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NOTE

SYNTHESIS AND THERMAL PROPERTIES OF A POLYSULFONIUM SALT WITH A COMB-LIKE STRUCTURE

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INTRODUCTION

Some strong acids and acid anhydrides are known to activate sulfoxides giving the sulfonium cations, which could undergo aromatic electrophilic substitution reactions [1]. This reaction has been applied to the polycondensation of methy phenyl sulfoxide derivatives to produce poly(arylenesulfonium salt)s [2, 3]. The polymers are useful as a soluble precursor for the preparation of high-molecular-weight poly(arylene sulfide)s [4, 5]. Several polysulfonium analogs with methyl, propyl, or phenyl substituents have also been prepared. Our objective is the development of these sulfonium-containing aromatic polymers as a novel class of functional polyelectrolytes. One of the successful examples is that the polymer acts as an efficient methylation reagent for phenol, aniline and benzoic acid [6].

Introducing long alkyl chains onto the hydrophilic polymers has been studied for the application of making a monomolecular layer by the Langmuir-Blodgett method [7-9]. The self-aggregation of the polymers via side group association in solution has also been examined [10]. Some of these polymers form a crystalline-amorphous layered structure in the solid, whose properties have been investigated for practical applications such as displays [11-14]. In this paper, we report a novel poly(arylenesulfonium salt) bearing *n*-octadecyl groups as the side chains, which was synthesized via the acid-induced polycondensation of alkyl an aryl sulfoxide. DSC analyses revealed that the polymer has two endothermic tran-

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sitions based on the rigid sulfonioarylene mesogen as the main chain and the flexible alkyl groups as the side chains.

EXPERIMENTAL

Materials

Dicholoromethane and acetonitrile were distilled over phosphorus pentoxide. Hexamethylphosporamide was purified by distillation under reduced pressure. Commercially available *n*-octadecyl mercaptan, sodium methoxide, 4-bromodiphenyl ether, nitric acid, potassium carbonate, tetraethylammonium bromide, and triflic acid were used as received.

Measurements

The ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JNM-LA500. The IR spectra were obtained using a JASCO FT-IR 5300 spectrometer with samples as potassium bromide pellets. The UV spectra were observed using a Shimadzu UV-2200 spectrophotometer. The GC mass spectra were recorded on a Shimadzu GCMS-QP5050 instrument with an ionization energy of 70 eV. The elemental analyses were performed using a Perkin-Elmer PE-2400 II and a Metrohm 645 DOSIMAT. Two parallel analyses were performed for each sample. The DSC measurements were carried out under a dry nitrogen atmosphere using a Seiko Model DSC/120 thermal analyzer with a sample weight of 7-10 mg at a heating rate of 10^{o}C/min. The molecular weight of the polymer was measured by high temperature (210^{o}C) gel permeation chromatography on a Senshu VHT-GPC SSC-7000 equipped with a GPC-3506 column (GL Sciences Inc.) and a Soma Optics S-3750 UV-VIS absorption detector set at 360 nm. 1-Chloronaphthalene was used as the eluent at a flow rate of 1.0 mL/min. Calibration was made using narrow-polydispersed polystyrene standards.

Synthesis

4-Octadecylsulfenylphenyl phenyl ether (**1**)

A solution of sodium methoxide (5.2 g, 96 mmol) in 50 mL methanol, at 25^{o}C under a nitrogen atmosphere, was added dropwise to the solution of *n*-octadecyl mercaptan (27.7 g, 97 mmol) in 50 mL methanol. The mixture was heated at 60^{o}C for 30 minutes and at 120^{o}C for 1 hour to evaporate methanol. The white powder of dry sodium *n*-octadecylthiolate was obtained in 100% yield. Sodium *n*-octadecylthiolate and 4-bromophenyl phenyl ether (21.8 g, 87 mmol) were dissolved in 100 mL of hexamethylphosporamide and heated at 150^{o}C for 5 hours. The mixture was poured into 1000 mL of water that produced a pale brown-colored precipitate. Crystallization of the crude product from ethanol gave a white crystal of 4-octadecylsulfenylphenyl phenyl ether (**1**) in 78% yield.

IR (KBr, cm^{-1}): 3041 (aromatic $\nu_{C\text{-}H}$), 2832, 2973 (alkyl $\nu_{C\text{-}H}$), 1582, 1490, 1455 ($\nu_{C=C}$), 1246 ($\nu_{C\text{-}O\text{-}C}$), 861 ($\delta_{C\text{-}H}$).

