Synthesis of polyesters from dimethyl terephthalate, ethylene glycol, poly(ethylene glycol) and 4,4'-bis(carbomethoxy)stilbene, and characterization by ^1H and 2-D n.m.r.

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Polyesters from dimethyl terephthalate, ethylene glycol, poly(ethylene glycol) and 4,4'-bis(carbomethoxy)-stilbene were synthesized via a thermal transesterification reaction. The assignment of proton frequencies was facilitated by 2-D n.m.r. techniques. The presence of ethylol end groups and the occurrence of a *cis* to *trans* stilbene monomer isomerization were observed and are reported herein.

(Keywords: ^1H n.m.r.; 2-D n.m.r.; poly(ethylene terephthalate); poly(oxyethylene terephthalate); 4,4'-bis(carbomethoxy)-stilbene; copolyester)

Introduction

Although poly(ethylene terephthalate)–poly(oxyethylene terephthalate) (PET-POET) copolyesters have been known for nearly four decades[1–5], little has been reported about their characterization by ^1H n.m.r. spectroscopy. Gilding and Reed[6] and Anan'eva *et al.*[7] described the ^{13}C n.m.r. spectra of PET–POET obtained in $CDCl_3$ and CD_3COCD_3, respectively. Ahn *et al.*[8] reported the ^1H n.m.r. spectra of PET-POET obtained in trifluoroacetic acid solution, but were only able to identify three characteristic resonances. Recently, PET-POET was investigated[9] by ^1H n.m.r. at 300 MHz. The improved spectral resolution has permitted the determination of the PET/POET mole ratio and the number of ethoxylate units in POET.

In the present study, we prepared[10] a series of polyesters derived from dimethyl terephthalate (**1**), ethylene glycol (**2**), poly(ethylene glycol) (**3**), and 4,4'-bis (carbomethoxy)stilbene (**4**)[11] (*Scheme 1*). This communication describes the characterization of poly (ethylene terephthalate)–poly(oxyethylene terephthalate)–poly(ethylene 4,4'-stilbenedicarboxylate) (PET-POET-PESC) (**5**) materials by ^1H n.m.r. spectroscopy.

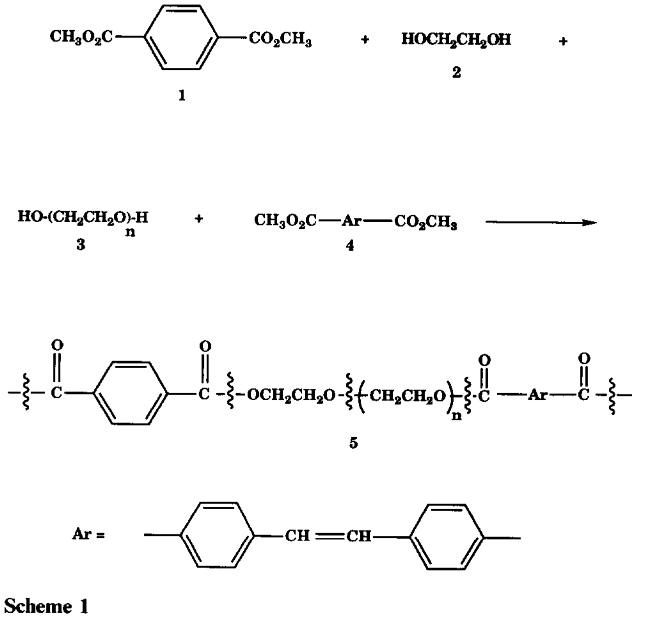
Experimental

^1H n.m.r. spectra were recorded on a Varian XL-300 MHz n.m.r. spectrometer at ambient temperature using 5 mm sample tubes. Samples were dissolved in $CDCl_3$ with tetramethylsilane as an internal standard. Acquisition parameters were: sweep width (s.w.) = 4000 Hz; pulse width = 56° (corresponding to 12.5 μs); acquisition time = 3.75 s; number of transients = 200.

