^{1}H-NMR Sequence Analysis of Poly(ethylene terephthalates) Containing Various Additional Diols

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SUMMARY

Homo- and copolyesters made up by terephtalic acid (T) on the one hand, and ethylene glycol (Et), diethylene glycol (Di), triethylene glycol (Tr), 1,4-butanediol (Bu) and 1,6-hexanediol (He), on the other hand, were investigated by means of 60, 90, 250 and 400 MHz ^{1}H-NMR spectra or by 22.63 MHz ^{13}C-NMR spectra. Copolyesters of ethylene, glycol and oligo(ethylene glycols) can be analyzed by means of ^{1}H-NMR spectra because of the fact that the terephthalic acid protons are sensitive to sequence effects, while the ^{13}C-NMR signals are insensitive. In contrast, sequences of ethylene glycol and 1,4-butanediol or 1,6-hexanediol are best analyzed by ^{13}C-NMR spectra, while ^{1}H-NMR spectra are rather useless in this case.

INTRODUCTION

In a previous paper one of us has demonstrated[1] that ^{13}C-NMR spectroscopy is a useful tool for the sequence analysis of various copolyesters, e.g. poly-(ethylene terephthalate) (PET)/polycaprolactone sequences. Other authors, studying the PET/PBuT system reached the same conclusion[2]. Because diethylene glycol is normally a component of industrially produced PET due to thermally induced side reactions, we were interested in the spectroscopic characterization of PET sequences containing diethylene glycol units (Di). Surprisingly, 22.63 MHz ^{13}C-NMR spectra measured with a digital resolution of 0.5 Hz/pt in various solvents did not reveal any sequence effects. However, already a 60 MHz ^{1}H-NMR spectrum of a PET/PDiT copolyester

exhibits a weak splitting of the terephthaloyl signal suggesting a sequence sensitivity of the aromatic protons. This observation prompted us to study the ^{1}H-NMR spectra of polyterephthalates in more detail.

RESULTS and DISCUSSION

The following polyesters were used for the NMR measurements:
1) homopolyesters of terephthalic acid and ethylene glycol, diethylene glycol, triethylene glycol, 1,4-butane diol and 1,6-hexane diol;
2) copolyesters with a regular sequence of ethylene glycol and diethylene glycol units: (Et-T-Et-T-Di-T-)$_n$ and (Et-T-Et-T-Di-T-Di-T-)$_n$ (the syntheses are described elsewhere [3,4]);
3) copolyesters with a random sequence of ethylene glycol and other diols, obtained by Ti(OBu)$_4$ catalyzed transesterification of homopolymer blends in the melt.

