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Application of Lanthanide Shift Reagents to the Determination of Sequences in an Aromatic Copolyterephthalate by ^{1}H-NMR-Spectroscopy

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SUMMARY

The 60 and 100 MHz ^{1}H-NMR spectra of a fully aromatic copolyterephthalate, prepared from 3,3'-dimethylbisphenol A and phenolphthalein as comonomers and terephthaloyl chloride as intermonomer, were recorded in the presence of $Eu(fod)_3$ or $Pr(fod)_3$ and used for the determination of diad, triad and tetrad signals.

INTRODUCTION

Sequence distribution investigations of condensation copolymers by means of high-resolution ^{1}H-NMR spectroscopy showed that such studies are generally possible in those cases in which the chemical shift of the homolinkages differ sufficiently from one another, e.g. one comonomer is aromatic while the other is aliphatic (KHRAMOVA et al. 1968, HAMB 1972, MURANO 1972, KORSHAK et al. 1973). By the addition of lanthanide shift reagents (LSR) (CHUJO et al. 1972) or the application of higher magnetic fields, using NMR instruments equipped with superconductive electromagnets (KRICHELDORF et al. 1981), signals of various sequences in more complicated cases can appear in the spectrum. Owing to the large dimensions and the relatively smaller influence of neighboring units in condensation copolymers, it was possible to distinguish only the compositional diads. In the case of condensation copolymers obtained from one intermonomer and two comonomers, e.g. copolyterephthalates, the compositional sequence distribution, i.e. the distribution of comonomer units along the macromolecular chain, could be statistically described in an analogous manner as the distribution of configurational sequences of a vinyl homopolymer chain or compositional sequences of a vinylidene copolymer (KLESPER and SIELAFF 1974).

The chain of the investigated copolyterephthalate, poly[4,4'-isopropylidene(3,3'-dimethyl)diphenylene-4,4'-phthalidylidenediphenylene terephthalate 50:50] (PDT/FT), consists of intermonomer, i.e. terephthalic (T), units separated by either comonomer unit, i.e. 3,3'-dimethylbisphenol A (D) or phenolphthalein (F). Since both comonomers and the intermonomer are

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symmetrical, there is no head-to-head and head-to-tail isomerism. The small anisotropic effect of the phenolphthalein unit configuration in the chain can also be neglected because in the case of PFT homopolyester neither the standard spectrum nor the spectra recorded in the presence of LSR, i.e. $Eu(fod)_3$ (MATLENGIEWICZ et al. 1979) and $Pr(fod)_3$ (Fig. 4c), exhibit splittings of the terephthalic proton signal. Therefore, differences in the copolyterephthalate microstructure are due only to comonomer unit distribution. Hence, comonomer units can be regarded in the same manner as α-carbons and intermonomer units as β-carbons in a vinylidene chain (Fig. 1). In the description of various sequences, intermonomer unit -T- may be omitted for clarity, e.g. DDD instead of -D-T-D-T-D-T- triad.

