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Preparation of new main-chain type poly(anthraquinone)s having alkoxyl groups and their liquid crystalline behaviour

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Abstract

New main-chain type poly(5,8-dialkoxyanthraquinone-1,4-diyl)s have been prepared by using a Ni(0) complex. They take an ordered structure assisted by side-chain crystallinity. The ordered structure has been elucidated by X-ray diffraction pattern. Their *d* spaces and the relationship between the *d* space and the number of carbon atoms in the alkoxyl side chain indicate that these polymers take an end-to-end packing mode and their main chain has an *s-trans* conformation. These polymers exhibit liquid crystalline behaviour at a wide range of temperature. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(anthraquinone); Liquid crystallinity; X-ray diffraction

1. Introduction

π-Conjugated poly(arylene)s have received much attention due to their interesting electronic and optical properties as well as their applicability to the present and future electronic and optical devices [1–3]. In contrast, quinone belongs to typical electron-accepting and redox-active aromatic compounds. In spite of many attempts to introduce quinone units into polymers [4–6], examples of main-chain type poly(quinone)s are still limited [7–10].

Many of the main-chain type poly(arylene)s have received a problem concerning their solubility in solvents, and introduction of alkyl side chains to poly(arylene)s has been carried out to improve their solubility and processibility [11–14]. It has also been demonstrated that π-conjugated poly(arylene)s can give liquid crystalline materials by introducing suitable side chains and the liquid crystalline polymers attain the processibility [12–14]. Pioneering studies on the liquid crystallinity of polymers which were composed of a rigid rod-like polyamide or polyester main chain and flexible side chains were carried out by Watanabe and his co-workers [15], and Ballauff [16].

On these bases, we have tried preparation of new main-chain type poly(anthraquinone)s with long alkoxyl substituents and herein report the results of the preparation and properties of the obtained polymers.

2. Experimental part

2.1. Materials

1,4-Dichloro-5,8-dialkoxyanthraquinones were prepared by modifying the literature methods [17,18] and analytically pure bis(1,5-cyclooctadiene)nickel, Ni(cod)$_2$, was prepared according to the literature [19].

2.2. Polymerization

Ni(cod)$_2$ 0.31 g (1.1 mmol), dist. DMF 45 cm^3, 1,5-cyclooctadiene 0.12 cm^3 (0.94 mmol), 2,2′-bipyridyl 0.18 g (1.1 mmol) and 1,4-dichloro-5,8-dihexyloxyanthraquinone 0.45 g (0.94 mmol) were mixed under N$_2$, and the reaction mixture was stirred at 60°C for 48 h. The reaction mixture was poured into methanol containing dilute HCl. The obtained polymer was washed with methanol containing dilute HCl, methanol containing dilute NH$_3$, water, and methanol repeatedly. It was purified by dissolving in a minimum quantity of chloroform and reprecipitation in methanol.

P(5,8-OMe-1,4-AQ): Yield = 42%; Anal. Found: C, 70.0; H, 3.6; Cl, 0.1%. Calcd for $(C_{16}H_{10}O_4)_n$: C, 72.2; H, 3.8%. P(5,8-OC$_6$H$_{13}$-1,4-AQ): Yield = 36%; Anal. Found: C, 76.9; H, 7.3; Cl, 0.0%. Calcd for $(C_{26}H_{30}O_4)_n$: C, 76.8; H, 7.4%. P(5,8-OC$_8$H$_{17}$-1,4-AQ): Yield = 62%; Anal. Found: C, 78.3; H, 8.7; Cl, 0.2%. Calcd for $(C_{30}H_{38}O_4)_n$: C, 78.7; H, 8.3%. P(5,8-OC$_{10}$H$_{21}$-1,4-AQ): Yield = 99%; Anal. Found: C, 78.4; H, 8.8; Cl, 0.1%. Calcd for $(C_{34}H_{46}O_4)_n$: C, 78.7; H,

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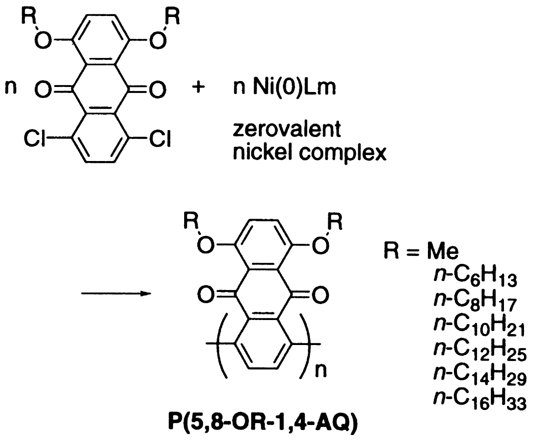

Scheme 1.