All ^{1}H-NMR measurements were run in a TFA/CDCl$_3$ mixture (1:2 by volume) because deuterated acids give broad lock signals, and because PET is insoluble in nonacidic solvents. When a blend of PET and PDiT (mole ratio 1,5:10) was measured, two aromatic signals were found. The downfield signal was attributed to PET owing to its greater intensity. The sequence polyester (Et-T-Et-T-Di-T-Di-T-)$_n$ as well as a random copolyester prepared by transesterification of PET and PDiT possess nearly identical spectra exhibiting three aromatic signals (δ =8.185, 8.145 and 8.110 ppm, Fig.1). Since both types of copolyesters contain the three diads Et-T-Et, Et-T-Di and Di-T-Di and because the concentration of the Et-T-Di(=Di-T-Et) triad must be twice as high as that of each other triad, the assignments shown in Fig.1 are obvious. They are confirmed
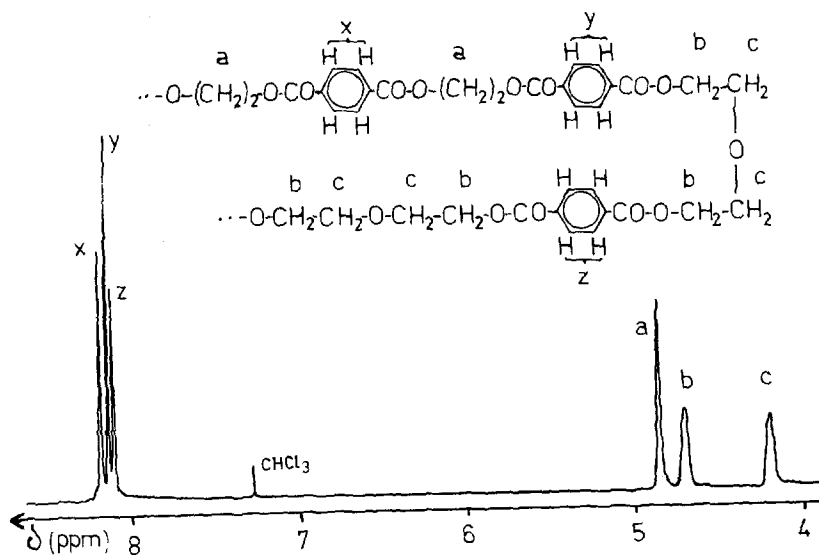
Fig.1 250 MHz ^{1}H-NMR spectrum of the sequence polyester (Et-T-Et-T-Di-T-Di-T-)$_n$ measured in TFA/CDCl$_3$ (1:2)
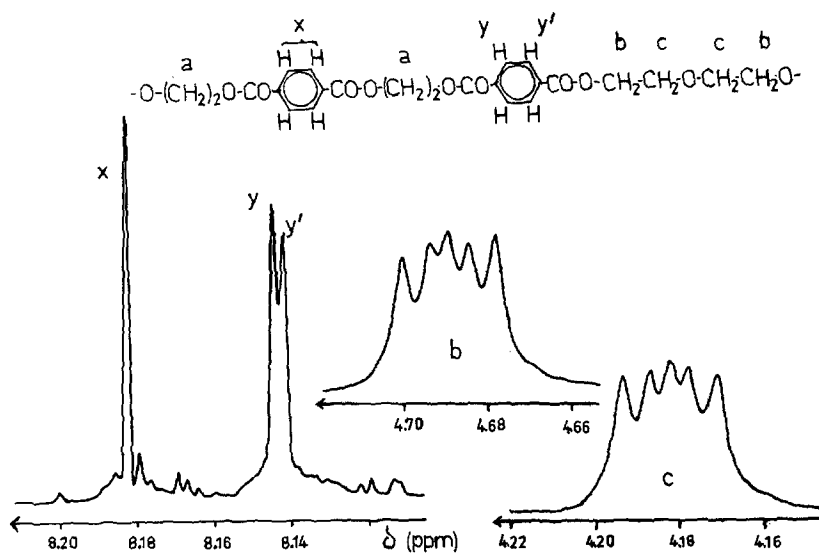

Fig.2 400 MHz ^{1}H-NMR spectrum of the sequence polyester (Et-T-Et-T-Di-T-)$_n$ in TFA/CDCl$_3$ (1:2): resolution enhanced signals of the aromatic protons and diethylene glycol protons

by the spectrum of the sequence polyester (Et-T-Et-T-Di-T)$_n$ which lacks the diad Di-T-Di, so that only two aromatic signals are observable (δ =8.185 and 8.145 ppm, Fig.2). The resolution enhanced 400 MHz ^{1}H-NMR spectrum (Fig.2) of the aromatic protons exhibits a symmetric splitting of the highfield signal which has a chemical shift identical with the central signal of the aromatic "triplet pattern" in Fig.1. Obviously, this splitting indicates that the two pairs of aromatic protons of the Et-T-Di diad are magnetically not equivalent. The complicated coupling pattern of the CH$_2$ groups of the diethylene glycol units is also shown in Fig.2.

A blend of PET and PTrT (poly(triethylene glycol terephthalate)) displays also two aromatic signals with PET absorbing downfield; yet their shift difference (0.06 ppm) is smaller than that of the PET/PDiT blend (0.08 ppm). A copolyester prepared from this blend by catalyzed transesterification shows the expected three aromatic ^{1}H-NMR signals, which represent the triads Et-T-Et, Et-T-Tr and Tr-T-Tr (Fig.3). The signal intensities of the three triad signals prove that the thermodynamical transesterification equilibrium was not yet reached, because a truely random sequence requires the Et-T-Tr signal beeing nearly twice as intensive as the signals of the two other triads. After resolution enhancement the aromatic protons show the interesting feature that the downfield signal is split into three peaks. Probably this splitting indicates a tetrad sensitivity.