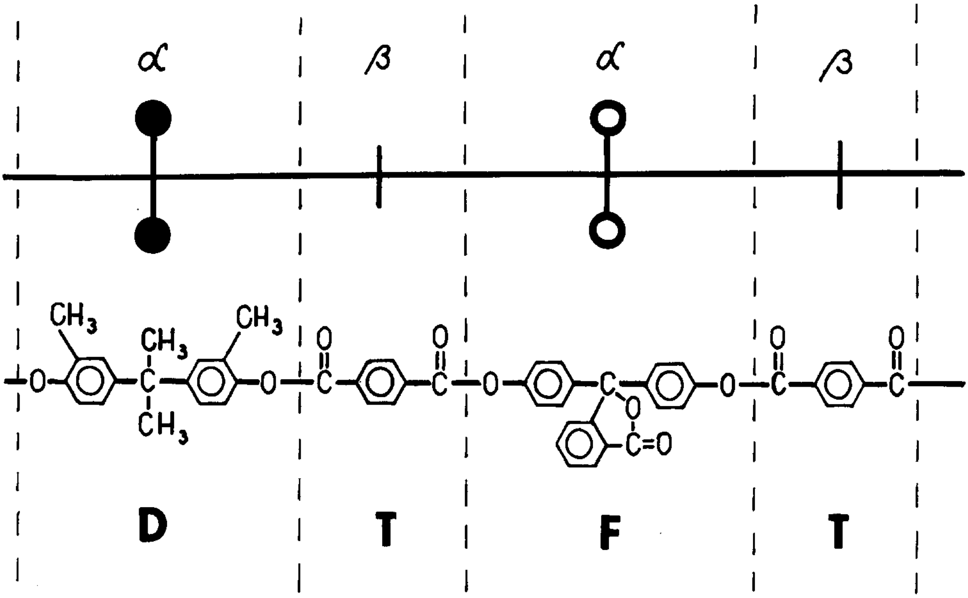

Fig. 1. Comparision of PDT/FT and vinylidene chains

Based on this analogy the intermonomer signal can be obviously used as a source of information on even compositional sequences, i.e. diads, tetrads and longer sequences of comonomer units whereas signals of comonomers supply information on odd compositional sequences, i.e. triads, pentads etc.

EXPERIMENTAL

The samples of PDT/FT copolyester were obtained from 3,3'-dimethylbisphenol A and phenolphthalein as comonomers and terephthaloyl chloride as intermonomer, used in the molar ratio 1:1:2, respectively. The high-temperature polycondensation was carried out in α-chloronaphthalene at 240°C, The molecular weight of the PDT/FT sample was about 16,000 as determined in THF by the Knauer Vapour Pressure Osmometer and the Waters Associates Instruments ALC/GPC-202/401 Chromatograph.

^{1}H-NMR spectra were recorded at 60 MHz with a JEOL JNM-C60H and at 100 MHz with a Varian XL-100 for 3-5 wt-% solutions in $CDCl_3$ at room temperature. $Eu(fod)_3$ and $Pr(fod)_3$ from Fluka AG were used as LSR. The concentrations of LSR were calculated with respect to the terephthalic units.

Simulations of tetrad fine splittings were performed with a Wang 2200 desk-top computer equipped with a Wang 2212 X-Y plotter. The experimental spectra were compared with the simulated ones drawn by the plotter by means of a program for superposition of 28 Lorentzian lines. The positions, heights and widths of some lines were evaluated from experimental spectra, while the remainder was calculated (MATLENGIEWICZ, to be published).

RESULTS AND DISCUSSION

The standard 100 MHz ^{1}H-NMR spectrum (i.e. in the absence of the chelate) of PDT/FT in $CDCl_3$ was observed to give no information about the various sequences of its macromolecular chain, because the intermonomer, i.e. terephthalic, signal at 8.36 ppm as well as both methyl signals of D units in the polymer chain at 1.74 and 2.24ppm are singlets while the region of aromatic signals of both comonomers at 7-8 ppm consisted of superimposed multiplets (Fig. 3a).

The incremental addition of solid LSR to PDT/FT solution in $CDCl_3$ was found to induce upfield [$Pr(fod)_3$] or downfield [$Eu(fod)_3$] shifts of all the signals of PDT/FT. The lanthanide-induced shifts of the terephthalic and methyl resonances vs. the molar ratio of [LSR]/[terephthalic units] are presented in Fig. 2. The magnitude of the induced shifts, which is most pronounced for the

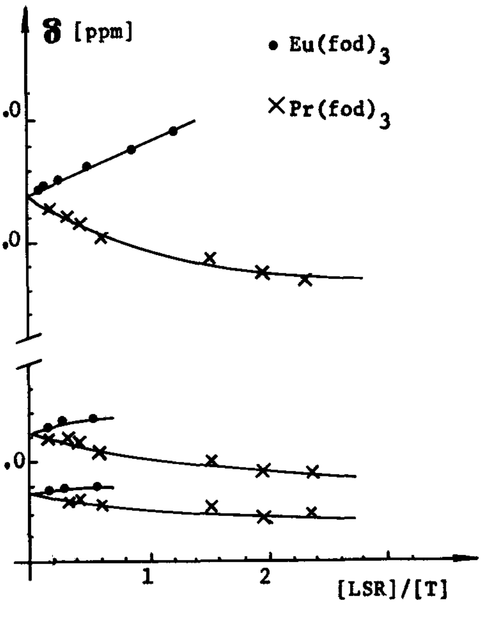

Fig. 2. Changes in the chemical shifts of terephthalic and methyl proton signals in the ^{1}H-NMR spectrum of PDT/FT in $CDCl_3$ upon the addition of $Eu(fod)_3$and $Pr(fod)_3$