The bond connectivity information was obtained from a symmetrized 45° COSY experiment. The acquisition parameters were: s.w.1 = 2623 Hz; s.w.2 = 2622 Hz; acquisition time = 0.195 s; pulse width = 90° (corresponding to 20 μs); first pulse = 90°; number of repetitions = 16; number of increments = 256. The free induction decays (f.i.d.s) were multiplied by a pseudo-echo function before Fourier transformation (*FT*). *FT* size was 1K × 1K.

For the homonuclear *J*-resolved experiment, the acquisition parameters were: s.w.1 = 4000 Hz; s.w.2 = 40 Hz; acquisition time = 0.512 s; pulse width = 90°; first pulse = 180°; number of repetitions = 4; number of increments = 64. The f.i.d.s were multiplied by a pseudo-echo function before *FT*. *FT* size was 4K × 256K.

General procedure for low (3000) molecular weight PET-POET-PESC polymers. To a 250 ml three-neck round bottom flask fitted with an overhead stirrer, distillation condenser and nitrogen inlet tube was added 19.41 g (0.01 mol) dimethyl terephthalate, 9.46 g (0.153 mol) ethylene glycol, 54.01 g (0.090 mol) poly(ethylene glycol) (M_w = 600), 7.40 g (0.025 mol) 4,4'-bis(carbomethoxy)stilbene (**4**), 0.135 g (0.876 mmol) $Ca(OAc)_2$, 0.135 g (0.463 mmol) Sb_2O_3 and 0.135 g (0.613 mmol)



Scheme 1

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2,6-di-tert-butyl-4-methylphenol. The reaction vessel was heated at 175°C for 2 h. The temperature was raised to 205°C, at which point MeOH was removed by distillation, and the reaction vessel was heated at that temperature for 5 h. The temperature was further raised to 220°C and the reaction vessel was heated at that temperature for an additional 19 h.

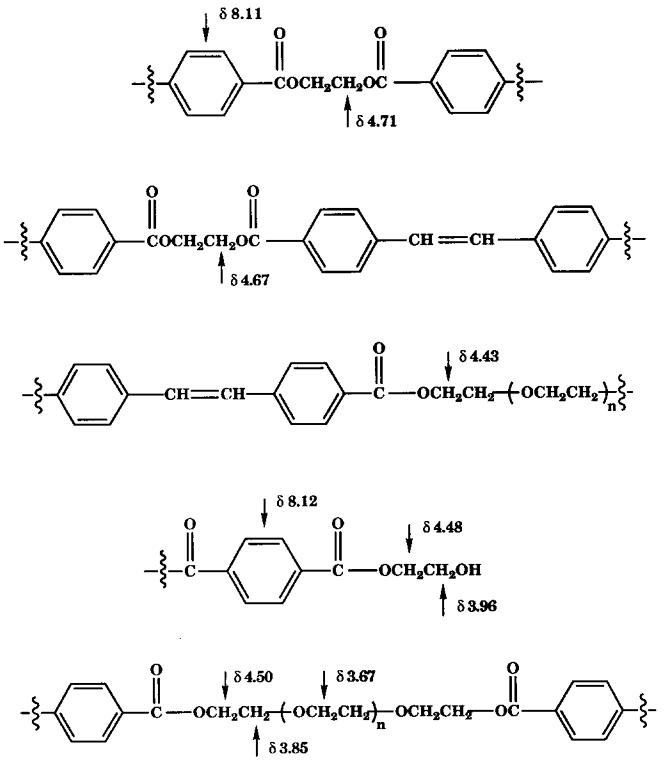
For the high molecular weight (50 000–75 000) PET-POET-PESC polymers, the above procedure was employed and the reaction vessel was heated an additional 5 h under vacuum (6.7×10^2 Pa).

Results and discussion

Although a series of polymers (**5**) could be synthesized ranging in stilbene loading and molecular weight[10], low (3000) and high (50 000) molecular weight samples of **5** containing 10 mol% stilbene were chosen for the following n.m.r. experiments. The frequency assignments are summarized in *Scheme 2*.

Ester region (3.8–5.0 ppm) and aromatic region (8.1–8.2 ppm). The ester features of low molecular weight PET-POET-PESC (*Figure 1a*) show some interesting differences from the high molecular weight analogue (*Figure 1b*). The signal at 4.49 ppm, assigned as the methylene group α to the carbonyl group in POET[9], exists as a triplet in the high molecular weight polymer but as a quartet in the low molecular weight polymer. In addition, the singlet at 3.97 ppm assigned as the methoxyl group of the unreacted dimethyl terephthalate starting material exists as a triplet in the low molecular weight polymer, but is absent from the high molecular weight polymer.

