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Determination of compositional sequences in PCT/FT aromatic copolyterephthalate by ^{1}H-NMR spectroscopy and Pr(fod)$_3$ lanthanide shift reagent

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SUMMARY

Standard 100 MHz ^{1}H-NMR spectrum of the PCT/FT copolyterephthalate gives little information on its microstructure and exhibits only slight splitting of the terephthalic signal which was found to be useful for evaluating distribution of compositional sequences. Application of Pr(fod)$_3$ provides clear splitting of this signal into lines of compositional diads with traces of compositional tetrads, while Eu(fod)$_3$ compresses the lines already split in the standard spectrum and yields one featureless broad terephthalic signal containing no microstructural information. The splitting induced by Pr(fod)$_3$ is comparable to that obtained using a superconducting spectrometer operating at 300 MHz.

INTRODUCTION

Previous investigations on the PDT/FT aromatic copolyterephthalate have shown that simultaneous application of a lanthanide shift reagent (LSR) to improve the 100 MHz ^{1}H-NMR spectra can provide in this case detailed information on the microstructure of the copolyterephthalate chain, based on the terephthalic signal splitting induced by the LSR (MATLENGIEWICZ and TURSKA 1982,1984; MATLENGIEWICZ 1984). The PCT/FT

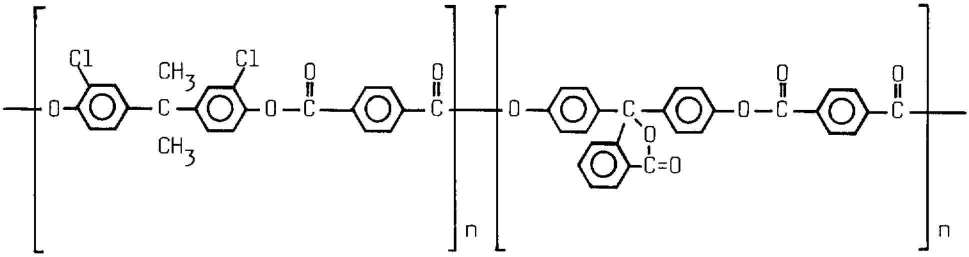

Fig. 1. Chemical structure of the PCT/FT copolymer

copolymer investigated in this work differs from previously studied PDT/FT copolymer only in substituents of bisphenol A, i.e. chlorine instead of methyl group. Therefore, the microstructural problems encountered here and the statistical description of respective sequences are identical with those employed for the PDT/FT chain (MATLENGIEWICZ and TURSKA 1982).

EXPERIMENTAL

The samples of 3,3'-dichlorobisphenol A/phenolphthalein copolyterephthalate [50:50] (PCT/FT) and homopolyterephthalates of 3,3'-dichlorobisphenol A (PCT) and phenolphthalein (PFT) were prepared from trephthaloyl chloride (Fluka AG) used as intermonomer and equimolar amounts of 3,3'-dichlorobisphenol A and phenolphthalein (POCh, Poland) as comonomers by polycondensation in solution of redistilled α-chloronaphthalene (Reachim, USSR) at 242°C under argon atmosphere.

The details of the 100 MHz ^{1}H-NMR spectra recording were as described previously (MATLENGIEWICZ and TURSKA 1982) and the 300 MHz ^{1}H-NMR spectrum was recorded on a Bruker MSL 300.

RESULTS AND DISCUSSION

The standard 100 MHz ^{1}H-NMR spectrum of PCT/FT gives slight diad splitting of terephthalic signal (Fig. 2), which is a little different from the standard spectrum of the previously investigated PDT/FT copolymer where this signal was a pure singlet. The three lines at δ 8.305, 8.335, and 8.365 ppm can be assigned to the FF, $\overleftrightarrow{\mathrm{CF}}$, and CC diad respectively, based on the comparision with the spectra of respective homopolytere-