8.9%. P(5,8-$OC_{12}H_{25}$-1,4-AQ): Yield = 69%; Anal. Found: C, 77.0; H, 9.2; Cl, 3.5%. Calcd for $(C_{38}H_{54}O_4)_n$: C, 79.4; H, 9.5%. P(5,8-$OC_{14}H_{29}$-1,4-AQ): Yield = 87%; Anal. Found: C, 78.5; H, 9.8; Cl, 0.1%. Calcd for $(C_{42}H_{62}O_4)_n$: C, 80.0; H, 9.9%. P(5,8-$OC_{16}H_{33}$-1,4-AQ): Yield = 92%; Anal. Found: C, 79.8; H, 9.8; %. Calcd for $(C_{46}H_{70}O_4)_n$: C, 80.4; H, 10.3%.

2.3. Measurements

IR spectra were recorded on a Jasco IR-810 spectrometer. ^{1}H-NMR spectra were obtained with JEOL JNM-FAX-400. Electrical conductivity was measured with an Advantest R8340 resistance meter. Cyclic voltammograms were obtained by using a Hokuto Denki HA-501 galvanostat/potensiostat and a Hokuto Denko KB-104 function generator. Powder X-ray diffraction patterns were recorded on a Philips PW1700 instrument.

Thermotropic liquid crystalline behaviour of these polymers was examined by differential scanning calorimetry (DSC). The DSC trace gave two peaks assigned to T_g and T_i (liquid-crystalline to isotropic phase transition temperature). Formation of liquid crystalline textures of the polymers were confirmed under crossed polarizers by using a Olympus Model BH-2 equipped with a Mettler FP82HT hot stage and Mettler FP90 central processor.

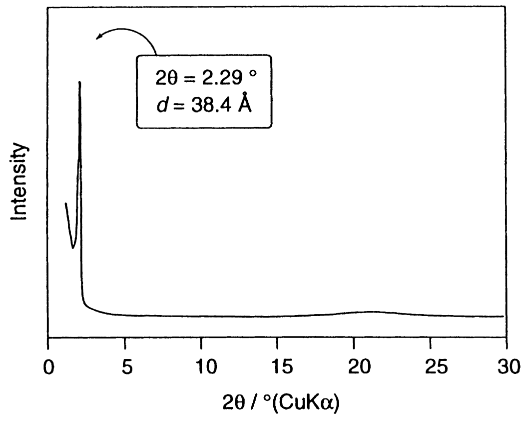

Fig. 1. Powder X-ray diffraction pattern of P(5,8-$OC_{16}H_{33}$-1,4-AQ).

Table 1
Powder X-ray diffraction peak of P(5,8-OR-1,4-AQ)s in the low angle region

Polymer	2θ(CuKα)
P(5,8-OC_6H_{13}-1,4-AQ)	5.97°
P(5,8-OC_8H_{17}-1,4-AQ)	3.64°
P(5,8-$OC_{10}H_{21}$-1,4-AQ)	3.17°
P(5,8-$OC_{12}H_{25}$-1,4-AQ)	2.82°
P(5,8-$OC_{14}H_{29}$-1,4-AQ)	2.68°
P(5,8-$OC_{16}H_{33}$-1,4-AQ)	2.29°

P(5,8-OC_6H_{13}-1,4-AQ): $T_g = -71.8$°C (2nd heating); $T_i =$ 243.1°C (2nd heating), 224.2°C (2nd cooling). P(5,8-OC_8H_{17}-1,4-AQ): $T_g = -64.0$°C (2nd heating); $T_i =$ 170.2°C (2nd heating), 156.2°C (2nd cooling). P(5,8-$OC_{12}H_{25}$-1,4-AQ): $T_g = -37.5$°C (2nd heating), -51.7°C (2nd cooling); $T_i = 158.7$°C (2nd heating), 153.5°C (2nd cooling). P(5,8-$OC_{16}H_{33}$-1,4-AQ): $T_g = -7.0$°C (2nd heating), -14.6°C (2nd cooling); $T_i = 174.2$°C (2nd heating), 160.6°C (2nd cooling).

All of the obtained polymers had high solubility in organic solvents including $CHCl_3$, CH_2Cl_2, benzene, toluene and THF.