In order to better understand the changes in molecular structure which lead to the new splitting patterns, we performed several 2-D n.m.r. experiments. The HOM2DJ data from the low molecular weight polymer (*Figure 2*) show that the line at 4.49 ppm is actually a pseudo quartet formed by the incidental overlap of two triplets. They are therefore two methylenes with very similar chemical shifts, one centred at 4.50 and the other at 4.48 ppm. The signal at 3.97 ppm is confirmed as a triplet.



Scheme 2

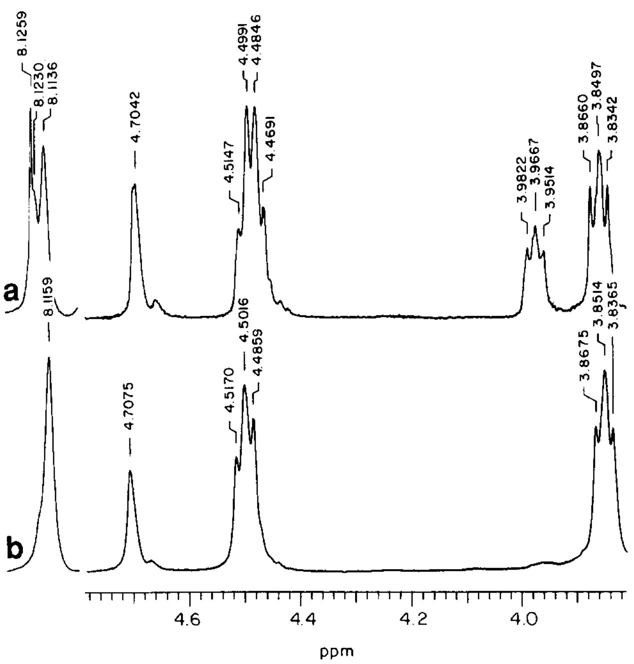


Figure 1 ^{1}H n.m.r. spectra of (a) low molecular weight (3000) PET-POET-PESC and (b) high molecular weight (50 000) PET-POET-PESC

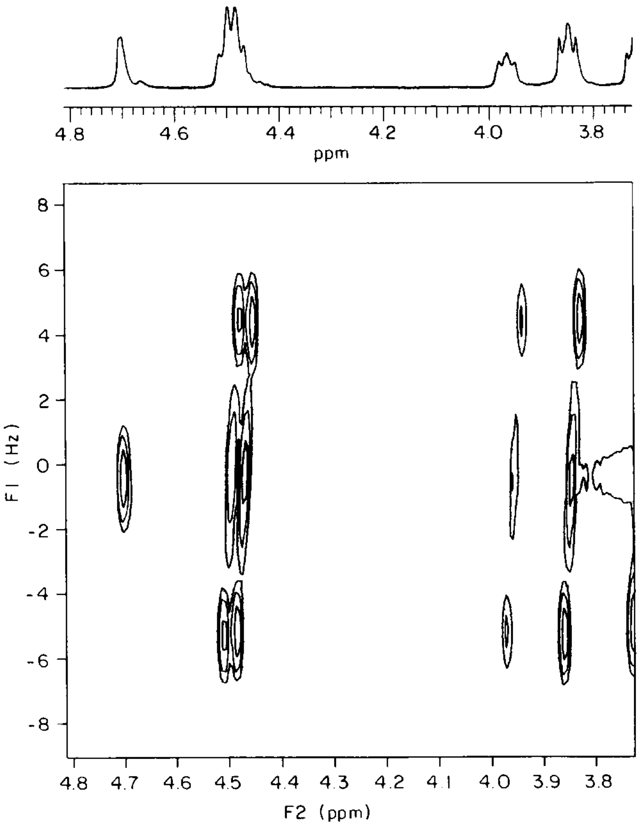


Figure 2 Contour plot of the HOM2DJ experiment of low molecular weight (3000) PET-POET-PESC

