and of GPC calibration polynomials (6 pages). Ordering information is given on any current masthead page.

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Synthesis and Characterization of a Water-Soluble Poly(*p*-phenylenevinylene) Derivative

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ABSTRACT: We report the preparation of a water-soluble poly(*p*-phenylenevinylene) (PPV) derivative, poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene], by a conventional precursor polymer approach. The conversion of the precursor polymer into fully conjugated PPV can be carried out in solution and in the solid state. We also describe a novel way to hydrolyze a sulfonyl chloride in the precursor polymer by refluxing with a small amount of DMF in water. Electronic spectroscopy reveals that the as-formed polymer is Brønsted acid doped and that it can be compensated (undoped) with ammonia.

Introduction

Highly conjugated polymers are generally insoluble, infusible, and intractable because of the stiffness of their backbones. The intractability makes it difficult to process electrically conductive polymers into useful objects such as fibers and films. One of the methods developed to solve this problem is the use of a processible precursor polymer that can be converted to the desired conjugated polymer without loss of the degree of polymerization and physical shape. Edwards and Feast's polyacetylene was synthesized by this approach.[1]

Highly conducting poly(*p*-phenylenevinylene) (PPV) has been obtained via pyrolysis of the soluble precursor polymer derived from *p*-xylene-α,α'-bis(dimethylsulfonium bromide) under an inert atmosphere.[2] Contrary to common observations that introduction of a substituent group to conjugated polymers results in a decrease in electric conductivity, unstretched, alkoxy-substituted PPV showed considerably higher conductivity than the corresponding, unstretched, PPV.[3] More recently, the first organic solvent soluble derivative of PPV, the dihexyloxy-substituted PPV, was developed through a novel route, where the precursor polymer was converted into a fully conjugated polymer in an organic solvent instead of in the solid state.[4]

The first water-soluble conducting polymers are poly(3-thiophenealkanesulfonates) invented in our group.[5] In these polymers, the counterions are covalently bound to the polymer backbone, leading to the self-doping concept.

In this paper we present the results on the first water-soluble PPV derivative.[6] This was achieved by the introduction of an alkanesulfonate group to the monomer. Such a modification not only did make the resulting PPV easily water soluble and self-doped but also lowered its band gap as in the case of alkoxy substitution of PPV.

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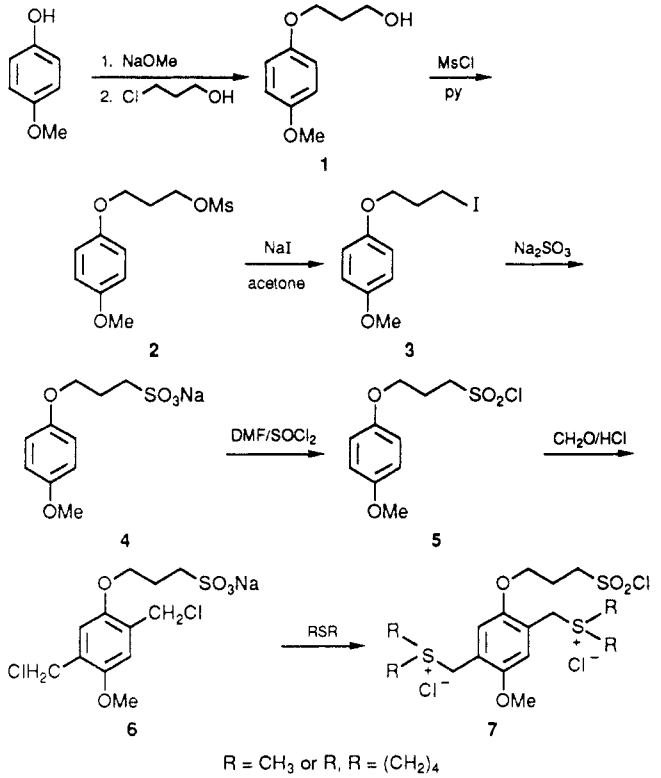
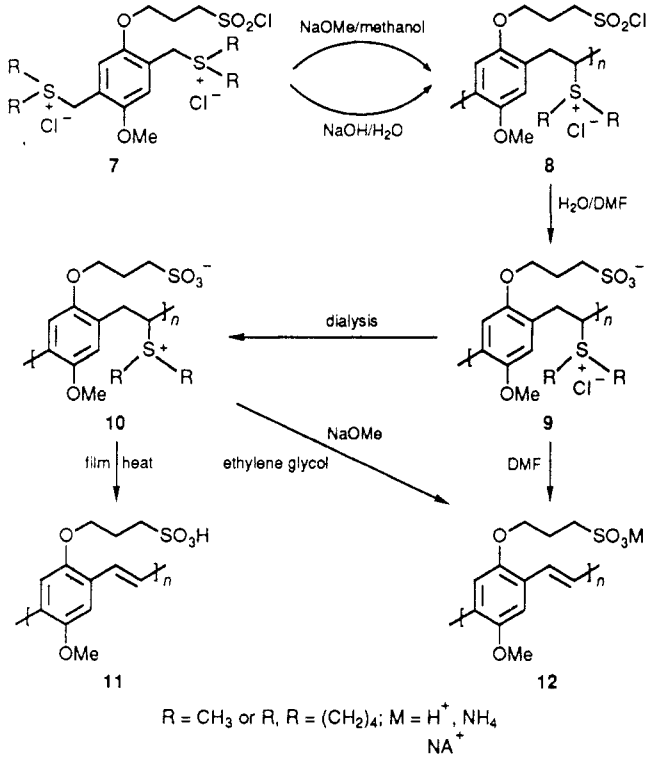
Scheme I



