Synthesis of a New Series of Polycations Based on Poly[oxy-2-[3-(trialkylammonio)propyl]-6-methyl-1,4-phenylene salts]

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ABSTRACT: A new poly(oxyphenylene) derivative containing a 3-(trialkylammonio)propyl substituent was synthesized via hydroiodinated poly(oxy-2-allyl-6-methyl-1,4-phenylene) followed by quaternization with trialkylamine. Poly(oxy-2-allyl-6-methyl-1,4-phenylene) obtained by oxidative polymerization of 2-allyl-6-methylphenol was allowed to react with bis(cyclopentadienyl)zirconium chloride hydride ($ZrCp_2HCl$) at room temperature in inert atmosphere in which the allyl group was converted to a terminally zirconocene-substituted propyl group. The activated propyl group can react with I_2 to yield the 3-iodopropyl group. The quaternization of the resulting polymer was performed through the Menshutkin reaction with a series of trialkylamines to obtain the poly[oxy-2-[3-(trialkylammonio)propyl]-6-methyl-1,4-phenylene iodide]. The resulting polyammonium salt as an ion exchange resin exhibits higher thermal stability than poly[oxy-2-[(trimethylammonio)methyl]-6-methyl-1,4-phenylene salt], *e.g.*, no decomposition in water below 100 °C for 24 h.

Introduction

Polyammonium salts, such as poly[4-[(trimethylammonio)methyl]styrene], poly(vinyl-*N*-methylpyridinium), or poly(*N*,*N*-dimethylammonioalkylene) (ionene), have been investigated as ion exchange resins, conducting materials, drug delivery systems, photographic dyes, and so on. Among them, poly[4-(trimethylammonio)-methyl]styrene-*co*-divinylbenzene], synthesized by suspension polymerization, is widely applied for practical use because of the easy processing in molding in the well-defined geometric shape of a bead. However, the low thermostability of these polymers above 60 °C as a practical temperature for utilization makes their applications narrow.

Poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO), which has been receiving much attention as a high-performance engineering plastic with excellent thermal and chemical resistance, is synthesized by oxidative polymerization using a copper–amine catalyst under oxygen atmosphere. The simple polymerization procedure results in the preparation of a variety of PPO derivatives. In addition, PPO has higher Tg (glass transition temperature) at 220 °C and higher Td (decomposition temperature) > 400 °C than those of divinylbenzene-cross-linked polystyrene (Tg = 90 °C, Td > 350 °C). And the amorphous characteristics with high Tg make it mechanically and thermally stable. The oxyphenylene unit which has electron-donating groups is expected to lead to a more stable ammonium group against the nucleophilic reaction. Therefore structurally modified PPO derivatives should be useful as the backbone of polycations with high thermal stability. Some attempts have been already reported on the modification of PPO based on this idea. Bromine-containing PPO was prepared by the polymerization of bromophenols[1] or by the direct bromination of PPO using bromine[2–5] or *N*-bromosuccinimide (NBS).[6] Poly[oxy-2,6-dimethyl-3-(chloromethyl)-1,4-phenylene], which can be converted to a polyammonium salt by the Menshutkin reaction, was synthesized by Friedel–Crafts reaction with chloromethyl methyl ether.[7,8] However, the methylene spacer between the phenyl and ammonium groups results in low chemical stability, *e.g.*, dissociation of amine or Hofmann degradation.[9] As an approach to the introduction of a functional group to produce a thermostable spacer, Hay and Yang have recently synthesized poly(oxy-2,6-diphenyl-1,4-phenylene) (P_3O) containing approximately 10 mol % ethynyl or phenylethynyl group on the pendant phenyls.[10] We have already reported the synthesis of PPO with unsaturated hydrocarbon substituents, such as 2-butenyl, prenyl, and geranyl groups.[11–13]

As an activation method of unsaturated hydrocarbon groups, hydrozirconation using bis(cyclopentadienyl)-zirconium chloride hydride ($ZrCp_2HCl$), Schwartz's reagent, has provided an attractive and convenient transformation into a variety of desirable organic compounds. The bulky size of the $ZrCp_2Cl$ group ensures that it will attach to the least hindered position of an olefin either by regiospecific addition of Zr–H to a terminal olefin or addition to an internal olefin followed by migration past primary or secondary carbons to the least hindered terminus of the alkyl chain. The organozirconium complexes can be reacted with electrophilic reagents to give the corresponding halides, alcohols, ketones, and so on.

In this paper, we describe the synthesis of a new series of polycations based on poly[oxy-2-[3-(trialkylammonio)propyl]-6-methyl-1,4-phenylene salts]. Oxidative polymerization of 2-allyl-6-methylphenol was performed to obtain poly(oxy-2-allyl-6-methyl-1,4-phenylene) in which the allyl group was hydroiodinated at the terminal position using $ZrCp_2HCl$ and iodine. The hydroiodinated polymer was quaternized by the Menshutkin reaction with trialkylamine. The thermal stability of the resulting polyammonium salts was compared with that of some polyammonium salts containing an oxyphenylene structure.

Experimental Section

Measurement. ^1H and ^{13}C NMR spectra were recorded on a JEOL GSX-400 or EX-270. IR spectra were obtained using KBr pellets on a JASCO FT/IR-5300 spectrometer. Elemental

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analysis was performed on a Yanagisawa MT3 CHN recorder. The molecular weight of the polymer was determined by gel-permeation chromatography (GPC) using a Shimadzu LC-9A system and Asahipac (GS510H and 310H) columns calibrated with polystyrene standards. Distilled THF was used as an eluent at 25 °C with a flow rate of 1.0 mL/min. The detector was a UV/vis spectrophotometer (Shimadzu SPD-6A, 265 nm). The inherent viscosity measurements were performed using a modified Ubbelohde dilution viscometer in chloroform at 20 °C. Thermogravimetric analysis (TGA) was carried out on a SEIKO TG/DTA 220C with a heating rate of 20 °C/min and a sample weight of 5 mg under nitrogen at a flow rate of 250 mL/min.

Materials. 2-Allyl-6-methylphenol was a commercial product (Aldrich Chemical Co., Inc.) which was purified by distillation under reduced pressure and stored under nitrogen. Copper(I) chloride (CuCl) was prepared by reduction of copper(II) chloride ($CuCl_2$) using ascorbic acid as a reductant. Pyridine, benzene, and other organic solvents were distilled in the usual manner before use. Commercial products of iodine, *N*-bromosuccinimide, and hydrogen bromide (30% solution in acetic acid) were used without further purification.