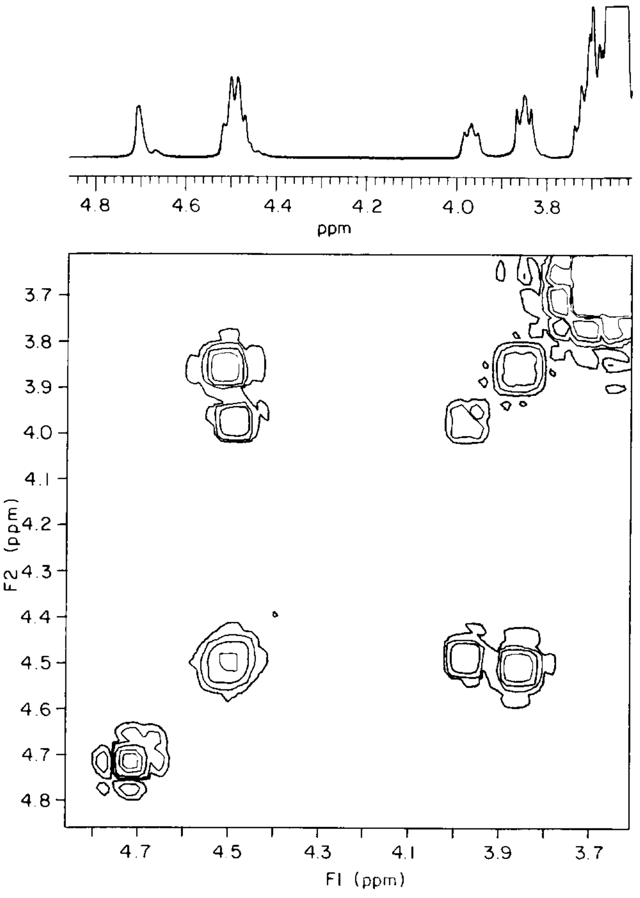


Figure 3 Contour plot of the COSY experiment of low molecular weight (3000) PET-POET-PESC

The COSY data from the low molecular weight polymer (*Figure 3*), reveal a cross-peak at 4.50 and 3.85 ppm. Since the latter peak had been assigned to the methylene group β to the carbonyl group in POET[9], the former must be the corresponding α methylene group. A second cross-peak at 4.48 and 3.97 ppm shows that these methylenes are also coupled. We speculated that these signals represented an ethylol (2-hydroxyethyl ester; $-CH_2CH_2OH$) end group resulting from incomplete diesterification of ethylene glycol. To verify the assignment, we collected a ^1H n.m.r. spectrum of bis(2-hydroxyethyl) terephthalate (sample obtained from Polysciences, Inc., Warrington, PA, USA). The two triplets at 4.50 and 3.99 ppm confirm the presence of the ethylol group, pertaining to its α and β methylene protons, respectively. It remains to be proven if the ethylol group in the polyester spectra is present as the end group on the copolyester of PET-POET-PESC or as bis(2-hydroxyethyl) terephthalate or both.

Comparison of the spectra of the low and high molecular weight polymers (*Figures 1a* and *b*) shows the simultaneous disappearance of the two triplets (4.48 and 3.97 ppm) and the aromatic singlet (8.126 ppm) from the spectrum of the high molecular weight polymer. This suggests that the signals may correspond to the same molecular fragment (e.g. ethylol end group) or the same molecule [e.g. bis(2-hydroxyethyl) terephthalate]. Closer examination of the high molecular weight polymer spectrum shows that the triplet at 3.97 ppm has not disappeared but has been reduced to a weak broad band. Also, in the high molecular weight polymer spectrum, the line at 8.126 ppm disappears while the shoulder at 8.123 ppm remains apparent. It is likely that a fair amount of the ethylol group present in the low molecular weight material is present as bis(2-hydroxyethyl) terephthalate which undergoes polyesterification at 6.7×10^2–26.8×10^2 Pa. The weak broad bands at 3.97 and 4.44 ppm, as well as the shoulder at 8.123 ppm, are therefore due to the ethylol end groups in the high molecular weight material.

