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Reductive transformations

14. Soluble polyesters derived from 9,10-anthracenediols (1)

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Summary: 2,3-Diheptyl- and 2,3,6,7-tetraheptyl-9,10-anthraquinone are reduced to the corresponding diols and subjected to esterification with the chlorides derived from mono- and diacids. The resulting polyesters are nicely soluble in organic solvents and can be characterized by vapor pressure osmometry and NMR spectroscopy.

Introduction

Polymers containing the 9,10-anthrylene unit exhibit attractive photochemical, electrical, and electrochemical properties (2,3,4). We have recently described the polymeric hydrocarbon 1 whose 9,10-anthrylene units are linked by flexible alkanediyl groups. The synthesis of 1 proceeds via the reductive alkylation of anthracene with 1,n-dihaloalkanes and dehydrogenation of the intermediate (poly-9,10-dihydroanthrylene)-compounds (5,6). It appears promising to compare 1 with the corresponding polyesters derived from either anthracene-9,-10-dicarboxylic acids (7) or anthracene-9,10-diols (2).

Attempts directed toward the synthesis of polymer structures such as 2 or 3 have suffered from various drawbacks among which the insolubility of the products in organic solvents was particularly severe (2,7). We reasoned that alkyl substituted anthraquinones such as 4 and 5 might constitute starting compounds for the synthesis of soluble polyesters. Herein, we describe the synthesis of polyesters 8 and 9 which are derived from 4 and 5. Furthermore, reductive esterification of 4 and 5 with monoacids such as heptanoic acid provides 2,3-diheptyl-9,10-diheptanoyloxyanthracene (10) and 2,3,6,7-tetraheptyl-9,10-diheptanoyloxyanthracene (11) which serve as suitable model compounds in the spectroscopic characterization of the polyesters 4 and 5. Attaching lateral substituents to the anthracene perimeter under formation of 9 and 11 might induce the formation of mesophases.

Experimental

The starting compounds 4 and 5 were prepared via Diels-Alder reaction between 2,3-diheptylbutadiene-1,3 and 1,4-naphthoquinone or benzoquinone, respectively, and dehydrogenation of the resulting adducts as described by us previously (8).

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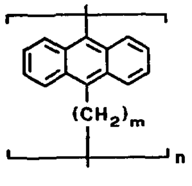
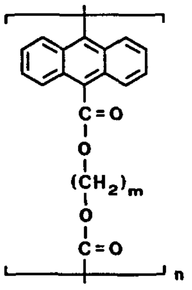


1



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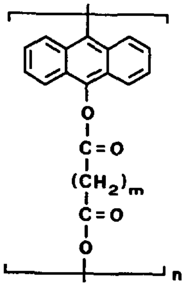
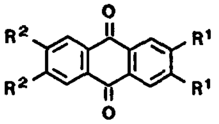