Bis(cyclopentadienyl)zirconium chloride hydride ($ZrCp_2HCl$) was purchased from Aldrich Chemical Co., Inc. (purity > 95%) or prepared by the following method. Bis(cyclopentadienyl)-zirconium dichloride ($ZrCp_2Cl_2$, 10.0 g, 34.2 mmol) was dissolved in 100 mL of dry THF under an inert atmosphere. To the solution was added 15 mL of 1.0 M $LiAlH_4$ solution in ether dropwise over a 30 min period at room temperature. The mixture was stirred for 1 h followed by the filtration under argon. The resulting white powder was washed with THF and ether several times and dried in vacuo to obtain $ZrCp_2HCl$ in > 80% yield with the purity of 95%. The formation of $ZrCp_2$-HCl was confirmed by ^1H NMR spectrum (Cp = 6.23 ppm).

2-(3-Methyl-2-butenyl)-6-methylphenol was synthesized by the following method. *o*-Cresol (5.40 g, 0.05 mol) was dissolved in 25 mL of dry ether, and metallic sodium (1.15 g, 0.05 mol) was added at room temperature. After the solution was stirred for 1 h, 1-chloro-2-methyl-2-butene (5.30 g, 0.05 mol) was added slowly to the solution, and the mixture was refluxed for 5 h. After the usual workup, a pale yellow oil was distilled under reduced pressure to obtain a pure colorless oil of 2-(3-methyl-2-butenyl)-6-methylphenol in 68% yield.

2-(3-Methyl-2-butenyl)-6-methylphenol: IR (KBr, cm^{-1}) 3495 (ν_{O-H}), 2965, 2920 (ν_{C-H}), 1607, 1468 ($\nu_{C=C}$), 855, 760 (δ_{C-H}); ^1H NMR ($CDCl_3$, ppm) 1.75 (s, CH_3, 3H), 1.77 (s, CH_3, 3H), 2.21 (s, CH_3, 3H), 3.33 (d, $-CH_2-$, 2H), 5.15 (s, OH, 1H), 5.31 (t, $-CH-$, 1H), 6.72–6.99 (phenyl, 3H); ^{13}C NMR ($CDCl_3$, ppm) 15.8 (methyl), 17.8 (methyl), 25.8 (methyl), 30.2 (methylene), 122.0 ($-CH=$), 134.8 ($-C=$), 120.2, 124.2, 126.1, 127.6, 129.0, 152.7 (phenyl). Anal. Calcd for ($C_{12}H_{16}O$): C, 81.77; H, 9.15. Found: C, 81.70; H, 9.24.

Preparative Polymerization of 2-Allyl-6-methylphenol (I). CuCl (0.70 g, 7 mmol) and pyridine (11.0 g , 0.14 mol) were dissolved in 430 mL of benzene. This solution was stirred under oxygen to oxidize Cu(I) to Cu(II). After the addition of $MgSO_4$ (0.077 mol, 9.27 g), 10.37 g (0.07 mol) of 2-allyl-6-methylphenol (**I**) was added dropwise to the catalytic solution under oxygen atmosphere at 10 °C over a 20 min period. The mixture was stirred for 8 h at 10 °C and then poured with stirring into 2 L of methanol containing 10% hydrochloric acid. The obtained white powder was washed with methanol several times and dried in vacuo for 10 h to obtain poly(oxy-2-allyl-6-methyl-1,4-phenylene) in 93% yield (**II**).

Poly(oxy-2-allyl-6-methyl-1,4-phenylene) (II): IR (KBr, cm^{-1}) 3079, 2963, 2917 (ν_{C-H}), 1607, 1468 ($\nu_{C=C}$), 1184 (ν_{C-O-C}), 860, 833 (δ_{C-H}); ^1H NMR ($CDCl_3$, ppm) 2.08 (s, CH_3, 3H), 3.20 (d, $-CH_2-$, 2H), 4.96 (t, $=CH_2$, 2H), 5.83 (m, $-CH=$, 1H), 6.48, 6.50 (phenyl, 2H); ^{13}C NMR ($CDCl_3$, ppm) 16.8 (methyl), 34.4 (methylene), 113.9 ($=CH_2$), 136.1 ($-CH=$), 115.0, 116.0, 132.8, 134.5, 144.9, 155.1 (phenyl). Anal. Calcd for ($C_{10}H_{10}O$): C, 82.16; H, 8.39. Found: C, 82.44; H, 8.48.

Hydroiodination of Poly(oxy-2-allyl-6-methyl-1,4-phenylene) (II). Poly(oxy-2-allyl-6-methyl-1,4-phenylene) (**II**, 0.46 g,3.15 mmol) was dissolved in 10 mL of well-degassed distilled benzene. This solution was added dropwise to a suspension of 2.26 g (8.76 mmol) of $ZrCp_2HCl$ in 5 mL of benzene in a dry argon atmosphere. The mixture was stirred at room temperature until the color of the solution turned yellow. After 2 h of reaction, a solution of iodine (2.38 g, 9.38 mmol) in 20 mL of benzene was added dropwise slowly to the mixture at 0 °C. The dark purple solution was stirred for 20 min at room temperature in argon and then poured into 200 mL of methanol containing 10% hydrochloric acid. The precipitate was washed with methanol and dried in vacuo for 10 h to give a pale brown powder of poly[oxy-2-(3-iodopropyl)-6-methyl-1,4-phenylene] (**IV**) in 97% yield. The resulting polymer comprised 94% 3-iodopropyl substituent and 6% *n*-propyl substituent per oxyphenylene unit.

Poly[oxy-2-(3-iodopropyl)-6-methyl-1,4-phenylene] (IV): IR (KBr, cm^{-1}) 2960, 2919 (ν_{C-H}), 1607, 1466 ($\nu_{C=C}$), 1202 (ω_{CH_2I}), 1186 (ν_{C-O-C}), 860 (δ_{C-H}); ^1H NMR ($CDCl_3$, ppm) 0.82 (t, CH_3, 0.18H), 1.65 (s, $-CH_2-$, 0.12H), 2.00 (m, $-CH_2-$, 2H), 2.09 (s, CH_3, 3H), 2.53 (s, $-CH_2-$, 1.88H), 3.10 (t, CH_2I, 1.88H), 6.51, 6.53 (phenyl, 2H).

Quaternization of (IV) with Trialkylamine through the Menshutkin Reaction. A typical procedure is as follows. Poly[oxy-2-(3-iodopropyl)-6-methyl-1,4-phenylene] (0.30 g) was dissolved in 20 mL of chloroform. Trimethylamine (0.25 g, 4.26 mmol) was added and the mixture was stirred at 60 °C for 20 h. The reaction mixture was poured into 200 mL of hexane precipitating the polymer which was washed with hexane and collected by filtration, and then dried for 12 h in vacuo.

Poly[oxy-2-[3-(trimethylammonio)propyl]-6-methyl-1,4-phenylene iodide] (V-1): IR (KBr, cm^{-1}) 2957, 2872 (ν_{C-H}), 1603, 1470 ($\nu_{C=C}$), 1190 (ν_{C-O-C}), 899, 862 (δ_{C-H}); ^1H NMR (CD_3OD, ppm) 0.82 (t, CH_3, 0.18H), 1.63 (m, $-CH_2-$ 0.12H), 2.03 (m, $-CH_2-$, CH_3, 5H), 2.51 (s, $-CH_2-$, 1.88H), 3.08 (s, CH_3, 8.46H), 3.43 (s, $-CH_2N^+-$, 1.88H), 6.47, 6.50 (phenyl, 2H).