While the aromatic protons are most useful for the sequence analysis, the aliphatic protons allow best the detection of low concentrations of diethylene glycol (or triethylene glycol) in commercial PET. Fig.4 shows a PET sample (provided by the BASF AG) containing

1.3% Di-units. From our measurements we may conclude that 400 MHz ^{1}H-NMR spectra allow to measure Di concentrations as low as 0.1% (mole percent relative to Et-units), whereas 60 MHz ^{1}H-NMR spectra can only be used for concentrations $\geq 1\%$[35]. In this connection it is worth noting, that ethylene glycol end-groups show chemical shifts similar to those of fully esterified diethylene glycol units. Obviously, esterification with TFA does not take place, when freshly prepared solutions of oligo- or poly(ethylene terephthalates) in TFA/CDCl$_3$ (1:2) are measured at room temperature. However, addition of trifluoroacetic acid anhydride leads to a rapid esterification of the OH end-groups. As a consequence, the two CH$_2$ signals of the ethylene glycol end-groups shift downfield and coalesce with the main signal at $\delta = 4.85$ ppm, while the diethylene glycol signals remain unchanged.

When blends of PET and PBuT or PHeT are measured, no sequence effects are detectable in 60 or 90 MHz ^{1}H-NMR spectra. Two aromatic signals with shift differences of 0.0045 ppm and 0.003 ppm respectively are observable in 400 MHz spectra. By virtue of these small shift differences ^{1}H-NMR spectra are rather useless for a sequence analyses of copolyesters made up by various alkane diols and ^{13}C-NMR spectra are more recommendable[2]. Indeed, when a copolyester obtained by Ti(OBu)$_4$ catalyzed transesterification of PET and PBuT was measured, only one aromatic signal without any fine structure was found.

Furthermore it is noteworthy that two series of transesterification experiments were conducted:
a) heating of the polyester blend without any catalyst at 260°C/6h; and
b) heating with Ti(OBu)$_4$ at 260°C/2h.

The homopolyesters used for these experiments were

reprecipitated from TFA/MeOH and dried at 80°C/0,1 torr
for 24h. Without added catalyst no transesterification
was observed; for example the ^{1}H-NMR spectrum of the
PET/PBuT blend displayed after heating without catalyst
the two aromatic signals characteristic for the star-
ting material. This finding demonstrates in agreement
with previous results[1] that purified and carefully
dried polyesters are rather stable against transesteri-
fication up to temperatures of 280°C. In this respect
our ^{1}H-NMR results were confirmed by DSC measurements
as demonstrated by Figs. 5 A-D. Sample A only reveals
the melting peak of the PET component. Upon transesteri-
fication this peak shifts to much lower temperatures,
proving that long PET sequences are not longer availa-
ble to form thick, and thus, high melting crystals. The
DSC curve of blend C shows the melting endotherms of
both components, PET and PBuT. Again, the peaks are
shifted to lower temperatures after the transesterifi-
cation. However, we still observe two peaks, because
even short PET and PBuT blocks are able to crystallize.

MEASUREMENTS

The 90, 250 and 400 MHz ^{1}H-NMR spectra were measured
on a Bruker WH-90, WH-250 and WM-400 Ft spectrometers in
5 mm o.d. sample tubes at 30-31°C. 50 mg polyester was
dissolved in ca. 1 ml solvent (TFA/CDCl$_3$ 1:2 by volume)
A pulse width of 2 μs(25°C) was used and 50-100 transients
were accumulated. 8 K data points/1.500 Hz spectral width
were used for the 90 MHz spectra, 16 K/3.500 Hz for the
250 MHz spectra and 32 K/5.400 Hz for the 400 MHz spectra.
Resolution enhancement was achieved by Gaussian multi-
plication of the FID.
DSC measurements were carried out with a DSC-2 (Perkin
Elmer Corp.) in unsealed aluminium pans under a nitrogen
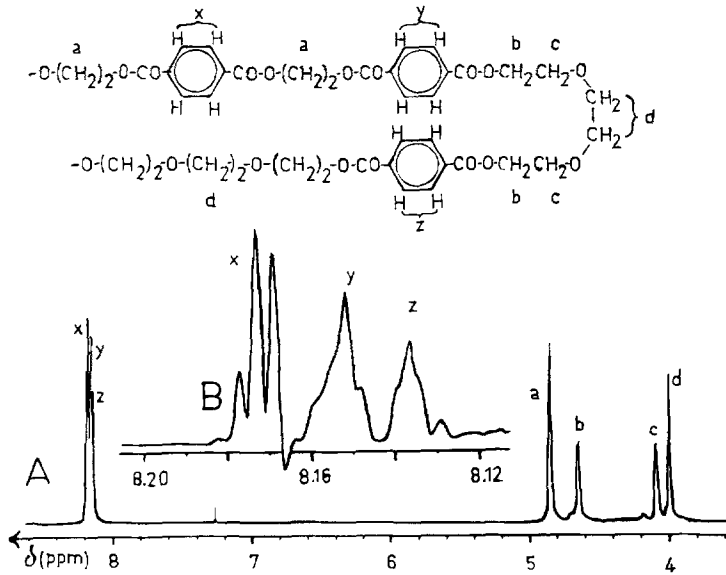atmosphere. For standards In and Sn were employed.