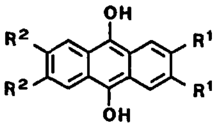
3

4 R^1 = n-heptyl

R^2 = H

5 R^1 = R^2 = n-heptyl

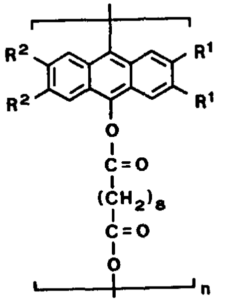




6 R^1 = n-heptyl

R^2 = H

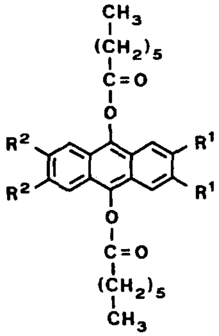
7 R^1 = R^2 = n-heptyl



8 : R^1 = n-heptyl

R^2 = H

9 : R^1 = R^2 = n-heptyl



10 : R^1 = n-heptyl

R^2 = H

11 : R^1 = R^2 = n-heptyl

Results and Discussion

Two well-known techniques were applied for the formation of the diols 6 and 7 from 4 and 5: Pd-catalyzed hydrogenation, e.g. in tetrahydrofuran (THF), and reduction with zinc in pyridine (9). According to the first procedure the catalyst was removed by filtration after the uptake of the calculated amount of hydrogen and THF was replaced by a mixture of toluene/pyridine which appeared as a suitable solvent for the subsequent esterification. While hydrogenation at 20°C only produced the anthracenediol, the same reaction at 40°C also affected the π-periphery. Addition of an excess of heptanoyl chloride to the reaction mixture gave 10 and 11 in 75 % and 49 % yield, respectively, after column chromatography and recrystallization. In the alternative procedure 4 and 5 were treated with zinc powder in boiling pyridine in the presence of heptanoic anhydride whereby the yields of 10 and 11 were 59 and 81 %, respectively (11: ^{1}H-NMR, δ_H = 7.57 (s, 4H, H-1,4,5,8), 2.89 (t, 4H, H-COCH$_2$), 2.72 (t, 8H, H-CH$_2$)). These compounds possess sharp melting points (10: 57°C, 11: 85°C) and fail to exhibit mesophases upon inspection with polarized light (10). It should be noted in this context that the formation of liquid crystals from 9,10-anthraquinone derivatives is only observed in the case of specific substitution patterns (11-14).

The polycondensation of the 9,10-dihydroxyanthracenes 6 and 7 (formed by hydrogenation of the quinones in THF) was performed in 1,1,2,2-tetrachloroethane in the presence of pyridine with the dichloride from decanedioic acid. The yield of polymer 8 (determined after precipitation with methanol) was 74 % and that of 9 60 %. The mean molecular weight of the polyesters 8 and 9, as determined by vapor pressure osmometry, was M_n = 3900 - 4500 ($P_n \approx$ 7 - 8) and M_n = 7900 ($P_n \approx$ 10), respectively. The relatively low chain length must be ascribed to the great tendency of 6 and 7 to undergo oxygenation. It is, thus, extremely difficult to maintain a 1:1-stoichiometry of the diol and diacid component. We have, therefore, made an attempt to replace the extremely labile dihydroxy compounds 6 and 7 by the corre-