Poly[oxy-2-[3-(triethylammonio)propyl]-6-methyl-1,4-phenylene iodide] (V-2): IR (KBr, cm^{-1}) 2960, 2925, 2872 (ν_{C-H}), 1603, 1470 ($\nu_{C=C}$), 1192 (ν_{C-O-C}), 895, 861 (δ_{C-H}); ^1H NMR (DMSO-d_6, ppm) 0.79 (t, CH_3, 0.18H), 1.09 (t, CH_3, 3.24H), 1.53 (m, $-CH_2-$, 0.12H), 1.94 (s, $-CH_2-$,2H), 2.01 (s, CH_3, 3H), 2.51 (s, $-CH_2-$, 1.88H), 3.13 (s, CH_2I, $-CH_2N^+-$, 4.04H), 6.50, 6.79 (phenyl, 2H).

Poly[oxy-2-[3-(tripropylammonio)propyl]-6-methyl-1,4-phenylene iodide] (V-3): IR (KBr, cm^{-1}) 2958, 2923, 2871 (ν_{C-H}), 1601, 1468 ($\nu_{C=C}$), 1191 (ν_{C-O-C}), 898, 860 (δ_{C-H}); ^1H NMR ($CDCl_3$, ppm) 0.83 (t, CH_3, 0.18H), 1.02 (t, CH_3, 1.98H), 1.48–1.87 (m, $-CH_2-$, 3.44H), 2.03 (s, CH_3, 3H), 2.57 (s, $-CH_2-$, 1.88H), 3.10 (s, CH_2I, 1.44H), 3.28 (s, $-CH_2N^+-$, 1.76H), 6.43, 6.46 (phenyl, 2H).

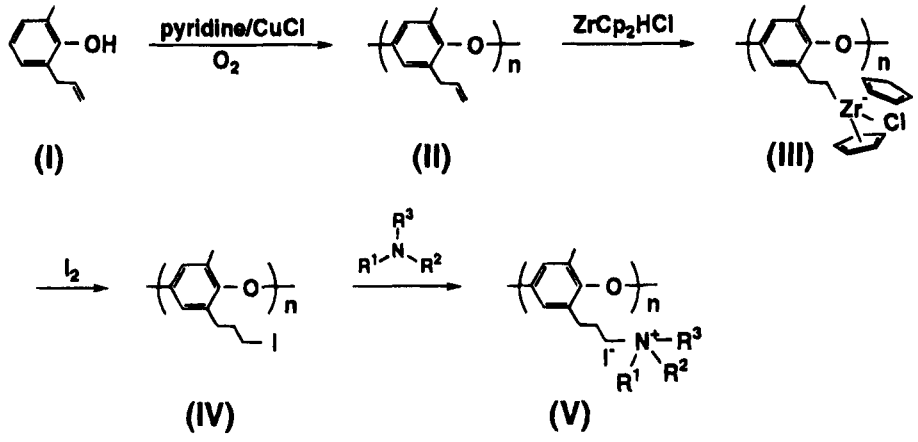
Poly[oxy-2-[3-(tributylammonio)propyl]-6-methyl-1,4-phenylene iodide] (V-4b): IR (KBr, cm^{-1}) 2958, 2920, 2871 (ν_{C-H}), 1600, 1469 ($\nu_{C=C}$), 1192 (ν_{C-O-C}), 890, 858 (δ_{C-H}); ^1H NMR (DMSO-d_6, ppm) 0.80 (t, CH_3, 0.18H), 0.94 (t, CH_3, 6.57H), 1.31 (s, $-CH_2-$, 4.38H), 1.55 (s, $-CH_2-$, 4.5H), 1.78–1.99 (m, $-CH_2-$, 2H), 2.03 (s, CH_3, 3H), 2.54 (s, $-CH_2-$, 1.88H), 3.15 (s, CH_2I, $-CH_2N^+-$, 6.26H), 6.53, 6.80 (phenyl, 2H).

Poly[oxy-2-[3-(tripentylammonio)propyl]-6-methyl-1,4-phenylene iodide] (V-5): IR (KBr, cm^{-1}) 2960, 2926, 2871 (ν_{C-H}), 1598, 1468 ($\nu_{C=C}$), 1192 (ν_{C-O-C}), 892, 858 (δ_{C-H}); ^1H NMR ($CDCl_3$, ppm) 0.83 (t, CH_3, 0.18H), 0.94 (t, CH_3, 1.35H), 1.38 (s, $-CH_2-$, 1.8H), 1.45–1.74 (m, $-CH_2-$, 0.9H), 1.91 (m, $-CH_2-$, 0.12H), 2.00 (m, $-CH_2-$, 2H), 2.03 (s, CH_3, 3H), 2.57 (s, $-CH_2-$, 1.88H), 3.11 (s, CH_2I, 1.58H), 3.30 (m, $-CH_2N^+-$, 1.2H), 6.48, 6.51 (phenyl, 2H).

Poly[oxy-2-[3-(trihexylammonio)propyl]-6-methyl-1,4-phenylene iodide] (V-6): IR (KBr, cm^{-1}) 2961, 2924, 2870 (ν_{C-H}), 1600, 1470, 1442 ($\nu_{C=C}$), 1190 (ν_{C-O-C}), 895, 861 (δ_{C-H}); ^1H NMR ($CDCl_3$, ppm) 0.90 (s, CH_3, 1.44H), 1.38 (s, $-CH_2-$, 2.52H), 1.43–1.74 (m, $-CH_2-$, 0.84H), 1.92 (m, $-CH_2-$, 0.12H), 2.00 (m, $-CH_2-$, 2H), 2.03 (s, CH_3, 3H), 2.56 (s, $-CH_2-$, 1.88H), 3.10 (t, CH_2I, 1.6H), 3.30 (m, $-CH_2N^+-$, 1.12H), 6.50, 6.53 (phenyl, 2H).

Poly[oxy-2-[3-(dimethylbutylammonio)propyl]-6-methyl-1,4-phenylene iodide] (V-7): IR (KBr, cm^{-1}) 3060, 2960, 2925, 2872 (ν_{C-H}), 1603, 1469, 1440 ($\nu_{C=C}$), 1191 (ν_{C-O-C}), 888, 860 (δ_{C-H}); ^1H NMR (DMSO-d_6, ppm) 0.80 (s, CH_3, 0.18H), 0.90

Scheme 1



(t, CH_3, 2.58H), 1.29 (m, $-CH_2-$, 1.72H), 1.60 (m, $-CH_2-$, 1.84H), 1.99 (m, $-CH_2-$, 2H), 2.03 (s, CH_3, 3H), 2.53 (s, $-CH_2-$, 1.88H), 3.02 (s, CH_3, 5.16H), 3.13 (s, CH_2I, 0.16H), 3.30 (m, $-CH_2N^+-$, 3.44H), 6.49, 6.83 (phenyl, 2H).