terephthalic and phenolphthalein protons, confirmed the generally accepted explanation that the carbonyl oxygen is the preferred coordination site for esters (COCKERILL et al. 1973). There exist three main coordination sites for LSR in the PDT/FT chain: two carbonyl oxygens at each terephthalic unit and one carbonyl oxygen at the phenolphthalein unit. This is the reason why the [LSR]/[T] ratio considerably exceeds unity. Hence, the [LSR]/[T] ratio is only a useful measure of the LSR concentration but it does not represent the composition of the complex formed, as is the case with monofunctional compounds. The plots are not linear over the entire range of [LSR]/[T] ratios because of competition between the phenolphthalein and terephthalic carbonyls. Nevertheless, linearity was observed for terephthalic protons in the range 0.2 - 1.2 for $Eu(fod)_3$ and 0.1 - 0.7 for $Pr(fod)_3$.

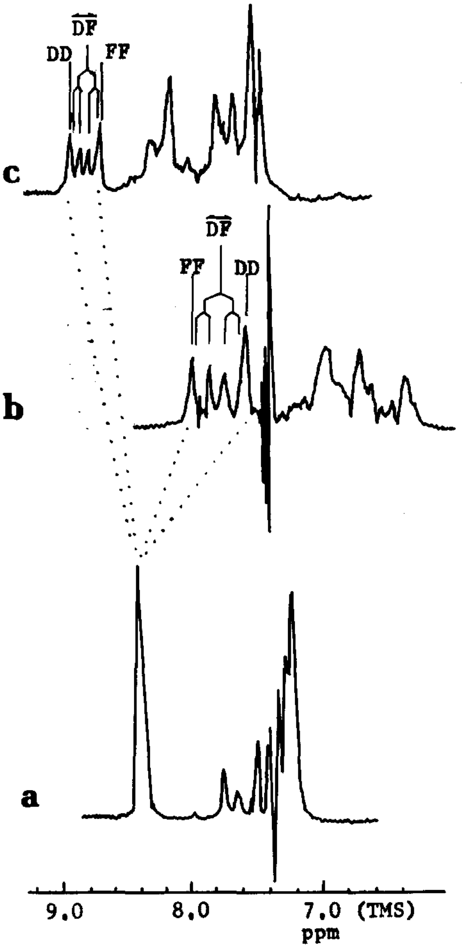

Fig.3. Changes in the aromatic proton region of the 100 MHz ^1H-NMR standard spectrum of PDT/FT in $CDCl_3$ (a) after the addition of $Pr(fod)_3$ (b) or $Eu(fod)_3$ (c)

Diads

The intermonomer, i.e. terephthalic, signal in the PDT/FT spectrum can provide information about the diad distribution. Addition of LSR to the solution of PDT/FT in $CDCl_3$ induces a shift of the signal but the different magnitudes of the induced shifts for various sequences result in the separation of the diad resonances. With increasing concentration of LSR, the single terephthalic signal splits into three and then into four components (Fig. 3).

$\underline{Eu(fod)_3}$ The addition of $Eu(fod)_3$ to the PDT/FT solution in $CDCl_3$ was found to induce a downfield shift and a separation of the terephthalic proton signals. It was possible to separate distinctly the outside signals by about 0.4 ppm and then, after an extra addition of Eu(fod)$_3$, the phenolophthalein signals (which are shifted more strongly) were superimposed on the terephthalic ones. Based on the experiments carried out with respective homopolyesters, the downfield outside signal in the terephthalic proton region of the PDT/FT spectrum was assigned to the DD homodiad (Fig. 3c) (MATLENGIEWICZ et al. 1979).