^{1}H NMR ($CDCl_3$): δ = 0.87, 0.88, 0.89 (3H, t, methyl), 1.23-1.65 (32H, m, methylene), 2.84 - 2.89 (2H, m, methylene), 6.92 - 7.34 (9H, m, phenyl). ^{13}C NMR ($CDCl_3$): d = 7.1, 14.3, 22.9, 28.8, 28.9, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 29.7, 29.8, 29.8, 29.8, 29.9, 32.1, 35.1 (octadecyl), 119.0, 119.7, 123.7, 129.8, 130.8, 132.1, 156.3, 157.5 (phenyl).

Elemental Analysis: Calcd. for $C_{30}H_{46}OS$: C, 79.24; H, 10.20; S, 7.05. Found: C, 79.48; H, 9.89; S, 7.12.

MS (m/z): 454 (M^+).

4-Octadecylsulfinylphenyl phenyl ether (**2**)

To a solution of **1** (26.5 g, 58 mmol) in dichloromethane (230 mL)/acetonitrile (40 mL) was added 700 mL of 20% nitric acid. The mixture was vigorously stirred at 25°C for 5 hours. After the reaction, potassium carbonate was added to the mixture until it became neutral. The product was extracted with three portions of 300 mL chloroform. The organic layer was evaporated to dryness to obtain the crude product. Crystallization from diethyl ether and *n*-hexane gave 4-octadecylsulfinylphenyl phenyl ether (**2**) as a white crystal in 78% yield.

IR (KBr, cm^{-1}): 3019 (aromatic $\nu_{C\text{-}H}$), 2837, 2912, 2958 (alkyl $\nu_{C\text{-}H}$), 1577, 1495, 1470 ($\nu_{C=C}$), 1248 ($\nu_{C\text{-}O\text{-}C}$), 1103, 1066, 1032 ($\nu_{S=O}$), 862 ($\delta_{C\text{-}H}$).

^{1}H NMR ($CDCl_3$): δ = 0.87, 0.88, 0.89 (3H, t, methyl), 1.26-1.78 (32H, m, methylene), 2.61-2.68 (2H, m, methylene), 7.38-7.77 (9H, m, phenyl).

^{13}C NMR ($CDCl_3$): δ = 7.1, 14.3, 22.7, 28.8, 28.9, 28.9, 29.0, 29.1, 29.1, 29.2, 29.4, 29.5, 29.6, 29.6, 29.7, 29.8, 31.9, 57.6 (octadecyl), 118.6, 119.8, 124.4, 126.0, 130.1, 137.5, 155.9, 160.2 (phenyl).

Elemental Analysis: Calcd. for $C_{30}H_{46}O_2S$: C, 76.54; H, 9.85; S, 6.81. Found: C, 76.65; H, 9.88; S, 6.53.

MS (m/z): 470 (M^+).

Poly(Octadecylsulfonio-1,4-phenyleneoxy-1,4-phenylene triflate) (**3**)

Compound **2** (5.0 g, 10.6 mmol) was put into a 200 mL round-bottom flask and triflic acid (13 mL) was dropwise added at -20°C. The mixture was allowed to stand at 25°C and stirred mechanically for 20 hours. The mixture was poured into 2000 mL of water with vigorous stirring to precipitate the white solid product. The precipitate was then filtered and washed with water several times. After drying in a vacuum at 35°C for 20 hours, poly(octadecylsulfonio-1,4-phenyleneoxy-1,4-phenylene triflate) (**3**) was obtained as a white solid in 99% yield.

IR (KBr, cm^{-1}): 3024 (aromatic $_{\text{C-H}}$), 2839, 2920, 2963 (alkyl $\nu_{\text{C-H}}$), 1584, 1496, 1474 ($\nu_{\text{C=C}}$), 1258, 639 ($\nu_{\text{C-F}}$), 1172 ($\nu_{\text{S=O}}$), 1030 ($\nu_{\text{O-S-O}}$), 862 ($\delta_{\text{C-H}}$).

^{1}H NMR (acetone-d$_6$): δ = 0.84, 0.85, 0.86 (3H, t, methyl), 1.26 (28H, br, methylene), 1.57 (2H, br, methylene), 1.81 (2H, br, methylene), 4.38, 4.39, 4.40 (2H, t, methylene), 7.43 (4H, br, phenyl), 8.28 (4H, br, phenyl).

^{13}C NMR (acetone-d$_6$): δ = 7.1, 14.3, 23.2, 25.2, 28.6, 29.5, 29.9, 30.0, 30.1, 30.2, 30.3, 30.3, 30.4, 30.4, 32.5, 45.7, 54.5, 69.4 (octadecyl), 118.4, 120.9, 123.1, 125.8 (CF$_3$), 120.6, 122.4, 134.4, 161.2 (phenyl).