Poly[oxy-2-[3-(dimethylcyclohexylammonio)propyl]-6-methyl-1,4-phenylene iodide] (V-8): IR (KBr, cm^{-1}) 3061, 2958, 2927, 2872 (ν_{C-H}), 1605, 1470, 1442 ($\nu_{C=C}$), 893, 858 (δ_{C-H}); ^1H NMR (DMSO-d_6, ppm) 0.80 (s, CH_3, 0.18H), 1.09–1.84 (m, $-CH_2-$, $-CH-$, 7.49H), 2.03 (s, $-CH_2-$, CH_3, 5H), 2.52 (t, $-CH_2-$, 1.88H), 3.01 (s, CH_3, 4.02H), 3,18 (s, CH_2I, 0.54H), 3.35 (m, $-CH_2N^+-$, 1.34H), 6.48, 6.85 (phenyl, 2H).

Synthesis of Poly[oxy-2-[(trimethylammonio)methyl]-6-methyl-1,4-phenylene bromide] (VII). Poly[oxy-2-(bromomethyl)-6-methyl-1,4-phenylene] was prepared by the previously reported method.[6] A typical procedure is as follows. Poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO, Mw = 137 000, Mn = 75 000) (22.0 g, 0.183 mol) was dissolved in 400 mL of carbon tetrachloride. To the refluxing solution was added 35.8 g (0.20 mol) of *N*-bromosuccinimide over a 10 min period while the solution was irradiated with two 100 W flood lamps at a distance of 10 cm. After 3 h, the reaction mixture was filtered to remove the succinimide. The filtrate was poured into 1500 mL of methanol containing 5% hydrochloric acid with vigorous stirring. After filtration, the precipitated polymer was washed with methanol and dried in vacuo for 12 h. The brominated polymer (**VI**) containing 1.00 Br per repeating unit was obtained in 100% yield. The Menshutkin reaction of **VI** with trimethylamine for quaternization was performed in a manner similar to that for **IV** to obtain poly[oxy-2-[(trimethylammonio)methyl]-6-methyl-1,4-phenylene bromide] (**VII**).

Poly[oxy-2-(bromomethyl)-6-methyl-1,4-phenylene] (VI): IR (KBr, cm^{-1}) 2960, 2922 (ν_{C-H}), 1610, 1468 ($\nu_{C=C}$), 1188 (ν_{C-O-C}), 862 (δ_{C-H}); ^1H NMR ($CDCl_3$, ppm) 2.08 (s, CH_3, 3H), 4.34 (s, $-CH_2-$, 2H), 6.44, 6.83 (phenyl, 2H). Anal. Calcd for (C_8H_7BrO): C, 48.27; H, 3.54; Br, 40.14. Found: C, 47.99; H, 3.49; Br, 40.40.

Poly[oxy-2-[(trimethylammonio)methyl]-6-methyl-1,4-phenylene bromide] (VII): IR (KBr, cm^{-1}) 2962, 2924 (ν_{C-H}), 1607, 1468 ($\nu_{C=C}$), 1192 (ν_{C-O-C}), 883 (δ_{C-H}); ^1H NMR (DMSO-d_6, ppm) 2.08 (s, CH_3, 3H), 2.76 (s, $-CH_2-$, 2H), 3.11 (s, CH_3, 9H), 6.59, 6.90 (phenyl, 2H). Anal. Calcd for ($C_{11}H_{16}BrNO$): C, 51.18; H, 6.25; Br,30.95; N, 5,43. Found: C, 51.44; H, 6.00; Br, 31.25; N, 5.33.

Synthesis of Poly[oxy-2-[3-methyl-3-(triethylammonio)butyl]-6-methyl-1,4-phenylene bromide] (IX). Oxidative polymerization of 2-(3-methyl-2-butenyl)-6-methylphenol was carried out as described previously[12] to obtain poly[oxy-2-(3-methyl-2-butenyl)-6-methyl-1,4-phenylene] in 94% yield. The resulting polymer was reacted with hydrogen bromide as follows. Poly[oxy-2-(3-methyl-2-butenyl)-6-methyl-1,4-phenylene] (8.0 g) was dissolved in 50 mL of chloroform. Hydrogen bromide in acetic acid (250 mL, 30%) was added to the solution and the mixture was stirred at room temperature for 10 h in the dark. After the reaction, the mixture was poured into 1000 mL of methanol to precipitate a light brown powder. The precipitate was washed with methanol several times and dried in vacuo for 10 h to obtain poly[oxy-2-(3-bromo-3-methylbutyl)-6-methyl-1,4-phenylene] (**VIII**) in 100% yield. The Menshutkin reaction of **VIII** with triethylamine was performed in DMF at room temperature for 20 h to obtain poly[oxy-2-[3-methyl-3-(triethylammonio)butyl]-6-methyl-1,4-phenylene bromide] (**IX**).

Poly[oxy-2-(3-methyl-2-butenyl)-6-methyl-1,4-phenylene]: IR (KBr, cm^{-1}) 3073, 2971, 2920, 2857 (ν_{C-H}), 1607, 1466 ($\nu_{C=C}$), 1188 (ν_{C-O-C}), 860 (δ_{C-H}); ^1H NMR ($CDCl_3$, ppm) 1.50 (s, CH_3, 3H), 1.62 (s, CH_3, 3H), 2.06 (s, CH_3, 3H), 3.12 (d, $-CH_2-$, 2H), 5.17 (t, $-CH-$, 1H), 6.43, 6.49 (phenyl, 2H); ^{13}C NMR ($CDCl_3$, ppm) 16.8 (methyl), 17.7 (methyl), 25.6 (methyl), 28.9 (methylene), 122.0 (—CH=), 132.8 (—C=), 113.6, 114.4, 132.5, 136.0, 144.8, 155.1 (phenyl). Anal. Calcd for ($C_{12}H_{14}O$): C, 82.72; H, 8.10. Found: C, 82.50; H, 8.11. Mw = 44 000, Mn = 9800.

Poly[oxy-2-(3-bromo-3-methylbutyl)-6-methyl-1,4-phenylene] (VIII): IR (KBr, cm^{-1}) 2967, 2924 (ν_{C-H}), 1607, 1468 ($\nu_{C=C}$), 1186 (ν_{C-O-C}), 860 (δ_{C-H}); ^1H NMR ($CDCl_3$, ppm) 1.66 (s, CH_3, 6H), 1.97 (t, $-CH_2-$, 2H), 2.09 (s, CH_3, 3H), 2.62 (t, $-CH_2-$, 2H), 6.46, 6.56 (phenyl, 2H); ^{13}C NMR ($CDCl_3$, ppm) 17.0 (methyl), 28.1 (methylene), 34.4 (methyl), 48.1 (CBr), 67.4 (methylene), 104.3, 104.9, 133.2, 136.1, 145.2, 155.5 (phenyl). Anal. Calcd. for ($C_{12}H_{15}BrO$): C, 56.49; H, 5.93; Br, 31.32. Found: C, 56.20; H, 6.11; Br, 31.02.