To investigate this matter further, we dialysed a sample of low molecular weight PET-POET-PESC through a 1000 molecular weight cut-off membrane against water. After dialysis, both the triplets at 4.49 and 3.97 ppm reduced in intensity. In the aromatic region, the line at 8.126 ppm disappeared while the shoulder at 8.123 ppm persisted. This suggested that some low (<1000) molecular weight terephthalate-based material, most likely bis(2-hydroxyethyl) terephthalate, was lost through the dialysis membrane. The remaining 3.97, 4.49 and 8.123 ppm signals are therefore likely to be related to ethylol end groups. These intensities are stronger in the low molecular weight material than in the high molecular weight material because of the longer chain length of the latter.

A weak signal at 4.67 ppm present in the PET-POET-PESC polyesters has been assigned to the ethylene protons of ethylene glycol copolymerized with dimethyl terephthalate on one end and 4,4′-bis-(carbomethoxy)stilbene on the other. That this signal is undetectable in PET-POET-PESC samples containing low levels (<0.5 mol%) of stilbene monomer is consistent with this assignment.

Olefinic region (6.6–8.1 ppm). 4,4′-Bis(carbomethoxy)-stilbene[11] synthesized via a Wittig[12,13] olefination was obtained as a 70:30 mixture of *cis*:*trans* isomers. Resonances from both stilbene isomers were present in the aromatic/olefinic region of the PET-POET-PESC spectrum. The chemical shifts of the signals in the aromatic/olefinic region for the PET-POET-PESC polymer are identical to those of 4,4′-bis(carbomethoxy)-stilbene and are likewise assigned (*Scheme 2*).

Interestingly, the ratio of the *cis*:*trans* isomers of stilbene moiety in the PET-POET-PESC polymer is different from that of the starting material charged in the reaction vessel. In the synthesis of the low molecular weight materials containing 5 and 10 mol% stilbene, respectively, 4,4′-bis(carbomethoxy)stilbene was employed as a 49:51 mixture of *cis*:*trans* isomers. The *cis*:*trans* ratio of the stilbene moiety in the final products was found by ^1H n.m.r. integration to be 37:63 and 27:73 for low and high molecular weight polymers, respectively. In other words, there was proportionally more *trans* than *cis* stilbene in the copolymer than in the 4,4′-bis(carbomethoxy)stilbene starting material.

The question is whether the predominance of *trans* 4,4′-bis(carbomethoxy)stilbene in the PET-POET-PESC polymer resulted from preferential incorporation of the *trans* over the *cis* form, or whether it resulted from *in situ cis* to *trans* isomerization, followed by transesterification. We had little reason to believe that there was any inherent preference for one isomer to be any more susceptible to nucleophilic attack over the other. However, only the *cis* form should be fully melted (m.p.$_{cis}$ = 109–111°C; m.p.$_{trans}$ = 227–228°C)[7] at the polymerization temperatures (205–220°C) and, under these circumstances, the preferentially incorporated monomer would likely be the *cis* form. For these reasons, we feel that a *cis* to *trans* isomerization of 4,4′-bis(carbomethoxy)stilbene took place under the reaction conditions.

To test our hypothesis, a low molecular weight polymer was synthesized using 5 mol% pure *cis* isomer according to the procedure described in the Experimental section. Characterization of this material by ^{1}H n.m.r. revealed that 34% of the incorporated stilbene was in the *trans* form. Since none of the stilbene starting material contained *trans* isomer, some of the *cis* form must have been isomerized under the reaction conditions. This is not at all surprising, since under the polymerization conditions the stilbene monomer is heated at temperatures >200°C in the presence of proton sources [ethylene glycol, poly(oxyethylene glycol) and methanol] and Lewis acid catalysts. This environment was likely to have promoted olefin protonation followed by free rotation about the sp^3–sp^3 σ bond and further followed by deprotonation and rehybridization to afford the thermodynamically favoured olefin.

Conclusions

^{1}H n.m.r. chemical shifts can be assigned for PET-POET-PESC polyesters. The presence of the ethylol end group has been verified with the aid of 2-D n.m.r. data. Interestingly, the *cis–trans* isomerization of the stilbene moiety which occurs under the polymerization conditions, can be detected and quantitated from n.m.r. experiments.

Acknowledgements

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