3. Results and discussion

Preparation of the polymers was carried out by dehalogenation polycondensation of corresponding dichloro derivatives with a zerovalent nickel complex [20,21] as shown in Scheme 1. Their IR and ^{1}H-NMR spectra agreed with the structures shown in Scheme 1. Data from elemental analysis also essentially agreed with the structure. They are considered to be mainly H-terminated, similar to previously prepared poly(anthraquinone)s [9], since they contain only a negligible amount of chlorine. Vapour pressure osmometric data of the polymers indicated that they had a number average molecular weight M_n of 2.1×10^3—3.7×10^3.

Fig. 1 shows powder X-ray diffraction (XRD) pattern of P(5,8-$OC_{16}H_{33}$-1,4-AQ). All the polymers, except for P(5,8-OMe-1,4-AQ), exhibit a sharp diffraction peak in a low-angle region (Table 1) and one broadened diffraction peak at about 2θ(CuKα) = 20°. Recently various π-conjugated poly(arylene)s with long side chains are reported to give a similar sharp diffraction peak in the low angle region [22–25].

The appearance of the sharp diffraction peak may be taken as an indication that the present polymers have an ordered structure. The polymers with the long alkoxyl groups is considered to take an ordered structure assisted by side chain crystallinity [26,27] (or cohesive force of the long alkoxyl groups). Their d space estimated from the low angle diffraction is assigned to the distance between core

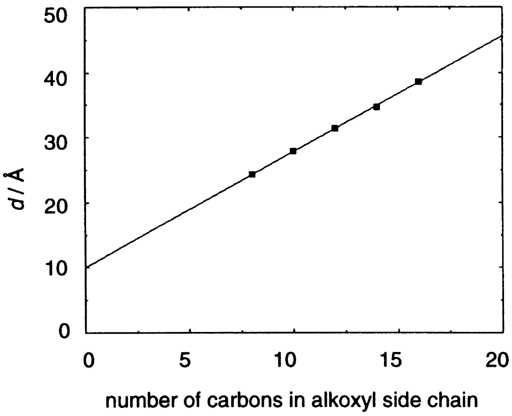

Fig. 2. Data of *d* space of P(5,8-OR-1,4-AQ)s vs. number of carbon in the alkoxyl side chain.

main chains of P(5,8-OR-1,4-AQ) separated by the OR group, and there holds a linear correlation between the *d* space and the number of carbons in OR as depicted in Fig. 2. The linear line in Fig. 2 gives an intercept of 9.5 Å, which is assigned to the thickness of the core main chain. The slope of the line, 1.8 Å/carbon, roughly agrees with these observed with regioregular poly(3-alkylthiophene-2,5-diyl) [22–24] and poly(4-alkylthiazole-2,5-diyl) [24] which are considered to take an end-to-end packing mode [26,27]. Due to a strong steric hindrance, the present polymers cannot take a coplanar main chain. However, these polymers are still considered to be loosely packed in a similar end-to-end mode.

Thermotropic liquid crystalline behaviour of these polymers was examined by DSC. These polymers having the long alkoxyl groups show enantiotropic liquid crystallinity between T_g and T_i; these temperatures are given in the experimental part.

One of the interesting properties of P(5,8-OR-1,4-AQ) is that these polymers have some dc conductivities ($\sigma = 7.9 \times 10^{-7}$–$4.9 \times 10^{-6}$ S cm^{-1} at room temperature; measured with a compressed powder) even at a non-doped state. Recently it has been reported that several π-conjugated polymeric compounds (e.g. poly(2,2′-bipyridine)-transition metal complexes [28] and poly(arylene)-*N*-oxides [29]) show similar intrinsic dc conductivity at the non-doped state, and their electrical conducting property has been attributed to the formation of carrier in the π-conjugated main chain by MLCT or by taking some resonance forms in the *N*-oxides. Evolution of carriers in the π-conjugation system of the anthraquinone unit bearing the OR group by taking analogous resonance structures is also conceivable, and the intrinsic conductivity may also be ascribed to the evolution of the carrier. The polymer films are redox active and a film of P(5,8-OC$_{16}$H$_{33}$-1,4-AQ) on a Pt plate show E_{pc}'s (or n-doping peaks) at -0.95 and -1.64 V vs. Ag/Ag$^+$, for example.

In addition, the present polymers with the long alkoxyl groups show piezochromism from yellow at 1 atm to dark red at 10 GPa. This piezochromism is reversible, and its details will be reported elsewhere.

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