Poly[oxy-2-[3-methyl-3-(triethylammonio)butyl]-6-methyl-1,4-phenylene bromide] (IX): IR (KBr, cm^{-1}) 2934, 2859 (ν_{C-H}), 1609, 1468 ($\nu_{C=C}$), 1186 (ν_{C-O-C}), 860, 837 (δ_{C-H}); ^1H NMR ($CDCl_3$, ppm) 1.44 (t, CH_3, 0.9H), 1.67 (s, CH_3, 6H), 1.95 (t, $-CH_2-$, 2H), 2.08 (s, CH_3, 3H), 2.62 (t, $-CH_2-$, 2H), 3.13 (q, $-CH_2-$, 0.6H), 6.45, 6.54 (phenyl, 2H).

Results and Discussion

Oxidative Polymerization of 2-Allyl-6-methylphenol. 2-Allyl-6-methylphenol (**I**) was oxidatively polymerized in the presence of copper–pyridine catalyst under oxygen in a manner similar to that for 2,6-xylenol (Scheme 1). The polymerization at 10 °C for 8 h gave a white powder of poly(oxy-2-allyl-6-methyl-1,4-phenylene) (**II**) in 93% yield on the basis of the monomer **I**. **II** is soluble in many organic solvents at room temperature, such as chloroform, dichloromethane, tetrahydrofuran, and *N*-methylpyrrolidone, as is PPO. The structure of the polymer was confirmed by the combination of elemental analysis and IR, ^1H, and ^{13}C NMR spectra. Elemental analysis revealed that the polymer had $C_{10}H_{10}O$ formula. In the IR spectrum of the polymer, a typical peak which is assigned to an aryl ether bond is observed at 1184 cm^{-1}. The existence of an allyl group is confirmed by the peak at 3079 cm^{-1} attributed to the alkene C–H stretching vibration. The existence of two peaks at 833 and 860 cm^{-1} attributed to the C–H out-of-plane vibration of isolated phenylene protons indi-

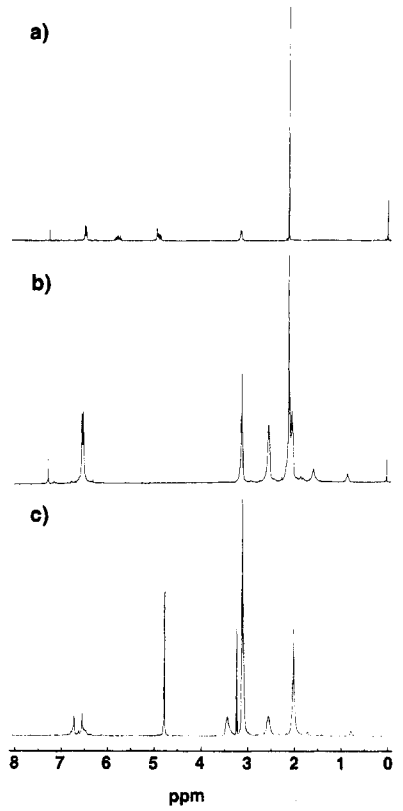


Figure 1. ^{1}H NMR spectra of (a) poly(oxy-2-allyl-6-methyl-1,4-phenylene) (**II**), (b) poly[oxy-2-(3-iodopropyl)-6-methyl-1,4-phenylene] (**IV**), and (c) poly[oxy-2-[3-(trimethylammonio)-propyl]-6-methyl-1,4-phenylene iodide] (**V-1**).

cates a 1,2,4,6-tetrasubstituted benzene structure. The ^{1}H NMR spectrum of **II** is shown in Figure 1a, where methyl proton (2.08 ppm), allyl protons (3.20, 4.96, 5.83 ppm), and phenyl protons (6.48, 6.50 ppm) are observed. The integration ratio of phenyl protons to methyl, methylene, and methyne protons is consistent with the proton numbers for the structure of an oxy-2-allyl-6-methyl-1,4-phenylene unit. In the ^{13}C NMR spectrum, a methyl carbon (16.8 ppm), allyl carbons (34.4, 113.9, 136.1 ppm), and six kinds of phenyl carbons (115.0, 116.0, 132.8, 134.5, 144.9, 155.1 ppm) are observed, which are well correlated with the structure of **II**. These spectroscopic data reveal the formation of a linear polymer with one allyl group per repeating unit.

I shows lower reactivity in the oxidative polymerization compared to 2,6-xylenol because of the increased steric hindrance of the allyl group adjacent to the hydroxyl group and the higher oxidation potential (2,6-xylenol = 1.6 V, 2-allyl-6-methylphenol = 1.9 V vs Ag/AgCl [14]). At −10 °C, only a low molecular weight polymer (Mw = 10 300, Mn = 4300) was produced due to the slow reaction rate (Table 1). The polymerization of **I** at 10 °C with a pyridine/copper molar ratio (N/Cu) = 100 provided the formation of **II** with Mw = 37 800 and Mn = 10 900. However, at higher temperature over 25 °C, the color of the reaction mixture was dark-brown which is different from that in the case at lower reaction temperature because of the side reactions such as the formation of diphenoquinone. The higher temperature condition results in promoting the formation of diphenoquinone. The addition of $MgSO_4$ whose molar ratio is 1.1 times that of the monomer promotes the polymerization and results in an increase in molecular weight of the polymer (Mw = 41 800, Mn = 13 300). The resulting water formed by the oxidative reaction with

Table 1. Oxidative Polymerization of 2-Allyl-6-methylphenol[a]

N/Cu[b]	T (°C)	$MgSO_4$ (mmol)	Mw	Mn
100	−10	0	10 300	4 300
100	10	0	37 800	10 900
100	25	0	30 000	9 700
100	35	0	28 300	8 600
100	10	77	42 600	13 800
20	10	77	88 000	22 300
2[c]	10	77	20 600	5 900
10[c]	10	77	26 000	9 800
50[c]	10	77	9 200	4 600

[a] Benzene = 430 mL, 2-allyl-6-methylphenol = 70 mmol, CuCl = 7 mmol, 8 h. [b] Molar ratio of pyridine to copper. [c] Molar ratio of TMEDA to copper.