Scheme II



Results and Discussion

Scheme I shows the synthetic route for the monomer **7**. We started from 4-methoxyphenol which was alkylated by 3-chloropropanol in the presence of sodium ethoxide to give 66% of **1**. The synthetic procedures for compounds **2**, **3**, and **4** were adopted from that of the thiophene analogue as reported by our group before.[5] Direct chloromethylation of **4** was unsuccessful. Changes in reaction conditions did not give us the desired material. Therefore **4** was converted first to **5** by treating with thionyl chloride in dry DMF. The sulfonyl chloride **5** was usually obtained in a yellow solid form, but sometimes as a yellow liquid, presumably due to the presence of residual DMF. In both forms, **5** was directly used in the next chloromethylation step to produce the dichloride compound **6** without further purification. Upon treatment with dimethyl sulfide or tetrahydrothiophene, **6** gave the hygroscopic bis(sulfonium) chloride **7** in quantitative yield, where **7** could be purified by recrystallization from methanol/acetone.

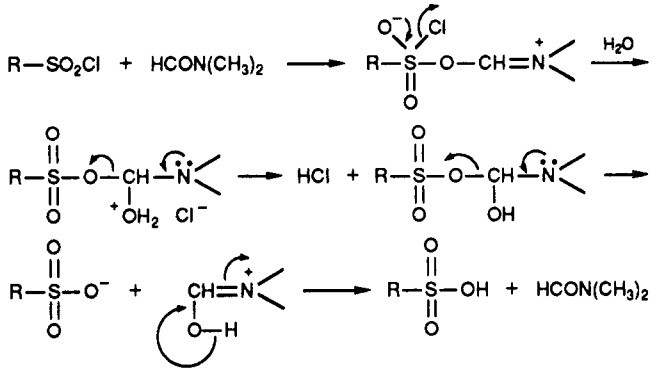
In the previous paper[6] we reported two possible ways to carry out the polymerization of monomer **7**. One was to do a pyridine-catalyzed hydrolysis of **7** in water to give the corresponding pyridinium sulfonate that was then polymerized with aqueous sodium hydroxide; the other was to effect the polymerization first with sodium methoxide in methanol, followed by hydrolysis in water with pyridine. Further investigation proved that when a "chewing-gum"-like viscous gel precursor polymer was obtained, pyridine failed to hydrolyze it; even if the monomer was "hydrolyzed" first, sometimes one still obtained an opaque aqueous solution after polymerization. Those facts clearly indicate that pyridine, as a catalyst, is not strong enough to totally hydrolyze the sulfonyl chloride group in the polymer or even in the monomer under those conditions. Therefore a stronger catalyst or more vigorous conditions were required.

Scheme II shows the polymerization procedure we developed recently for monomer **7**. The monomer **7** was polymerized either in methanol or in water with sodium methoxide or sodium hydroxide, respectively. A viscous gel or "chewing-gum" precursor polymer could be obtained depending on the concentration of the base used in the polymerization processes. As in all other poly(*p*-phenylenevinylene) derivatives, because the monomer **7** goes through a reactive *p*-xylylene intermediate that undergoes an anionic[7] or radical addition polymerization,[8] the purity of the monomer is crucial to produce a narrow-polydispersity, high molecular weight polymer. To get pure monomer **7**, we first purified the bis(chloromethyl) precursor **6** by repeated recrystallization from benzene, followed by conversion to monomer **7** by reaction with a large excess of dimethyl sulfide or tetrahydrothiophene. The resulting monomer **7** was further purified by recrystallization from methanol/acetone.