UV (acetonitrile): λ_{max}/nm (ε/(L mol^{-1} cm^{-1})) = 280 (12400)

Elemental Analysis: Calcd. for $C_{31}H_{45}O_4S_2F_3$: C, 61.77; H, 7.52; S, 10.64. Found: C, 61.62; H, 7.37; S, 10.81.

Dealkylation of **3**

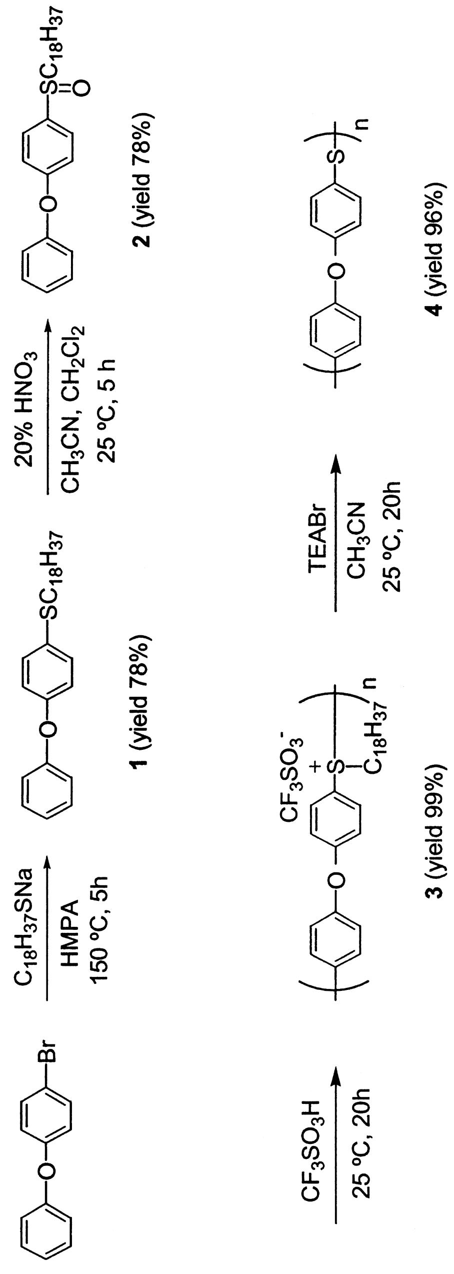
The nucleophilic dealkylation of the polymer **3** was carried out using tetraethylammonium bromide in acetonitrile at 25°C according to a previously descibed method [15]. Poly(oxy-1,4-phenylenethio-1,4-phenylene) (**4**) was obtained as a white powder in 96% yield.

IR (KBr, cm^{-1}): 3050 (aromatic $\nu_{\text{C-H}}$), 1580, 1480, 1432 ($\nu_{\text{C=C}}$), 1246 ($\nu_{\text{O-C-O}}$), 831 ($\nu_{\text{C-H}}$) cm^{-1}.

Elemental Analysis: Calcd. for $C_{12}H_8OS$: C, 71.97; H, 4.03; S, 16.01. Found: C, 71.72; H, 4.12; S, 15.85.

RESULTS AND DISCUSSION

The aryl sulfoxide monomer bearing an *n*-octadecyl group (4-octadecylsulfinyldiphenyl ether, **2**) was prepared by the nucleophilic substitution reaction of sodium octadecylthiolate and 4-bromophenyl phenyl ether followed by the oxidation with 20% nitric acid (Scheme 1). Compounds **1** and **2** were characterized by IR, ^{1}H, and ^{13}C NMR, and elemental analyses. Compound **2** was polymerized in triflic acid. The progress of the polymerization was confirmed by the increase in the viscosity of the navy blue solution. After the precipitation from water, poly(arylenesulfonium triflate) (**3**) was obtained in 99% yield as a white powder having the empirical formula $C_{31}H_{45}O_4S_2F_3$. In the ^{1}H NMR spectrum (Figure 1a), the triplet peak at 4.38, 4.39, and 4.40 ppm assigned to the methylene groups bonded to the sulfonium cation was observed at a lower magnetic field than that of the sulfinylmethylene groups of **2** (2.84-2.89 ppm). The peaks for the aromatic protons at 7.43 and 8.28 ppm indicate the linear (1,4-phenylene) structure of the polymer bonded with alternating ether and sulfonio groups. In the ^{13}C NMR spectrum (Figure 1b), four aromatic peaks at 120.6, 122.4, 134.4, and 161.2 ppm are definitely assigned to the structure of **3**. The 18 peaks at 7.1-69.4 ppm are attributed to the *n*-octadecyl groups. The IR spectrum of the polymer indicates the exis-


C18H37SNa
HMPA
150 °C, 5h
1 (yield 78%)
20% HNO3
CH3CN, CH2Cl2
25 °C, 5 h
2 (yield 78%)
CF3SO3H
25 °C, 20h
3 (yield 99%)
TEABr
CH3CN
25 °C, 20h
4 (yield 96%)

Scheme 1.