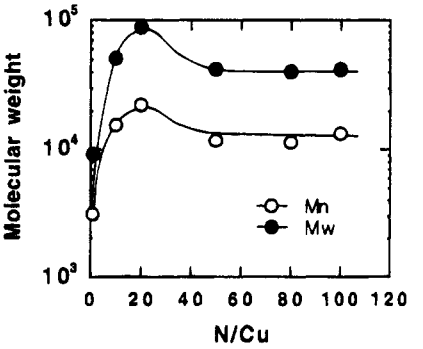


Figure 2. Effect of the ratio of nitrogen atoms to copper atoms on the molecular weight of **II** for polymerization at 10 °C for 10 h.

oxygen results in the deactivation of the catalysts through the hydrolysis. The molecular weight of the resulting polymer also increases with a decrease in N/Cu ratio, and the highest molecular weight (Mw = 88 000, Mn = 22 300) and the highest inherent viscosity ([η] = 0.37 dL/g) were achieved at a N/Cu ratio of 20 (Figure 2). At a N/Cu ratio larger than 50, the molecular weight decreases to Mw = 41 800 and Mn = 13 300. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA) which is a well-known effective ligand for the oxidative polymerization of 2,6-xylenol was employed, however, increase in molecular weight did not take place (N/Cu = 10; Mw = 26 000, Mn = 9800). The polymerization with higher N/Cu ratio (>10) results in a decrease of the molecular weight, *e.g.*, Mw = 9200, Mn = 4600 (N/Cu = 50) because of the insolubility of PPO in TMEDA.

The Mark−Houwink−Sakurada parameters, K and α, for **II** in chloroform at 20 °C were determined by measuring the inherent viscosity of several samples in determining the molecular weight by GPC. The plot of log [η] versus log Mn or log Mw shows a good linear relationship given by

$$[\eta] = (6.48 \times 10^{-5})\mathrm{Mn}^{0.86}$$

$$[\eta] = (3.26 \times 10^{-3})\mathrm{Mw}^{0.41}$$

This result not only confirms the essential linearity of the polymer but also suggests that the conformation of poly(oxy-2-allyl-6-methyl-1,4-phenylene) in solution is similar to that of poly(oxy-2,6-dimethyl-1,4-phenylene) ($K = 4.83 \times 10^{-4}$ dL/g, $\alpha = 0.64$ at 25 °C in chloroform).[15]

Synthesis of Poly[oxy-2-(3-iodopropyl)-6-methyl-1,4-phenylene]. **II** was allowed to react with $ZrCp_2HCl$ to obtain the hydrozirconated polymer **III**. The reaction was carried out in dry benzene at room temperature to avoid decomposition of **III** by water. The addition of the zirconium compounds was monitored by

Table 2. The Menshutkin Reaction of IV with Trialkylamines for Quaternization[a]

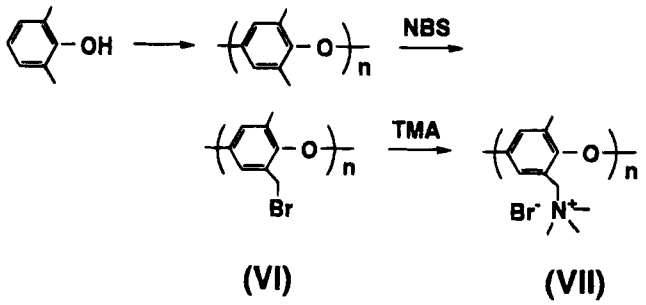
no	$R_1R_2R_3N$	pK_a	conversion (%)	ammonium group[c] (%)	δ_{CH_2}[d] (ppm)
V-1	$N(CH_3)_3$	9.8	100	94	3.43
V-2	$N(CH_2CH_3)_3$	11.0	38	36	3.38
V-3	$N(CH_2CH_2CH_3)_3$	10.7	23	22	3.29
V-4a	$N(CH_2CH_2CH_2CH_3)_3$	9.9	35	33	3.32
V-4b[b]	$N(CH_2CH_2CH_2CH_3)_3$	9.9	78	73	3.32
V-5	$N(CH_2CH_2CH_2CH_2CH_3)_3$		16	15	3.32
V-6	$N(CH_2CH_2CH_2CH_2CH_2CH_3)_3$		15	14	3.32
V-7	$(CH_3)_2NCH_2CH_2CH_2CH_3$		91	86	3.32
V-8	$(C_6H_5)(CH_3)_2N$		71	67	3.32

[a] Reaction time = 20 h. [b] Reaction time = 72 h. [c] Ammonium group per repeating oxyphenylene unit. [d] ^1H NMR chemical shift of the methylene proton adjacent to the ammonium group.

the disappearance of the peaks at 4.96 and 5.83 ppm assigned to allyl protons and the appearance of the peaks at 1.20 and 1.57 ppm assigned to the 3-zirconated propyl group in the ^1H NMR spectrum. This observation indicates the complete hydrozirconation within 2 h through the preferential addition of $ZrCp_2HCl$ at an unhindered part of the allyl group. The polymer **III** is susceptible to hydrolysis and electrophilic reaction by an aqueous acid or a halogen. To obtain a polymer substituted by a 3-iodopropyl group, **IV**, **III** was reacted *in situ* with iodine as postulated in Scheme 1. The progress of the reaction of the 3-zirconated propyl group with iodine could be confirmed by the disappearance of the intense purple color of iodine. The reaction was completed within 20 min and a pale brown powder was precipitated by pouring into hydrochloric acid–methanol. In the IR spectrum of the resulting polymer, a sharp peak attributed to the CH_2I group is observed at 1202 cm^{-1} which does not exist in the IR spectrum of the original polymer **II**. In the ^1H NMR spectrum (Figure 1b), the peaks at 1.20 and 1.57 ppm disappeared, which suggests the complete reaction of the zirconated propyl group with iodine. The appearance of a new triplet peak at 3.10 ppm assigned to iodomethylene protons and the absence of a peak around 4.2 ppm attributed to a iodomethyne proton support the structure of a 3-iodopropyl group attached to a main chain oxyphenylene unit. Iodination on the methyl group at the 2-position and the phenyl ring or degradation of the polymer main chain was not confirmed in the ^1H NMR spectrum. However, the formation of the *n*-propyl group was confirmed by the two minor peaks at 0.82 and 1.65 ppm.[16] The integral ratio of the peaks suggests that the resulting polymer **IV** comprised 94% 3-iodopropyl substituents and 6% *n*-propyl groups per repeating oxyphenylene unit.

Synthesis and Thermal Stability of Poly[oxy-2-[3-(trialkylammonio)propyl]-6-methyl-1,4-phenylene]. The Menshutkin reaction of **IV** with a series of trialkylamines was performed in chloroform at reflux temperature for 20 h (Table 2). The resulting polymers **V** are soluble in dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF) and slightly soluble in chloroform. **V-1** is also soluble in methanol. In the IR spectrum of **V-1**, the peaks at 2957 and 2872 cm^{-1} attributed to the alkyl C–H stretching vibration appears stronger than that of **IV**, which suggests the introduction of trimethylamine. The quaternization of the 3-iodopropyl group with trimethylamine is also confirmed by the disappearance of the peak at 1202 cm^{-1} assigned to the CH_2–I group. Figure 1c shows the ^1H NMR spectrum of **V-1** in CD_3OD, where a strong peak attributed to the trimethylammonium proton is

Scheme 2



observed at 3.14 ppm. The peak attributed to the methylene proton at the 3-position of the propyl substituent is shifted downfield from 3.10 ppm to 3.43 ppm by the quaternization due to the strong electron-withdrawing ammonium group. The peak at 2.03 ppm is assigned to the methyl proton at the 6-position on the phenylene ring and the methylene proton at the 2-position of the propyl group. It was determined from the ^1H NMR integration ratio that the polymer **V-1** contains 94% 3-(trimethylammonio)propyl group per repeating unit (in 100% conversion).