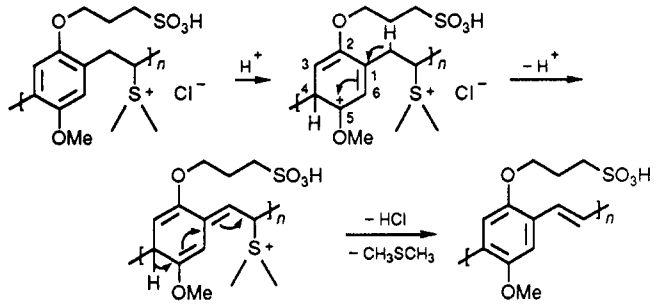
We found that polymer **8** obtained from either water or methanol could be hydrolyzed under vigorous condition by refluxing with DMF/water to give polymer **9**. There was no detectable hydrolysis in the absence of the cosolvent. A rationalization for the hydrolysis is depicted in Scheme III, where DMF serves as a catalyst and a cosolvent. The resulting precursor polymer was usually colorless, but if more than 1 equiv of base was used in the previous polymerization process, the resulting polymer **9** solution was strongly fluorescent pale yellow greenish, due to partial elimination of the sulfonium group. Also under these conditions, polymer **9** was produced in its sodium salt form instead of acid form. After the precursor polymer **9** solution was dialyzed against deionized water, a zwitterionic precursor polymer **10** solution was obtained.

There are three ways to convert the precursor polymer into fully conjugated PPV (see Scheme II). Method A is to heat the precursor polymer film under vacuum at 200 °C for 4 h to give the fully conjugated PPV derivative, polymer **11**, after thermal elimination of dimethyl sulfide or tetrahydrothiophene. This method is the gen-

Scheme III



Scheme IV



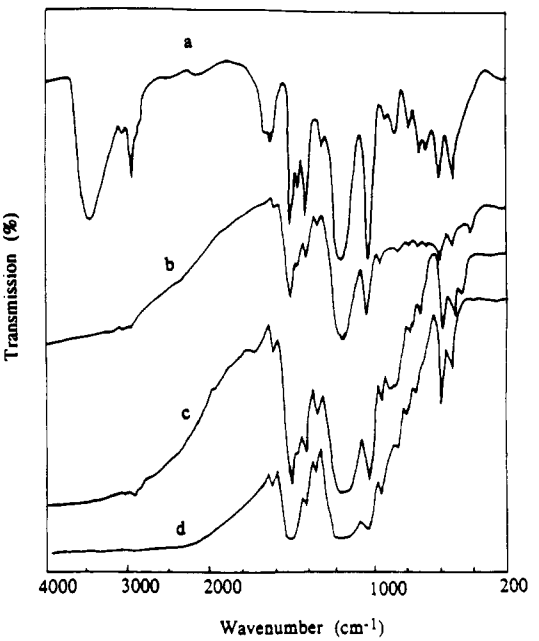


Figure 1. IR spectra of (a) precursor polymer film, (b) polymer 11 film after compensation with NH_3, (c) polymer 12 film, and (d) polymer 11 film.

eral one employed to prepare PPV[8] and its derivatives.[2,3] Method B and method C are similar to the one recently developed in our laboratory for the preparation of soluble dihexyloxy-substituted PPV.[4] A slight difference is that here acid or base is also used besides heat treatment.

In method B, the precursor polymer **9** solution in DMF/H_2O or precursor polymer **10** solution in water was heated to reflux under nitrogen in the presence of a small amount of acid for 4 h to yield a red solution of polymer **12** (in its acid form). The acids that can be used here are nonoxidative strong acids such as hydrochloric acid, dilute sulfuric acid, methanesulfonic acid, trifluoromethanesulfonic acid, etc. Oxidative strong acids, such as concentrated sulfuric acid or nitric acid, produce a black, insoluble material. We also noted if polymer **8** was indeed obtained in its acid form, it could be converted to polymer **12** just by heating in aqueous solution without addition of extra acid, where the acidic proton of the polymer served as a self-catalyst. It was surprising to find that if base was employed instead of acid, no conversion of the precursor polymer to its fully conjugated form was observed in DMF/H_2O even after refluxing for a few hours; also, if the precursor **8** was treated with concentrated acid before it was hydrolyzed, the elimination of the sulfonium salt occurred immediately to yield an insoluble black polymer that could not be hydrolyzed by DMF. Although the details of the acid-catalyzed reaction are still not clear, we propose a possible mechanism as follows (see Scheme IV). A protonation at the 4- or 6-position in the aromatic ring may occur first, followed by loss of the proton in the position α to the sulfonium group to give an unstable methylene cyclohexadiene-type of intermediate which, upon loss of the 4- or 6-position proton and dimethyl sulfide or tatrahydrothiophene, could afford the phenylenevinylene skeleton.