Pr(fod)$_3$ The addition of Pr(fod)$_3$ to PDT/FT solution in CDCl$_3$ was found to induce an upfield shift of the terephthalic protons. It was possible to separate the outside signals of the homodiads by about 0.45 ppm and then, after further addition of the Pr(fod)$_3$, the terephthalic proton signals were superimposed on the CDCl$_3$ signal occupying an unshifted position. The assignment of the outside signals to the respective homodiads was performed in the same way as in the case of the europium-shifted spectra (MATLENGIEWICZ et al. 1979). A comparision of the magnitude of the induced shifts of the terephthalic protons in the PDT/FT copolyester (Fig. 4a), PDT and PFT homopolyesters (Fig. 4b and 4c, respectively) and in a mixture of the homopolyesters (PDT : PFT = 1:3 w/w, Fig. 4d) after the addition of the same amount of Pr(fod)$_3$ to each sample showed that in all these cases the signal of the terephthalic protons of PDT homopolyester was strongly shifted upfield. Hence, the signal at highest field in the terephthalic proton region of the PDT/FT

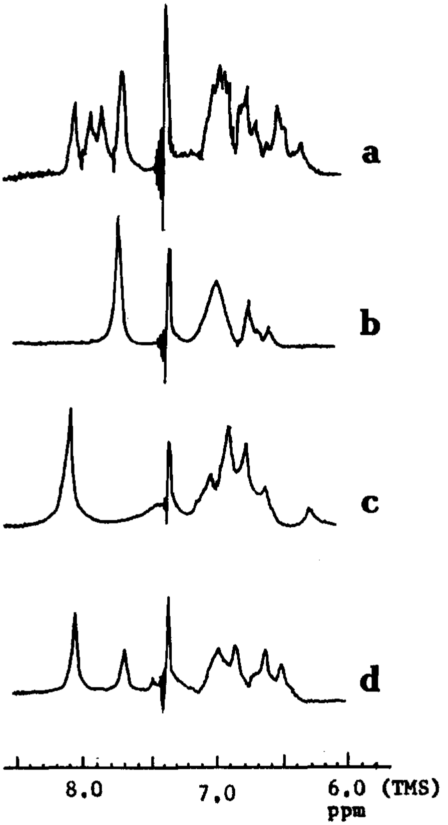

Fig.4.Assignment of the terephthalic proton signals of PDT/FT to the respective diads. 60 MHz ^{1}H-NMR spectra after the addition of equal amounts of Pr(fod)$_3$:

(a) PDT/FT copolyester
(b) PDT homopolyester
(c) PFT homopolyester
(d) PDT:PFT = 1:3 w/w homopolyester mixture

spectrum recorded in the presence of Pr(fod)$_3$, must be assigned to the DD homodiad.

In the case of both LSR's, the DD homodiad signals were found to be shifted outermost from their initial position in the standard spectrum, and the central signal (quartet) was found to be that of the $\overleftrightarrow{DF}$ heterodiad signal $[P(\overleftrightarrow{DF}) = P(DF) + P(FD)]$.

Triads

Comonomers (i.e. signals of D and F units) in the spectrum of PDT/FT can give information about the triad distribution. Since the aromatic signals due to D and F are bunched together in a featureless clustered multiplet (especially after the addition of LSR) only the methyl signals of D could be utilised for the triad analysis. In the standard PDT/FT spectrum, the methyl signal of the propylidene unit of D (the so-called "aliphatic" one) and the signal of the methyl group attached to the aromatic ring (the so-called "aromatic" one) at 1.74 and 2.24 ppm, respectively, were observed as singlets. After the addition of LSR, the methyl signals were also found to be displaced from their respective positions in the standard spectrum. Only minor traces of the splittings of the signals, due to the various triads, were observed.

Eu(fod)$_3$ The addition of Eu(fod)$_3$ to a PDT/FT solution in CDCl$_3$ was found to induce larger shifts of the "aromatic" methyl groups while the other methyl signal did not change its position significantly. For instance, at the ratio [Eu(fod)$_3$]/[T] = 0.28, the signal of the "aromatic" methyl group of D was shifted from 2.24 to 2.33 ppm, i.e. 0.09 ppm, while the other methyl groups were recorded at 1.76 ppm (0.02 ppm displacement). Therefore, an increase in the Eu(fod)$_3$ concentration was shown to result in an increase of the distance in the spectrum between these signals. Up to the highest available concentration of Eu(fod)$_3$, triad splittings were not observed. At higher concentrations of Eu(fod)$_3$, the increasing intensity of the t-Bu signal of fod chelate at 1.45 ppm was observed to significantly interfere with the "aliphatic" methyl signal and deform both its shape and intensity.