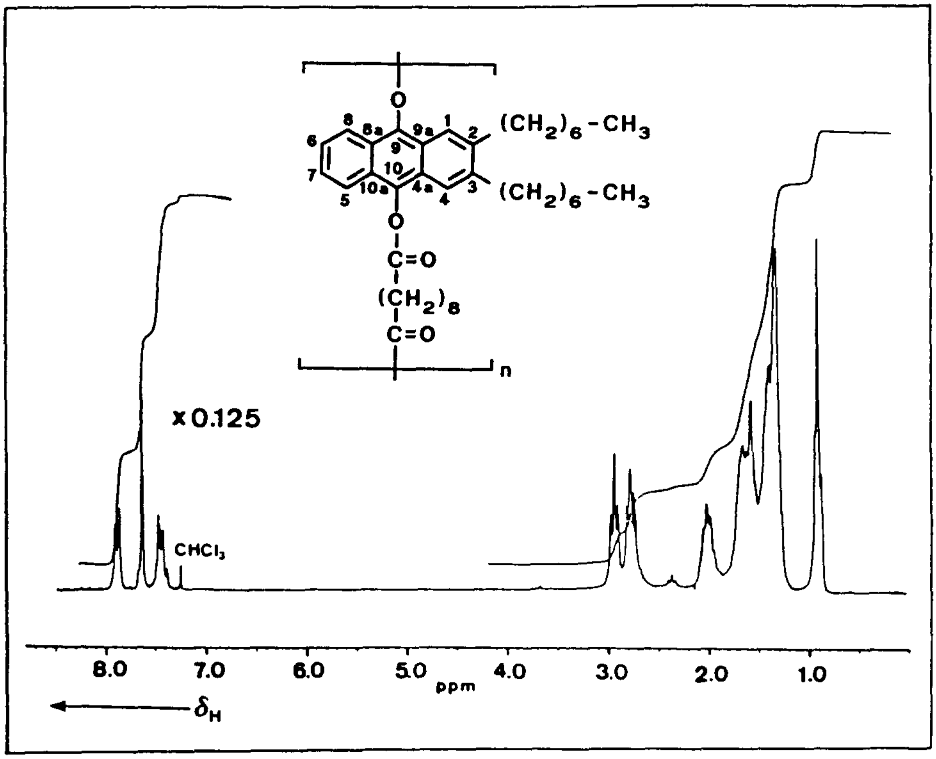


Fig. 1a: ^{1}H-NMR spectrum (200 MHz) of 8 in CDCl$_3$

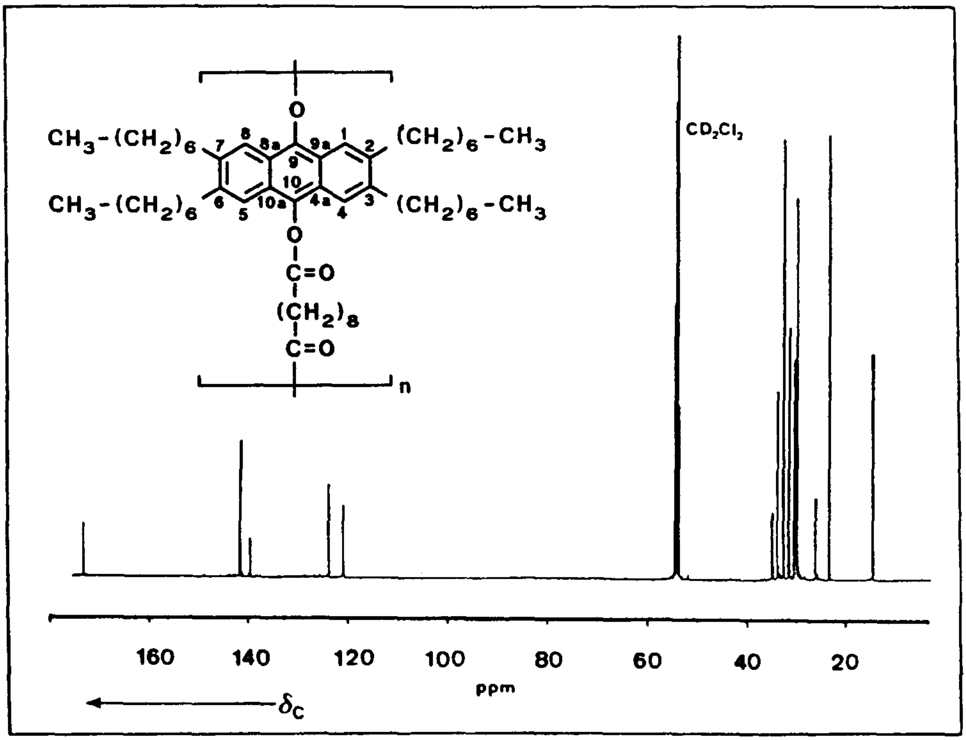


Fig. 1b: ^{13}C-NMR spectrum (50 MHz) of 9 in CD_2Cl_2

sponding diacetoxy derivatives and to achieve polyester formation by a trans-esterification. The latter reaction, however, requires temperatures of about 170°C which also induces decomposition of the starting compounds.

Compounds 8 and 9 are nicely soluble in organic solvents and exhibit well resolved ^{1}H- (Fig. 1a) and ^{13}C- (Fig. 1b) NMR spectra. In the ^{1}H-NMR spectrum of 8 the signals of the AA'-BB'-spin system of the aromatic protons H-5 - H-8 can, clearly, be detected. As expected from the structural formula and from the comparison with model compound 11 the ^{13}C-NMR spectrum of 9 shows the carbonyl resonance at $\delta = 172.7$ and four signals of aromatic carbons at $\delta = 141.0, 139.1, 123.3, 120.4$. The aliphatic domain exhibits eleven signals from which four can be assigned to the bridging groups and seven to the lateral heptyl groups of the anthracene units. DSC measurements for polymers 8 and 9 fail to give evidence for the formation of mesophases.

One concludes that the formation of polyesters from 4 and 5 provides an interesting structural alternative to polyanthrylenes such as 1 and to polyesters derived from 2,6-dihydroxyanthracene and related compounds (15). However, alkyl substitution of the starting compounds is essential for the synthesis of soluble and tractable polymeric material.

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