The quaternization reaction is highly affected by trialkylamines used for the reaction. The reaction of **IV** with trimethylamine proceeds rapidly to 100% conversion within 20 h; however, the conversion decreases with an increase in the alkyl chain length of the amine (**V-2**–**V-6**). When trihexylamine is used, only 15% of the 3-iodopropyl substituent is converted through the quaternization. The result did not correspond to the basicity (pK_a) of the amines. We suggest that the lower reactivity of bulky alkylamines is simply due to the steric hindrance. The steric hindrance between the iodopropyl group and the alkyl chain of the amine results in a low rate of the Menshutkin reaction. *N,N*-Dimethylbutylamine (**V-7**, 91%) and *N,N*-dimethylcyclohexylamine (**V-8**, 71%) which are less bulky than triethylamine or tripropylamine react with higher conversion. Longer reaction time is required to achieve the quantitative conversion for bulky amines, *e.g.*, the quaternization with tributylamine proceeded to 78% conversion in 72 h (**V-4b**).

As a typical polyoxyphenylene containing a bound ammonium group with a methylene spacer, poly[oxy-2-[(trimethylammonio)methyl]-6-methyl-1,4-phenylene bromide] (**VII**) was prepared as follows (Scheme 2). Poly(oxy-2,6-dimethyl-1,4-phenylene) (Mw = 137 000, Mn = 75 000) which was prepared by oxidative polymerization of 2,6-xylenol was brominated with *N*-bromosuccinimide (NBS). The free radical bromination gave PPO containing a bromomethyl group **VI** in 100% yield. In the ^1H NMR spectrum of **VI**, a strong singlet peak appeared at 4.34 ppm which is assigned to the bromomethylene proton. Methyl proton and phenyl protons are also observed at 2.08, 6.44, and 6.83 ppm, respectively. The integration ratio of the peaks reveals that the polymer contains 1.00 Br per repeating oxyphenylene unit. The Menshutkin reaction of **VI** with trimethylamine was performed in chloroform at 60 °C to obtain poly(oxy-2-[(trimethylammonio)methyl]-6-methyl-1,4-phenylene bromide) (**VII**) in 100% yield. **VII** is soluble in polar organic solvents, such as methanol and dimethyl sulfoxide (DMSO). The ^1H NMR spectrum of **VII** in DMSO-d_6 shows peaks at 2.08, 2.76, 3.11, 6.59, and 6.90 ppm (Figure 3a). The strong characteristic peak at 3.11 ppm indicates the existence of the trimethylammonium group. The combination of the in-

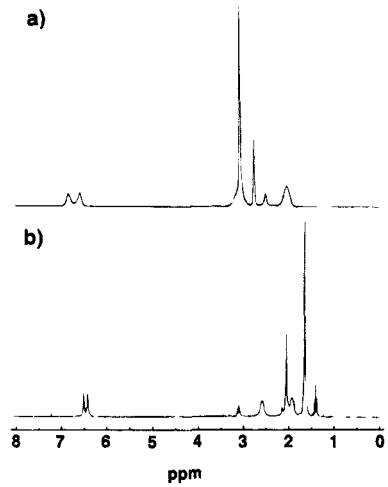
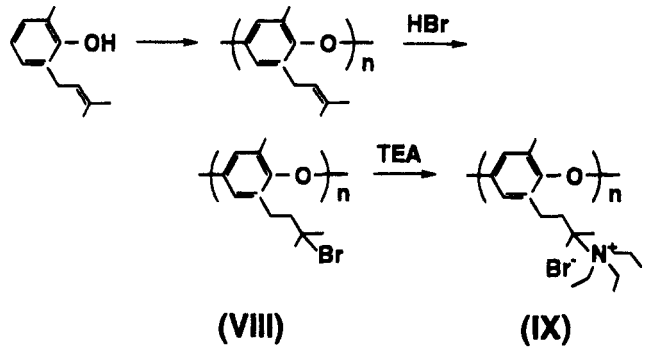


Figure 3. ^{1}H NMR spectra of (a) poly[oxy-2-[(trimethylammonio)methyl]-6-methyl-1,4-phenylene bromide] (**VII**) and (b) poly[oxy-2-[3-methyl-3-(triethylammonio)butyl]-6-methyl-1,4-phenylene bromide] (**IX**).

Scheme 3



tegration ratio of the peaks, the disappearance of the peak of the bromomethylene proton at 4.34 ppm, and the appearance of the peak of the ammoniomethyl proton at 2.76 ppm reveals that the conversion in the quaternization reaction was 100%.

Poly[oxy-2-(3-methyl-2-butenyl)-6-methyl-1,4-phenylene] (Mw = 44 000, Mn = 9800) was also prepared by oxidative polymerization as a reference for an isopentyl spacer type polyammonium **IX** (Scheme 3). Hydrobromination of the polymer was carried out with 30% hydrogen bromide in acetic acid at room temperature in the dark. The hydrobromination proceeds efficiently according to the Markovnikov rule, and a pale brown powder of poly[oxy-2-(3-bromo-3-methylbutyl)-1,4-phenylene] (**VIII**) was obtained in 100% conversion. ^{1}H and ^{13}C NMR spectra of the polymer are well-correlated with the structure of **VIII**. **VIII** was allowed to react with triethylamine in DMF at room temperature for 20 h. The ^{1}H NMR spectrum of the resulting quaternized polymer **IX** in $CDCl_3$ is shown in Figure 3b. Introduction of triethylammonium is confirmed by the peaks at 1.44 ppm (methyl proton) and at 3.13 ppm (methylene proton) which are at a lower magnetic field than that of triethylamine[17] due to the strong electron-withdrawing ammonium group. However, the conversion determined by the integration ratio of the peaks was only 10% because of the lower reactivity of the bulky 3-bromo-3-methylbutyl group. Extending the reaction time and heating to 60 °C did not result in an increase in the conversion because Hofmann degradation occurs as a side reaction.