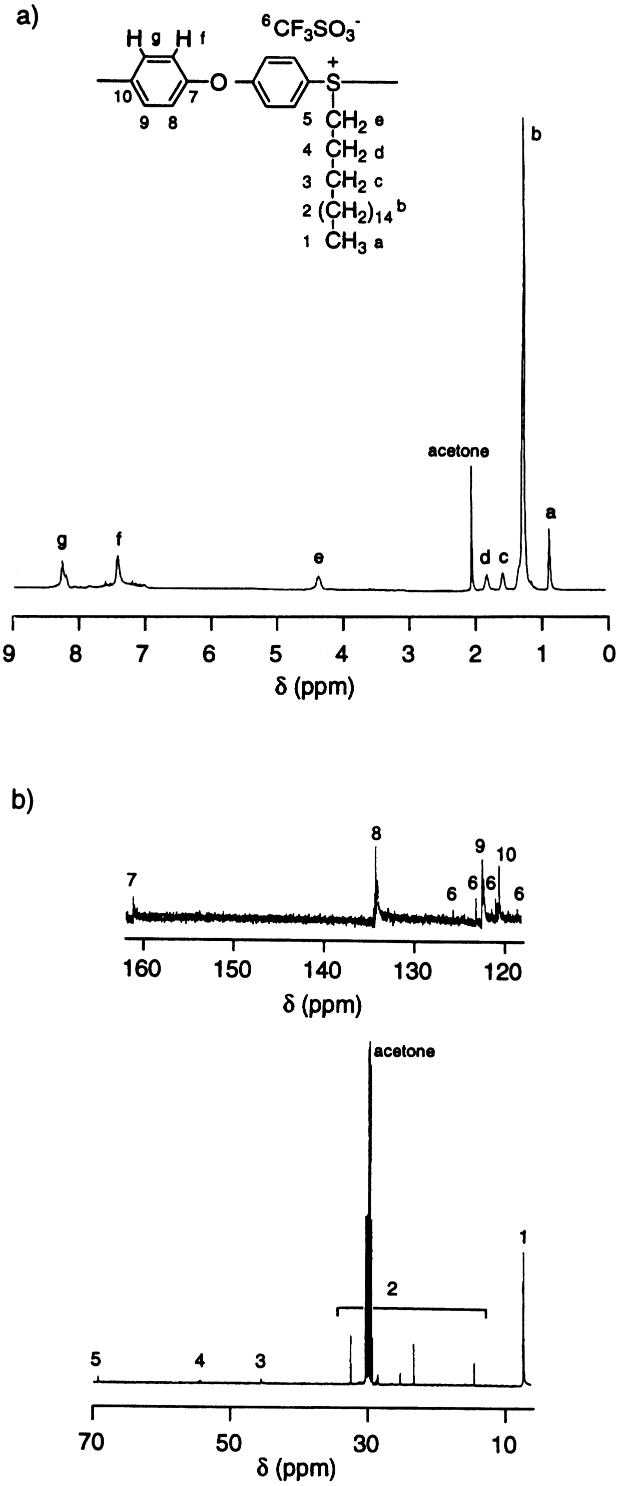


Figure 1. (a) ^{1}H and (b) ^{13}C NMR spectra of the polymer **3** in acetone-d_6.

tence of the triflate anion (1258 and 639 (n_{C-F}) cm^{-1}) and the alkyl groups (2839, 2920, 2963, (n_{C-H}) cm^{-1}). These spectroscopic data support the structure of poly (octadecylsulfonio-1,4-phenyleneoxy-1,4-phenylene triflate).

The solubility of the polymer **3** is different from that of the polymer analogs with methyl or propyl substituents. Poly(methylsulfonio-1,4-phenylenethio-1.4-phenylene triflate) and poly(propylsulfonio-1,4-phenylenethio-1.4-phenylene triflate) prepared by a similar procedure are soluble in polar organic solvents (e.g., acetonitrile, acetone and DMF) but not in halogenated hydrocarbons. The polymer **3** shows better solubility in less polar solvents such as chloroform due to the long alkyl side chains. It is soluble in benzene, dichloromethane and chloroform. A transparent and flexible thin film was obtained by casting from the chloroform solution.