In method C, the precursor polymer **10** was treated with excess sodium methoxide in ethylene glycol and then heated to 190 °C under nitrogen for 26 h to afford a red solution of polymer **12** (in its sodium salt form). After water dialysis, films could be cast at room temperature under nitrogen from aqueous polymer **12** solution obtained from either method B or method C. As judged from the IR and UV–vis spectra of the corresponding polymers, essentially both methods, B and C, resulted in the same polymer (polymer **12**), but in different forms. One is in its acid form, the other in its sodium salt form. Both forms are interchangeable. Since method B is much easier to carry out than method C, polymer **12**, in this paper, hereafter was prepared by method B.

Figure 1 shows the IR spectra of polymers **10**, **11**, and **12**. A broad dispersion peak from 1800 to 4000 cm^{-1}, which is a characteristic of doped conducting polymers, appears in the IR spectra of polymers **11** and **12**. Therefore it seemed to us that some kind of doping processes had occurred in both polymer **11** and **12** films. A similar doping phenomenon has been observed in the synthesis of soluble dibutoxy-substituted PPV with strong acids.[10] After compensation with ammonia vapor, the IR spectra of polymers **11** and **12** exhibited a large decrease in absorption intensity between 1800 and 4000 cm^{-1}. As the precursor polymer was converted into polymer **11** and polymer **12** by either method A or method B, a new weak absorption peak around 960 cm^{-1} was observed in their IR spectra. That peak, a typical out-of-plane bending mode of a trans vinylene C–H group which is normally a strong peak but considerably weaker in substituted PPV's, indicates that polymers **11** and **12** have the *E* configuration in their vinylene units.

The UV–visible spectra (see Figure 2) of polymers **11** and **12** films show a similar pattern: one major broad peak with maximum absorption around 500 nm and one small broad peak with maximum absorption around 720 nm. The latter absorption peak, due to partial doping of the polymer, disappears totally after the polymer is compensated with ammonia vapor. The π–π^* transition onset in both polymer films is around 600 nm (2.07 eV), which is identical with that of alkoxy-substituted derivatives of PPV[2,4] but red-shifted with respect to that of the parent PPV by about 0.43 eV. The UV–visible spec-

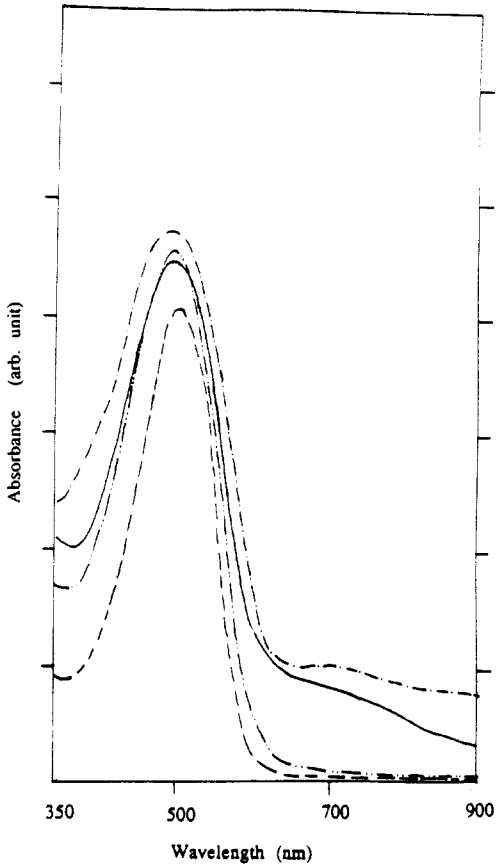
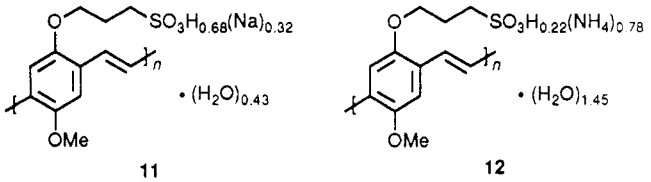


Figure 2. UV spectra of polymer **12** film (– · –), polymer **11** film (—), polymer **11** film after compensation with NH3 (– ·· –), and polymer **12** aqueous solution (– –).

Chart I



11 **12**

trum of an aqueous solution of polymer **12** shows a maximum absorption around 508 nm with a sharp onset at 595 nm and a small tail extending up to 900 nm.