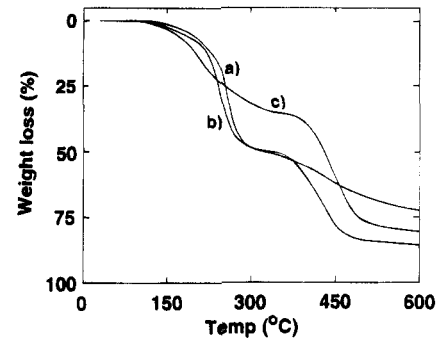


Figure 4. TG curves of (a) poly[oxy-2-[3-(trimethylammonio)propyl]-6-methyl-1,4-phenylene iodide] (**V-1**), (b) poly[oxy-2-[(trimethylammonio)methyl]-6-methyl-1,4-phenylene bromide] (**VII**), and (c) poly[oxy-2-[3-methyl-3-(triethylammonio)butyl]-6-methyl-1,4-phenylene bromide] (**IX**).

In order to investigate the effect of an alkyl spacer between the phenyl ring and the ammonium group on the heat resistance of the polyammonium salts, thermal gravimetric analysis of **V-1**, **VII**, and **IX** was carried out as shown in Figure 4. The degradation of the polyammonium salts is considered to consist of two processes. The first process is a weight loss of the trialkyl ammonium group at 100–380 °C and the second is a degradation of the oxyphenylene main chain above 380 °C. **V-1** and **VII** lose approximately 50% of their original weight which corresponds to the proportion of trimethylammonium iodide or bromide in the polymers, respectively. **IX** retains 63% of its original weight at 380 °C, where 37% weight loss is attributed to 10% of a triethylammonium bromide group and 90% of an unquaternized bromine per oxyphenylene unit. **VII** and **IX** begin to decompose at 101 and 118 °C, respectively, while **V-1** does not decompose up to 129 °C. $Td_{10\%}$ (the temperature for 10% weight loss) of **V-1** is 221 °C and the highest among these three polyammonium salts.

The thermal stability of the polyammonium salts was also examined in hot water at 70 °C for 24 h. After the treatment, **VII** shows no decomposition which was supported by no change in the ^{1}H NMR spectrum. However, in the case of poly(oxy-2-[(dicyclohexylmethylammonio)methyl]-6-methyl-1,4-phenylene bromide) obtained from **VI** and *N,N*-dicyclohexylmethylamine, dissociation of 6% amine was detected in the ^{1}H NMR spectrum , where a sharp peak at 2.21 ppm was assigned to the methyl proton of free amine. The dissociation of 20% bis(3-cyclohexylpropyl)methylamine was also confirmed in the corresponding polyammonium salts. The stability of the polyammonium salts having a methylene spacer decreases with an increase in the bulkiness of the ammonium group. The polyammonium salt having an isopentylene spacer (**IX**) is quite unstable because of the tertiary carbon adjacent to the ammonium group. In the ^{1}H NMR spectrum of **IX** after heating in water, the characteristic peaks of the alkene proton at 4.62 and 5.15 ppm are observed. This result suggests Hofmann degradation of the 3-methyl-3-(triethylammonio)butyl group to 3-methyl-3-butenyl and 3-methyl-2-butenyl groups. One hundred percent degradation was determined by the integration ratio of the peaks. In contrast, in the case of a series of the polyammonium salts having a propylene spacer **V**, free amine was not formed after heating in water at 100 °C for 24 h. The ^{1}H NMR spectrum of the resulting polyammonium salts **V** agrees with that of the virgin polymers, where allyl methylene and methyne protons do not exist. These results suggest that the polymers

V are stable up to 100 °C without Hofmann degradation and dissociation of the amine. The introduction of a propyl group between the oxyphenylene chain and the ammonium group results in an increase in hydrolitic stability of the polyammonium salt.

The stability of the polyammonium salts was also evaluated by monitoring the chemical shift of the methylene proton adjacent to the ammonium group in ^{1}H NMR spectrum, because it relates to the electron density of the methylene group. The δ_{CH_2} of the polyammonium salts having a propylene spacer stands in the range of 3.29 to 3.43 ppm, whose lower magnetic field than that of a methylene spacer (2.76 ppm) means a lower electron density on the methylene carbon. This result indicates that the ammonium group is less susceptible to be attacked by OH^- and is bonded more covalently with the methylene group in the case of propyleneammonium salts than in the case of methylene ones. As a result, dissociation of amine and Hofmann degradation does not take place easily.

Conclusions

Allyl-substituted poly(oxy phenylene) with Mw = 88 000, Mn = 22 300 and $[\eta]$ = 0.37 dL/g was prepared by oxidative polymerization of 2-allyl-6-methylphenol. The allyl group was converted to an iodopropyl group by hydrozirconation with $ZrCp_2HCl$ (Schwarz's reagent) followed by the reaction with iodine. The iodination proceeds preferentially at the terminal methylene to give a PPO containing 94% 3-iodopropyl group and 6% *n*-propyl group per phenylene unit. The polymer was quaternized by the Menshutkin reaction with a series of trialkylamines in high conversion. The resulting polyammonium salt is more stable than that having a methylene or isopentylene spacer.

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References and Notes

(1) Staffin, G. C.; Price, C. C. *J. Am. Chem. Soc.* **1960**, *82*, 3632.
(2) Hay, A. S.; Blanchard, H. S.; Endres, G. F.; Eustance, J. W. *J. Am. Chem. Soc.* **1959**, *81*, 6335.
(3) Hay, A. S. U. S. Patent 3,306,874, 1967.
(4) Hay, A. S. U. S. Patent 3,306,875, 1967.
(5) Hay, A. S. *Adv. Polym. Sci.* **1967**, *4*, 496.
(6) White, D. M.; Orlando, C. M. *ACS Symp. Ser.* **1975**, *6*, 178.
(7) Daly, W. H.; Chotiwana, S.; Nielsen, R. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1979**, *20*, 835.
(8) Daly, W. H. *J. Macromol. Sci.-Chem.* **1985**, *A22*, 713.
(9) Aosaki, Y.; Ito, T.; Kiba, H.; Onozuka, T.; Shindo, M. *Ion Exch. Soc. Jpn., Prepr.* **1994**, 11.
(10) Yang, H.; Hay, A. S. *J. Macromol. Sci.-Pure Appl. Chem.* **1994**, *A31*, 155.
(11) Nishide, H.; Suzuki, Y.; Tsuchida, E. *Makromol. Chem.* **1981**, *182*, 2361.
(12) Nishide, H.; Minakata, T.; Tsuchida, E. *Makromol. Chem.* **1982**, *183*, 1889.
(13) Hyun, S. H.; Nishide, H.; Tsuchida, E. *Polymer Bulletin*, **1987**, *18*, 283.
(14) The potential of the reference electrode (Ag/AgCl) was adjusted by using a ferrocene/ferrocenium redox couple to be 0.42 V in dichloromethane.
(15) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; 1989; VII/21.
(16) It is supposed that the *n*-propyl group was formed by the reduction of allyl group with bis(cyclopentadienyl)zirconium dihydride ($ZrCp_2H_2$), which is a contaminant of $ZrCp_2HCl$.
(17) ^{1}H NMR chemical shifts of triethylamine in $CDCl_3$ are as follows: 1.03 ppm (t, CH_3, 9H), 2.54 ppm (q, $-CH_2-$, 6H)

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