The polymer **3** could be converted to poly(oxy-1,4-phenylenethio-1,4-phenylene) (**4**) by the dealkylation with tetraethylammonium bromide in acetonitrile solution. During the dealkylation reaction, the mixture became suspended and then formed a white precipitate product. The polymer **4** was isolated in 96% yield based on the theoretical formula of $C_{12}H_8OS$. The IR spectrum is consistent with that of the previously reported polymer prepared by the thermal polymerization of bis[4-[(4-bromophenyl)oxy]phenyl] disulfide [16]. The absorption assigned to the alkyl group and the triflate anion was not observed in the spectrum, indicating that the dealkylation was complete. The typical absorption at 831 cm^{-1} assigned to the C-H out-of-plane vibration supports the 1,4-phenylene structure of the polymer. The polymer **4** shows poor solubility, being only soluble in halogenated hydrocarbons above 100°C. The molecular weight of the polymer was determined to be $M_w = 3.5 \times 10^4$ and $M_n = 8.4 \times 10^3$ by high temperature GPC.

In order to examine the thermal properties of the polymer **3**, a microscopic observation was carried out upon heating during which the two transitions were confirmed. At the first transition (T_1), the solid crystalline phase changed to the fluid liquid crystalline mesophase, and at the second transition (T_2), the polymer enters into the isotropic melting phase. The transition behavior was further analyzed by DSC as shown in Figure 2. During the first heating, the polymer shows two clear endothermic peaks of T_1 at 43°C (ΔH = 14 J/g) and T_2 at 60 °C (ΔH = 10 J/g). The T_1 peak should be attributed to the transition from the crystalline to the mesophase based on the *n*-octadecyl chains. The second T_2 peak is due to the isotropic melting behavior of the polymer. The two transitions were reversible and detected during the cooling and second heating measurements. From these results, we assume that this comb-like polysulfonium salt **3** bearing long alkyl group is potentially available as a high-molecular-weight thermotropic liquid crystalline polymer.

CONCLUSION

A novel poly(arylenesulfonium salt) with *n*-octadecyl groups as the side chains was synthesized via the polycondensation of 4-octadecylsulfinyldiphenyl

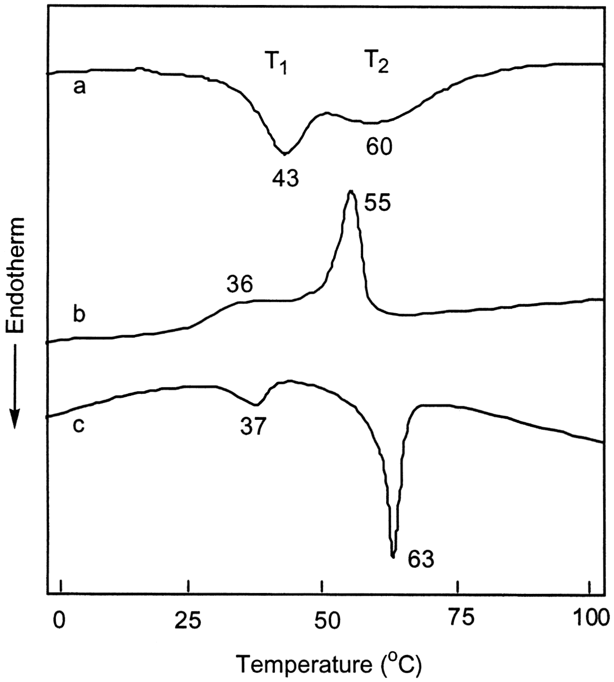


Figure 2. DSC thermograms of the polymer **3** at a heating (or cooling) rate of 10°C/min. (a) First heating; (b) cooling, and (c) second heating.

ether (**2**). The polymerization takes place in triflic acid to produce poly(octadecylsulfonio-1,4-phenyleneoxy-1,4-phenylene triflate) (**3**) in quantitative yield. The polymer was converted to poly(oxy-1,4-phenylenethio-1,4-phenylene) (**4**) by the dealkylation of which molecular weight was determined to be $M_w = 3.5 \times 10^4$ and $M_n = 8.4 \times 10^3$ by means of GPC analysis. The polymer **3** with a comb-like structure shows a mesophase between 43 and 60°C.

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