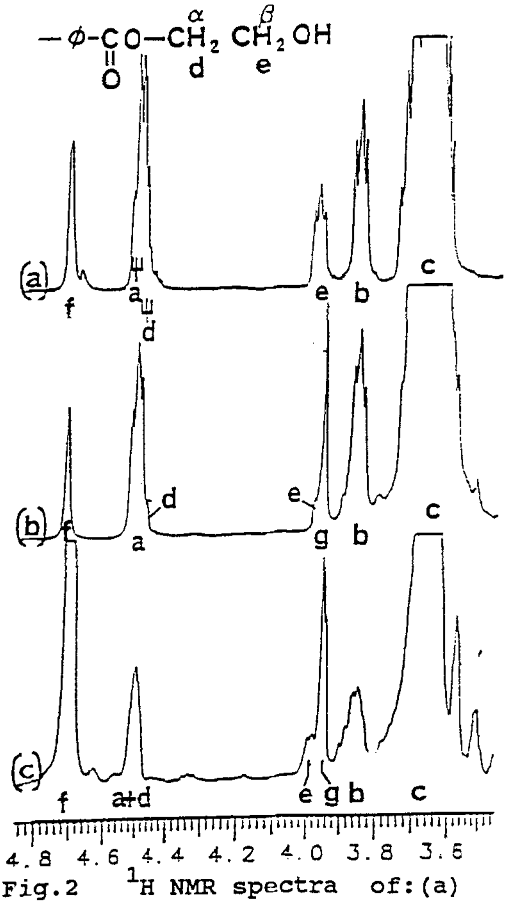


Fig.2 ^{1}H NMR spectra of:(a) PET-POET-PESC with PEG 600(6); (b) PET-POET Sample 2 with negligible amount of ethylol; (c) PET-POET Sample 5 with tangible amount of ethylol (For labels a,b,c,f,see Fig.1)

All samples examined in this study have long chain lengths and the relative amount of end-caps is small. Hence, the spectral evidence for end-cap was not apparent and its presence was not recognized in the spectra initially. In a related study (6), the polyester of poly(ethylene terephthalate)-poly(oxyethylene terephthalate)-poly(ethylene 4,4'stilbenedicarboxylate) (PET-POET-PESC) was synthesized and studied by ^{1}H NMR. There, in the spectrum of a low m.w. PET-POET-PESC sample, several spectral features in the ether/ester region were noted as significantly different from those observed in this study. Using 2D NMR techniques, they were identified as those of ethylol(-CH_2CH_2OH) end-caps. Subsequently, the spectral data of the present study were re-examined and weak ethylols were also found.

The presence of ethylol is illustrated in Figure 2. Fig. 2a is that of a low m.w. sample of PET-POET-PESC(6). Due to its shorter chain length, the relative amount of ethylol becomes substantial and the spectral features of the ethylol (d,e) are therefore more prominent. Sample 2 of PET-POET(Fig. 2b) has a negligible amount of ethylol whose presence is indicated by its a methylene(d) a 4.47 ppm which appears as a small upfield shoulder on (a) and by its b methylene(e) at 3.99 ppm, a small downfield shoulde on (g). Sample 5(Fig. 2c) has a tangible amount of ethylol whose presence is indicated by the large b methylene shoulde at 3.99 ppm(e). The corresponding a methylene(d) is completely masked by the broad resonance at 4.50 ppm. Nevertheless, (d) can be estimated because it is equivalent to (e). Since the total area of the 4.50 ppm line is (a+d), the area due to the a methylenes of POET(a) is therefore: (a+d)-e.

The determination of PET/POET mole ratio

Fig. 2b and 2c are used to illustrate the determination of PET/POET mole ratio. The copolyester is designated to have x moles of PET and y moles of POET(Scheme 1). For a copolyester sample with negligible amount of ethylol (Sample 2, Fig. 2b), there are 4x moles of methylene protons in PET responsible for the area of (f) at 4.71 ppm. In POET, there are 4y moles of methylene protons responsible for the resonance at 4.50 ppm. Since the amount of ethylol is negligible, the area of this resonance may be considered to be entirely due to the methylene protons of POET, i.e. area of (a). Thus,

$$\frac{4x}{4y} = \frac{x}{y} = \frac{f}{a} \qquad (1)$$

For a copolyester sample with a tangible amount of ethylol (Sample 5, Fig. 2c), the area of the 4.50 ppm resonance is due to the a methylene protons of POET(a) and ethylol(d), i.e (a+d). As indicated above, the area due to the a methylen protons of POET(a) is (a+d)-e. Thus,

$$\frac{4x}{4y} = \frac{x}{y} = \frac{f}{(a+d)-e} \qquad (2)$$

The mole ratios of PET/POET determined as described above are compared with the feed ratios of EG/PEG in Table 2 below:

TABLE 2 PET/POET mole ratio

SAMPLE	M.W. PEG	FEED RATIO OF PEG:EG:DMT	FEED RATIO EG/PEG	^{1}H NMR EXPTL. RATIO PET/POET
1	600	0.70 : 1.08 : 1.00	1.54	0.44
2	450	0.69 : 1.07 : 1.00	1.55	0.32
3	3350	0.71 : 1.08 : 1.00	1.52	0.25
4	3350	0.12 : 1.08 : 1.00	9.00	3.36
5	3350	0.06 : 1.08 : 1.00	18.00	6.33*

* Under-estimated due to under-estimation of ethylol end-caps.