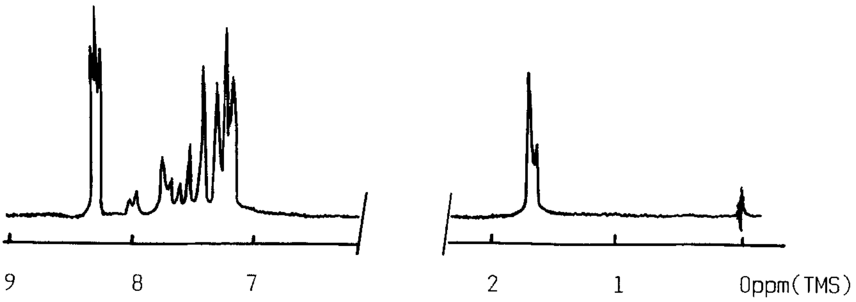

Fig. 2. Standard 100 MHz ^{1}H-NMR spectrum of the PCT/FT copolymer

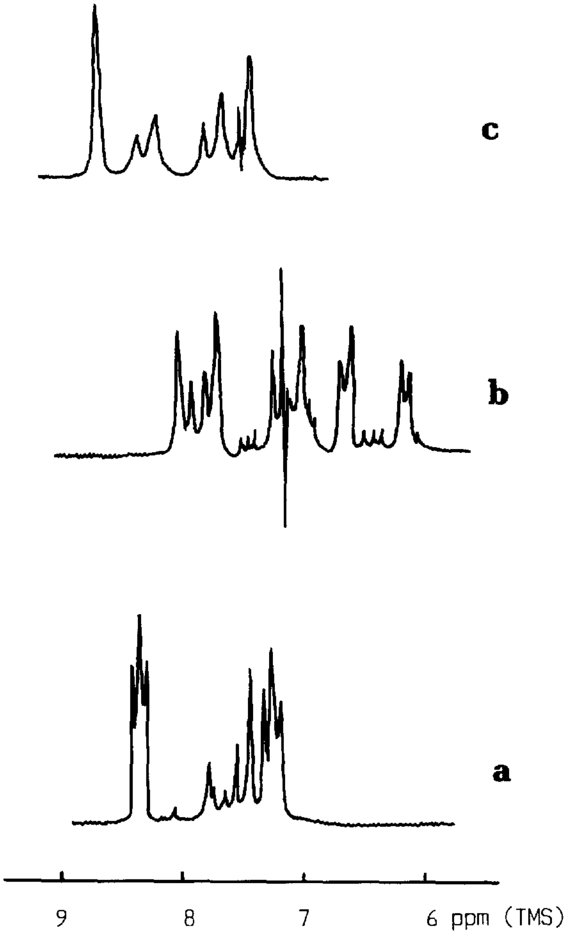

Fig. 3. Changes in the aromatic region of the standard 100 MHz ^{1}H-NMR spectra of PCT/FT copolyterephthalate (a) upon the addition of Pr(fod)$_3$ (b) and Eu(fod)$_3$ (c).

phthalates (MATLENGIEWICZ 1986). Application of Pr(fod)$_3$ confirms such an assignment (see next paragraph). Addition of either lanthanide shift reagent, Eu(fod)$_3$ or Pr(fod)$_3$, shifts the terephthalic signal upfield or downfield, respectively. For higher concentrations of LSR the terephthalic lines superimpose with the rest of aromatic signals.

Addition of Pr(fod)$_3$

Addition of Pr(fod)$_3$ to the PCT/FT solution in CDCl$_3$ was found to induce an upfield shift and clear separation of the lines of the terephthalic proton signal. The individual lines of the terephthalic signal were assigned to respective diads based on the experiments carried out with respective homopolyesters and mixture of homopolyesters . After addition of the same amounts of Pr(fod)$_3$ to the solutions of the copolymer and homopolymers in CDCl$_3$ it can be seen (Fig. 4) that in the region of terephthalic signal, the line at the highest field can be assigned to the FF homodiad, while that at the lowest field to the CC homodiad. The CF heterodiad gives a quartet with central two lines visible between the lines of homodiads and the two outer lines of the heterodiad superimposed with the lines of homodiads. Since the lanthanide induced shift for the FF diad is higher than that for the CC diad, it indicates easier access of the Pr(fod)$_3$ molecule to this unit of the chain.

Further addition of Pr(fod)$_3$ makes it possible to observe the splitting of the terephthalic signal into tetrad lines (Fig.5), however, superposition with remaining aromatic signals and broadening of the lines caused by Pr(fod)$_3$ did not allow to perform detailed tetrad analysis since uncertainty of computer simulation exceeded 10% in this case. Therefore, tetrad analysis requires further splitting of the spectrum, e.g., recording at higher magnetic field.