The conductivity of the polymer **11** film is around 2×10^{-6} S cm^{-1} (300 K, air), yet the conductivity of the polymer **12** film, which is relative humidity dependent, ranges from 10^{-4} to 10^{-2} S cm^{-1}. As is observed with other sulfonated polyelectrolytes,[9] both polymers are very hygroscopic. Elemental analysis indicates polymer **11** contains 0.43 mol of water and 0.32 mol of sodium per repeat unit (see Chart I), while polymer **12** has 1.45 mol of water and 0.78 mol of ammonium per repeat unit, where the ammonium ion resulted from the deliberately added ammonia to stabilize the polymer. It has been estimated from GPC using pulluan as a standard that the weight-average molecular weight ($\bar{M}_w$) of polymer **12** is around 1.12×10^6 with a polydispersity of 16.

Although the polymer **12** films cast from aqueous solution can be easily redissolved in water, polymer **11** films are found to be insoluble in any solvent. The reason could be that the high-temperature treatment in the solid state during the formation of polymer **11** may cause some interchain cross-linking, which makes polymer **11** insoluble. The fact that mechanically polymer **11** films are much stronger than polymer **12** films is evidence that some cross-linking has happened in polymer **11** films. Since monomer **7** is unsymmetrically substituted, the regioselectivity of the polymerization, i.e. head-to-head or head-to-tail placement, is still not known. Further investigation of the physical properties of this novel conducting polymer is under way.

Summary

Hydroquinone monomethyl ether was converted in few steps to a monomer of the first water-soluble, substituted poly(phenylenevinylene). The precursor polymer polyelectrolyte could be converted to the conjugated polymer in homogeneous solution as well as in the solid state. The latter process invariably led to insoluble, high strength films, indicating cross-linking. The former process afforded a soluble conjugated polymer that could be cast into films from water. Typical in situ spectroscopic doping studies of conjugated polymer films could be carried out with this polymer. This special dialkoxy PPV could also be doped with Brønsted acids (e.g. HCl) and compensated with ammonia. Subjects to be pursued with this polymer are voltage-dependent ion exchange, transport properties, and electrochromic properties.

Experimental Section

General Information. IR spectra were obtained with a Perkin-Elmer 1330 spectrophotometer and are reported in cm^{-1}. UV–visible spectra were recorded on a Perkin-Elmer Lambda 5 and Lambda 9 spectrophotometers and are reported as λ_{max} in nm. ^{1}H NMR spectra were obtained with a Varian EM 360L (60 MHz) instrument and are reported in δ (ppm) values with TMS as an internal standard (unless otherwise noted). Mass spectra were obtained on a VG 70-250-HF mass spectrometer in either low-resolution electron-impact or chemical ionization. Elemental analyses were conducted by University of California, Microanalysis Laboratory, Berkeley, CA. Measurements of the conductivity were performed by a standard four-probe technique. Unless specified otherwise, reagent grade reactants and solvents were obtained from chemical suppliers and used directly.

3-(4-Methoxyphenoxy)propanol (1). To 200 mL of absolute ethanol was added 10.5 g of sodium pellets (456.5 mmol) at room temperature. After the sodium was completely consumed, a solution of 22.32 g of 4-methoxyphenol (180 mmol) in 80 mL of absolute ethanol was added. The resulting solution was stirred for 10 min followed by treatment with 38.0 mL of 3-chloropropanol (456.5 mmol). The mixture was allowed to reflux for 16 h before the solvent was removed under vacuum, and the residue was taken up in 200 mL of ether. After filtration over charcoal, the filtrate was concentrated to about 25 mL and a large amount of white solids crystallized out to give 21.5 g of pure **1** (66%). Anal. Calcd for $C_{10}H_{11}O_3$: C, 65.93; H, 7.69; Found: C, 65.78; H, 7.74. IR (KBr): 3300, 3050, 2960, 2940, 2880, 2840, 1520, 1480, 1450, 1400, 1300, 1245, 1185, 1065, 1040, 950, 830, 730. ^{1}H NMR (CD_3OD): 1.6–2.0 (q, 2 H), 3.5–4.0 (m, 7 H), 6.7 (s, 4 H). MS (*m/z*, %): 182 (M^+, 41), 124 (100), 109 (61).