Pr(fod)$_3$ The addition of Pr(fod)$_3$ to a PDT/FT solution in CDCl$_3$ was also found to induce larger shifts of the "aromatic" methyl signals. Therefore, an increase in

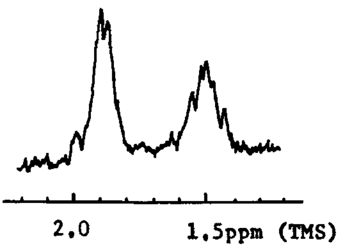

Fig. 5. Triad splittings of the methyl signals of PDT/FT in the presence of Pr(fod)$_3$

the Pr(fod)$_3$ concentration resulted in a decrease of the distance between the methyl signals in the spectrum. At higher concentrations of Pr(fod)$_3$, traces of weak splittings of both methyl signals (into three resonances each) were observed, but small shift differences (o.03 ppm) cannot be used for a triad analysis.

Tetrads

At higher concentrations of LSR, the highly resolved terephthalic proton signals were found to exhibit tetrad fine splittings.

Eu(fod)$_3$ was found to induce tetrad resonances sufficiently distinct for performing a tetrad analysis (Fig. 6). Assignment of the single lines to the respective tetrads was performed by computer simulation. A more detailed discussion of the tetrad assignment procedure and distribution of them will be presented elsewhere. Tetrad signal separation was found to be more pronounced than that found for the triads. This fact confirmed the generally accepted findings about the coordination of LSR at the carbonyl oxygen.

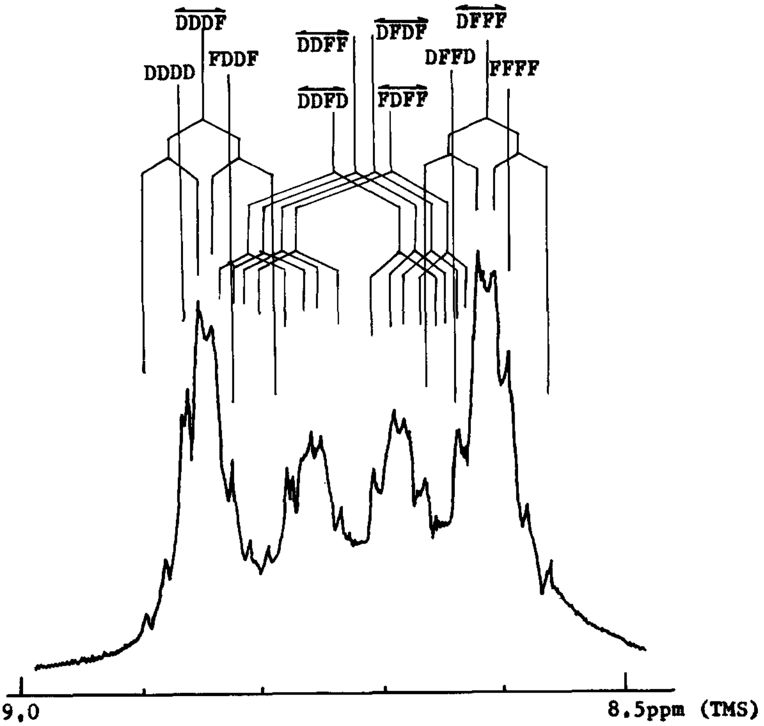

Fig. 6. Tetrad resonances of terephthalic proton signals in the 100 MHz ^{1}H-NMR spectrum of FDT/FT in the presence of Eu(fod)$_3$

$Pr(fod)_3$ was found to produce a significant broadening of the terephthalic signals and hence the signals tended to overlap and the fine splittings of tetrads were not observed.

CONCLUSIONS

Lanthanide shift reagents have become a valuable tool in the simplification of NMR spectra. It was shown in this work that they can be applied to a sequence distribution analysis of copolyesters if the standard spectrum furnishes no information about the various sequences. Conventional NMR instruments operating at frequencies up to 100 MHz for protons can be used succesfully for this purpose. The application of higher magnetic fields should also improve the separation of the various sequence signals.

In the case of copolyterephthalates, the terephthalic proton signal was found to be a useful source of information about the distribution of even compositional sequences, i.e. diads and tetrads.In certain particular cases, comonomer signals, e.g. methyl signals of PDT/FT, can be used for the determination of odd compositional sequences, i.e. triads or higher. For copolyterephthalates the coordination of LSR takes place on the carbonyl oxygen and hence the tetrad separation was found to be more pronounced than that observed for the triads (as in the case of PDT/FT).

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