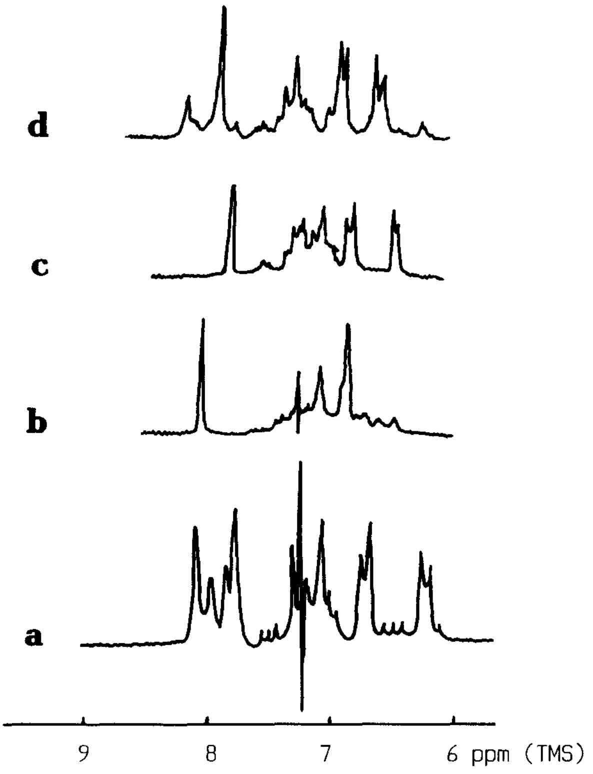

Fig. 4. Assignment of diads in the terephthalic proton signals recorded after addition of the same amount of Pr(fod)$_3$.
[Pr(fod)$_3$]/[T] = 2.4.
(a) PCT/FT copolyester
(b) PCT homopolyester,
(c) PFT homopolyester,
(d) PCT:PFT = 1:5 (w/w) homopolymer mixture.

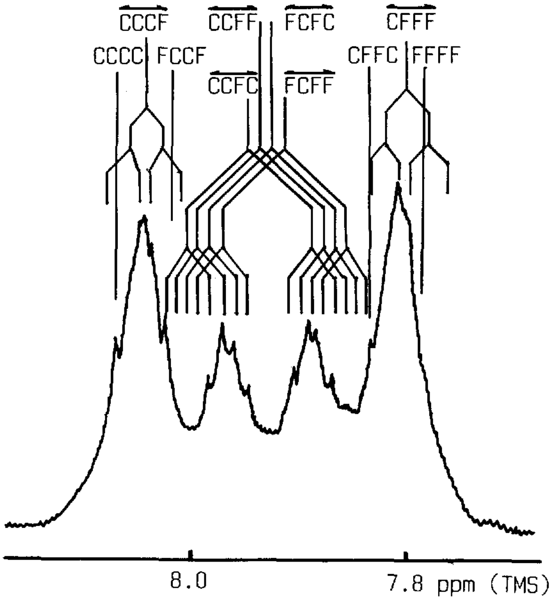

Fig. 5. Traces of tetrads in the terephthalic signal split in the presence of $Pr(fod)_3$.

Addition of $Eu(fod)_3$

Addition of $Eu(fod)_3$ leads to a compression of the terephthalic signal, already split in the standard spectrum, into one broad line featureless from the point of view of microstructure determination (Fig. 3b).

Application of higher magnetic field

Introductory ^{1}H-NMR investigations performed at 300 MHz have shown that in the case of the PCT/FT copolymer the terephthalic protons are already split in the standard spectrum into signals of diads and the signal separation is comparable to that obtained for 100 MHz instrument with simultaneous addition of $Pr(fod)_3$, however, there are no tetrad lines observed in this spectrum.

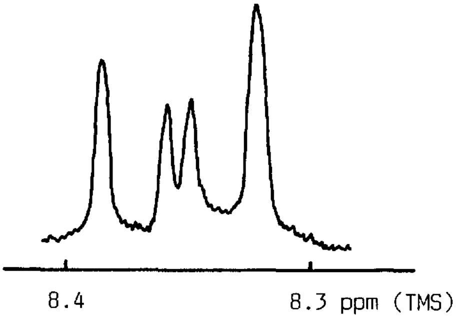

Fig. 6. Terephthalic protons signal in the 300 MHz ^{1}H-NMR spectrum of the PCT/FT copolymer.

CONCLUSIONS

The PCT/FT copolymer investigated in this work differs from previously investigated PDT/FT copolymer only in substituents of the 3,3'-disubstituted bisphenol A comonomer, i.e. chlorine instead of methyl group and this change introduces significant decrease in accuracy of determining the microstructure of its macromolecular chain compared to the PDT/FT copolymer, even though the terephthalic signal used for the microstructure studies is split into diad lines already in the standard 100 MHz spectrum. Application of $Pr(fod)_3$ lanthanide shift reagent induces clear separation of signals of compositional diads with traces of tetrad lines, too small, however, to perform detailed tetrad analysis. Simultaneous application of $Pr(fod)_3$ and higher magnetic field should enable recording of better resolved tetrad signals. Nevertheless, even the diad splittings alone are quite sufficient to distinguish differences between the samples of PCT/FT synthesized at various temperatures, which exhibit differences in their chain microstructure. This is to be presented in the next paper.

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