3-(4-Methoxyphenoxy)propyl Methanesulfonate (2). To a solution of 5.10 g of 3-(4-methoxyphenoxy)propanol (**1**) (28 mmol) in 20 mL of freshly distilled pyridine was added 3.26 mL of methanesulfonyl chloride in 5 mL of pyridine. The reaction mixture was stirred at room temperature overnight and then poured into a separatory funnel containing 80 mL of water and 80 mL of ether. The layers were separated, and the aqueous layer was extracted twice with 40 mL of ether. The combined organic layers were extracted twice with 40 mL of 10% hydrochloric acid followed by washing twice with 40 mL of H_2O and dried with sodium sulfate for 2 h. After evaporation of the solvent, a light brown oil was obtained which, upon passing through a 16 × 2.5 cm silica gel column using $CHCl_3$ as eluent, gave 6.04 g of light yellow oil (65%). IR (KBr): 3020, 2960, 2940, 2880, 2840, 1600, 1510, 1470, 1450, 1360, 1300, 1240, 1180, 1110, 1060, 980, 950, 830. ^{1}H NMR ($CDCl_3$): 2.0–2.4 (q,

2 H), 3.1 (s, 3 H), 3.8 (s, 3 H), 3.9–4.2 (t, 2 H), 4.3–4.6 (t, 2 H), 6.8 (s, 4 H). MS (*m/z*, %): 260 (M^+, 1), 203 (45), 202 (10), 201 (15), 200 (11), 165 (25), 137 (12), 125 (19), 124 (21), 123 (100), 95 (4).

3-(4-Methoxyphenoxy)propyl Iodide (3). To a solution of 6.75 g of NaI (45 mmol) in 100 mL of acetone was added 3.9 g of **2** (15 mmol). The mixture was allowed to react at room temperature for 24 h. The CH_3SO_3Na that had precipitated was separated by filtration. The filtrate was poured into water and extracted with chloroform, and the organic layer was dried with $MgSO_4$. Evaporation of the solvent afforded 4.073 g of light brown oil (93%). IR (KBr): 3020, 3000, 2950, 2870, 2820, 1600, 1510, 1470, 1450, 1390, 1300, 1230, 1180, 1110, 1040, 830, 740. ^1H NMR ($CDCl_3$): 2.1–2.4 (m, 2 H), 3.2–3.5 (t, 2 H), 3.7–4.1 (m, 5 H), 6.8 (s, 4 H). MS (*m/z*, %): 292 (M^+, 25), 202 (15), 200 (39), 124 (100), 123 (71), 109 (61), 95 (25), 81 (11), 77 (11), 64 (11), 63 (13), 52 (12).

Sodium 3-(4-Methoxyphenoxy)propanesulfonate (4). To 80 mL of an aqueous solution of 15.36 g of Na_2SO_3 (122 mmol) was added 17.8 g of **3** (61 mmol), and the reaction mixture was heated to 70 °C for 45 h. The resulting solution was extracted with $CHCl_3$ to remove unreacted iodide (1.98 g). The aqueous layer was distilled in a rotatory evaporator to remove water. The residue was washed with anhydrous acetone to remove sodium iodide. The remaining solid was a mixture of the desired sodium salt contaminated with excess sodium sulfite and was used in the next step without further purification. For characterization, the mixture was dissolved in water and passed through Amberlite IR-120 (plus) ion-exchange resin. The solution was concentrated under vacuum at 80 °C and was neutralized with 0.5 N NaOH solution. After evaporation of the solvent, 14.38 g of gray-white solid was obtained (88%). IR (KBr): 3020, 2960, 2920, 2880, 2840, 1520, 1480, 1450, 1300, 1250, 1230, 1200, 1120, 1070, 1040, 830, 740, 640. ^1H NMR (D_2O, δ relative to DSS): 2.1–2.4 (q, 2 H), 2.9–3.3 (t, 2 H), 3.8 (s, 3 H), 4.0–4.2 (t, 2 H), 7.0 (s, 4 H).

3-(4-Methoxyphenoxy)propanesulfonyl Chloride (5). To a stirred suspension of 20.5 g of the above mixture in 80 mL of DMF was added dropwise 20 mL of thionyl chloride at 0 °C. After the mixture had been stirred at room temperature for 45 min, it was quenched with 400 mL of ice water and extracted with 300 mL of ether. The ether layer was washed four times with 200 mL of cold water and dried with $MgSO_4$. Evaporation of the solvent afforded 13.3 g of yellow liquid which, on cooling, gave crystalline solid product. IR (KBr): 3050, 3000, 2950, 2880, 2840, 1600, 1510, 1480, 1450, 1380, 1300, 1240, 1170, 1110, 1050, 930, 830, 750, 730, 700. ^1H NMR ($CDCl_3$): 2.2–2.6 (m, 2 H), 3.8–4.3 (m, 7 H), 6.9 (s, 4 H). MS (*m/z*, %): 266 ($M^+ + 2$, 16), 265 ($M^+ + 1$, 5), 264 (M^+, 40), 143 (20), 141 (54), 137 (20), 124 (59), 123 (100), 109 (44), 95 (23).