Fig.3   400 MHz ^{1}H–NMR spectrum of a polyterephthalate
with a nearly random sequence of ethylene glycol and
tri(ethylene glycol) units(mole ratio 1.2:1.0):

A) standard expansion and resolution,
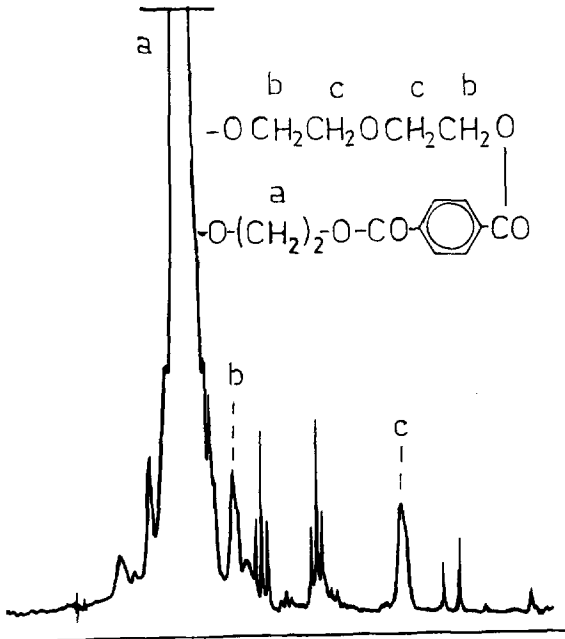B) resolution enhanced aromatic prorons.

Fig.4   400 MHz
^{1}H NMR spectrum
of the aliphatic
protons of an in-
dustrially produ-
ced PET sample
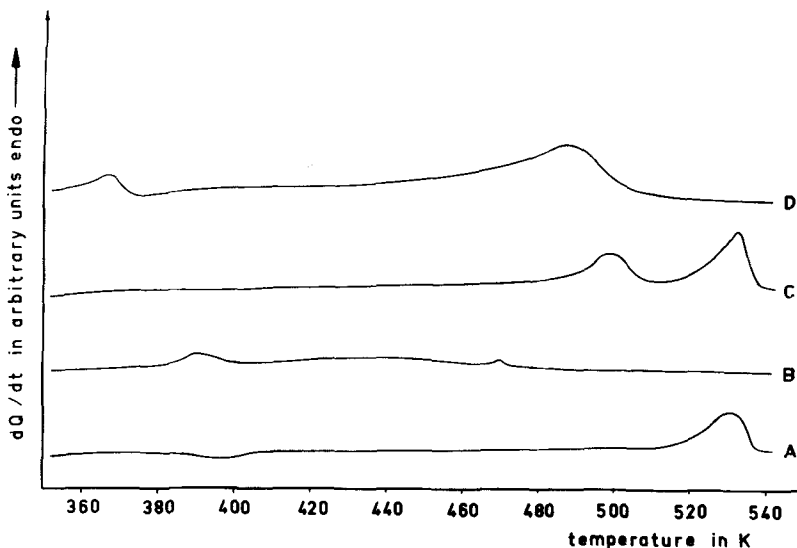containing 1.3
mol% di(ethylene
glycol)

Fig.5 DSC traces of polyterephthalates (samples repre-
cipitated from TFA/MeOH; sample weights 3-4 mg; heating
rate 20 K/ min):

A) Blend of PET and PTrT (1.2:1.0)

B) Above blend after transesterification with Ti(OBu)$_4$

C) Blend of PET and PBuT (1.5:1.0) heated without catalyst

D) Above blend after transesterification with Ti(OBu)$_4$

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