The determination of EO number

For y moles of POET(Fig. 2b,2c), the area of (c) represents 4my moles of protons(see Fig.1 for definition of m). With similar reasoning used in Eqs. 1 and 2, for a copolyester with a negligible amount of ethylol (Sample 2, Fig. 2b),

$$\frac{4my}{4y} = m = \frac{c}{a} \tag{3}$$

For a copolyester with a tangible amount of ethylol (Sample 5, Fig. 2c),

$$\frac{4my}{4y} = m = \frac{c}{(a+d)-e} \tag{4}$$

For the total number of EO, n(Scheme 1), the two moles of EO units with a and b methylenes(see Fig.1) should be account for, i.e.

$$n = m + 2 \tag{5}$$

The EO numbers(n), as determined from ^{1}H NMR data, are compared with the expected EO numbers based on the molecular weights of the PEG used(Table 3). Since EO is not lost under the conditions of polymerization, a comparison of these two sets of EO numbers should provide an indication of the validity of the above calculations.

Table 3 Comparison of the expected and measured number of ethoxylate (EO) in POET

SAMPLE	M.W. OF PEG USED	EXPECTED EO # FROM M.W. OF PEG	EXPTL. EO # FROM ^{1}H NMR DATA
1	600	13.2	13.5
2	1450	32.5	35.0
3	3350	75.7	164.4
4	3350	75.7	70.4
5	3350	75.7	59.1

Acceptable agreement is obtained between the experimentally determined EO number and the expected EO number for Samples 1, 2 and 4. However, for Samples 3 and 5, deviations from the expected values are observed. For Sample 3, the experimentally determined EO number is more than twice of that of the expected number. One possible explanation is that, for Sample 3, there is a large amount of unreacted PEG. The bulk EO chemical shift of unreacted PEG will be indistinguishable from the EO incorporated in POET, making (c) much larger, which in turn, leads to a larger m and n.

To verify this speculation, GPC data were collected for the PET-POET samples 3, 4 and 5, all of which use PEG-3350 as one of the starting materials. The chromatograms produced by

Samples 4 and 5 exhibit very similar distribution(see Fig. 3c, 3d). For Sample 4, the EO number determined from ^{1}H NMR data agrees with that of the expected value. For Sample 5, the EO number determined from ^{1}H NMR data is actually less than that of the expected value. This suggests that unreacted PEG was unlikely to be present. The chromatogram of Sample 3(Fig. 3b), on the other hand, is distinctly different from those of Samples 4 and 5. Its strongest GPC peak has the same elution time as that of unreacted PEG(Fig. 3a),indicating a substantial contribution from unreacted PEG. Thus the GPC data of Sample 3 support the view that a fair amount of unreacted PEG could skew results from ^{1}H NMR data.

For Sample 5, the experimentally determined EO number is noticeably less than the expected EO number. This could be due to an under-estimation of the area of (e) during the deconvolution procedure. It is evident from Eqs. 4 and 5 that such an under-estimation would lead to an underestimation of m and n.

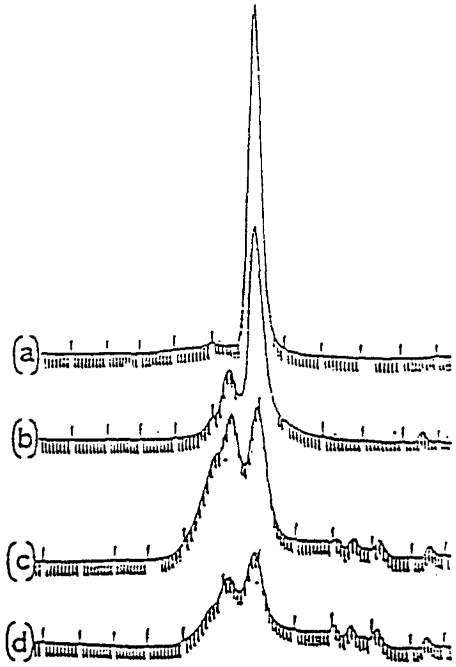


Fig.3 GP chromatograms:
(a) PEG 3350; (b) PET-POET Sample 3;(c)PET-POET Sample 4; (d) PET-POET Sample 5

CONCLUSIONS

In this study, we showed how ^{1}H NMR can be used to characterize PET-POET by providing the PET/POET mole ratio and the EO number in POET. When ethylol end-caps are present, a correction factor should be applied to either calculation to ensure accuracy. The presence of unreacted PEG will distort the EO number determination. Thus, PET-POET samples should always be examined by GPC in order to ascertain the presence of unreacted PEG.

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