5-Methoxy-2-(3-(chlorosulfonyl)propoxy)-1,4-xylene α,α′-Dichloride (6). To 150 mL of 37% formaldehyde aqueous solution was added 100 mL of concentrated hydrochloric acid at 0 °C. The mixture was saturated with hydrogen chloride gas for 15 min before addition of 15 g of the above sulfonyl chloride **5** (56.7 mmol) in 80 mL of dioxane. The resulting mixture was allowed to stir at room temperature for 6 h. The white solid that formed was collected by filtration and was recrystallized from benzene to give 17.4 g of white product (92%). Anal. Calcd for $C_{12}H_{15}Cl_3O_4S$: C, 39.83; H, 4.15. Found: C, 40.01; H, 4.22. IR (KBr): 3060, 3000, 2980, 2940, 2880, 2840, 1520, 1470, 1420, 1400, 1360, 1320, 1270, 1240, 1160, 1070, 1050, 1030, 940, 920, 870, 800, 730, 690, 600. ^1H NMR ($CDCl_3$): 2.4–2.8 (q, 2 H), 3.8–4.3 (m, 7 H), 4.6 (s, 4 H), 6.9 (s, 2 H).

5-Methoxy-2-(3-(chlorosulfonyl)propoxy-1,4-xylene-α,α′-bis(tetrahydrothiophenonium chloride) (7). To 922 mg of **6** (2.55 mmol) in 5 mL of acetone and 5 mL of methanol was added 5 mL of tetrahydrothiophene. The mixture was stirred at 50 °C for 24 h under nitrogen. After the solvent was removed, the residue was precipitated with acetone and dried under vacuum to afford 1.041 g of **7** (76%). Compound **7** was further purified by recrystallization from methanol/acetone. Anal. Calcd for $C_{20}H_{31}Cl_3O_4S_3$: C, 44.65; H, 5.77; S, 17.86. Found: C, 44.92; H, 6.01; S, 17.85. IR (KBr): 3000, 2910, 2840, 1510, 1470, 1425, 1400, 1320, 1230, 1190, 1150, 1040, 940, 900, 870, 730, 700, 600. ^1H NMR (CD_3OD): 2.3–2.7 (m, 10 H), 2.9–3.2 (t, 2 H), 3.5–3.8 (m, 8 H), 4.0 (s, 3 H), 4.2–4.5 (t, 2 H), 4.8 (s, 4 H), 7.5 (s, 2 H).

Polymerization of 7. Method A. To a solution of monomer **7** (1.075 g, 2 mmol) in 5 mL of MeOH was added 0.48 mL of 25% NaOMe in MeOH at 0 °C under nitrogen. A viscous gum of **8** was formed immediately. After a reaction time of 15 min, the solvent was decanted and 8 mL of water and 2 mL of DMF were added. The resulting mixture was heated to reflux for 5–10 min to give a clear colorless solution. The solution wad dialyzed against deionized water with Spectropor membrane tubing of 6000 MWCO for 24 h to remove the low molecular weight reactants and products. The precursor polymer **10** was cast into films from aqueous solution. IR (film): 3450 (H_2O), 3080, 3010, 2950, 2880, 1650, 1510, 1470, 1420, 1330, 1210 (broad), 1045, 940, 880, 800, 730, 690, 610, 530. UV (film): 370.

Method B. To a 0.4 N solution of monomer **7** in water was added 1.2 equiv of aqueous sodium hydroxide at 0 °C under nitrogen; a viscous milky gel was formed immediately. The milky gel became a homogeneous solution after being refluxed with a small amount of DMF. Upon water dialysis, an aqueous solution of the precursor polymer **10** was obtained. The film cast from the solution has the same IR spectrum as that from method A.

Conversion of Precursor Polymer into the Substituted PPV. Method A. The precursor polymer **10** was cast into films from aqueous solution. The films were then heated to 200 °C and maintained at this temperature for 4 h in vacuo to yield an insoluble and infusible black film with brilliant appearance. Anal. Calcd for $(C_{12}H_{13.68}Na_{0.32}O_4S)\cdot(H_2O)_{0.43}$: C, 50.57; H, 5.11; Na, 2.58; S, 11.24. Found: C, 50.55; H, 4.98; Na, 2.61; S, 11.52. UV (film): 500, 700. IR (film): 4000–2000 (broad dispersion), 1610, 1520 s, 1410, 1350, 1210 (broad), 1040 s, 960, 850, 800, 750, 600.

