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

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SUMMARY

Homo- and copolyesters made up by terephthalic acid (T) on the one hand, and ethylene glycol (Et), diethylene glycol (Di), triethylene glycol (Tr), 1,4-butane-diol (Bu) and 1,6-hexanediol (He), on the other hand, were investigated by means of 60, 90, 250 and 400 MHz 1H-NMR spectra or by 22.65 MHz 13C-NMR spectra. Copolyesters of ethylene glycol and oligo(ethylene glycols) can be analyzed by means of 1H-NMR spectra because of the fact that the terephthalic acid protons are sensitive to sequence effects, while the 13C-NMR signals are insensitive. In contrast, sequences of ethylene glycol and 1,4-butanediol or 1,6-hexanediol are best analyzed by 13C-NMR spectra, while 1H-NMR spectra are rather useless in this case.

INTRODUCTION

In a previous paper one of us has demonstrated1) that 13C-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 conclusion2). 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 13C-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 1H-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 ($\delta$=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