Method B. The aqueous solution of the polymer **9** (0.2 N) was treated with a few drops of concentrated hydrochloric acid. The mixture was heated to reflux for 4 h to yield a red solution. After water dialysis, a red aqueous solution of substituted PPV was obtained. Anal. Calcd for $(C_{12}H_{16.34}N_{0.78}O_4S)\cdot(H_2O)_{1.45}$: C, 46.55; H, 6.22; N, 3.53; S, 10.36. Found: C, 46.53; H, 6.11; N, 3.52; S, 10.74. UV: 500, 700 (for film); 508 (for aqueous solution). IR (film): 4000–2000 (broad dispersion), 1610, 1520, 1410, 1350, 1210, 1040, 960, 850, 800, 750, 600.

Method C. An aqueous solution of the precursor polymer **10** (0.2 N) was mixed with the same volume of ethylene glycol and excess of sodium methoxide in methanol. The mixture was heated to the boiling point. After all the water was removed, the temperature of the solution was increased to 190 °C and the solution turned red. The solution was maintained at reflux for 26 h under nitrogen, then cooled, and dialyzed against deionized water for 24 h to afford a red aqueous solution of substituted PPV from which a hygroscopic black film can be cast on a plastic weighing bowl at room temperature in vacuo. The polymers obtained from method C had the same UV and IR spectra as that from method B.

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Water-Soluble Copolymers. 30. Effects of Molecular Structure on Drag Reduction Efficiency

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ABSTRACT: Four series of high molecular weight, water-soluble acrylamide copolymers with specific compositions have been synthesized, characterized, and tested for drag reduction effectiveness. The comonomers sodium acrylate, sodium 2-(acrylamido)-2-methylpropanesulfonate, sodium 3-(acrylamido)-3-methylbutanoate, and diacetone acrylamide were utilized in appropriate molar ratios to provide tailored structures with varying degrees of hydrophobicity, ionic character, and propensity to form inter- or intramolecular associations. Drag reduction properties were measured in a modified rotating disk and a tube flow apparatus. A simple method of analyzing drag reduction performance was developed on the basis of hydrodynamic volume fraction normalization. This method allows comparison of diverse polymer types by efficiency curve superimposition utilizing an empirical shift factor. Drag reduction data were also analyzed by several conventional methods. Results demonstrate the dependence of drag reduction effectiveness on polymer structure as well as the importance of polymer–solvent interactions. Structure-performance analysis suggests that predictive theoretical models might be improved by inclusion of parameters reflective of solvent and associative interactions as well as hydrodynamic volume.

Introduction

It has been known for a number of years that certain additives can reduce energy loss due to friction in turbulent flow.[1] Drag reducing additives include low concentrations of high molecular weight polymers, micellar systems, and suspensions of fibers or other solids.[2] A large number of possible commercial applications for drag reduction (DR) have been the impetus for continued research in this area.[3] Despite the abundance of theoretical, experimental, and practical studies of the phenomenon that have appeared in the literature, many unanswered questions remain and no comprehensive, universally accepted model exists that explains the drag reduction mechanism.[4,5] In particular, the role of polymer microstructure and solvent interactions is not clear.

It is generally thought that macromolecular extension is involved in polymeric drag reduction.[6] Polymer molecules are thought to be elongated by shear forces in the turbulent flow regime. There is disagreement, however, as to whether the friction reduction results from an increased elongational viscosity or from an alteration of the energy balances in turbulent flow.[7,8]

Many researchers accept the proposal put forth by Lumley[9-11] which suggests that a fluid layer of substantially increased viscosity is present in the turbulent flow regime near the wall due to polymer elongation. In the layer of increased viscosity, damping of small dissipative eddies and reduced momentum transport from the buffer zone occur. In the viscous sublayer next to the wall, however, macromolecules are not greatly extended and viscosity is not increased appreciably above that for solvent alone.

Ryskin[12,13] recently developed a predictive theory incorporating Lumley's ideas and his own "yo-yo" model of polymer dynamics. The polymer effect on viscosity enhancement, ζ_{turb}, is given in eq 1,

$$\zeta_{turb} \simeq 0.05\alpha^3 N_A a^3 N^2 C/M_a \quad (1)$$

where N_A = Avogadro's number, M_a = molecular weight repeat unit, a = length of a repeat unit, α = ratio of chain length to that of a fully extended chain, C = polymer concentration, N = degree of polymerization. Ryskin relates ζ_{turb} to Virk's slope increment, δ_v (a measure of drag reduction effectiveness[14]), by eq 2. The δ value used

$$\delta = 2(1 + \zeta_{turb})^{1/2} - 2 \quad (2)$$

by Ryskin in eq 2 is half that of Virk's. Combination of eq 1 and 2 and rearrangement give eq 3, where molecular weight, M, is equal to M_aN. This relationship enables

$$[(\delta^2 + 4\delta)/2]^{1/3} = \alpha\{aN[N_A C/2M]^{1/3}\} \quad (3)$$

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