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Zwitterion Polymerization of Tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium Hydroxide Inner Salt

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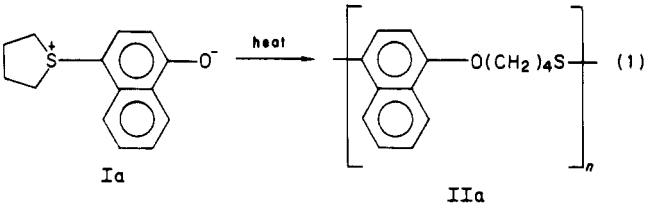
ABSTRACT: The zwitterion tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide inner salt (I) was synthesized from tetrahydrothiophene and 1-naphthol and characterized by ^1H and ^{13}C NMR and IR spectroscopy. Thermal polymerization of the zwitterion was studied over the temperature range 60–200 °C. Polymerization gave a mixture consisting of about three-fourths linear polymer and one-fourth oligomer. The polymer was identified as poly(oxytetramethylenethio-1,4-naphthylene) (II) based on ^{13}C and ^1H NMR and IR. Gel permeation chromatography showed $\bar{M}_n$ to vary with temperature in the range 6300–21 680. NMR identified the linear polymer fraction as consisting of molecules containing 4-hydroxy-1-naphthyl groups at one end and either 3-butenylthio or (4-hydroxybutyl)thio groups at the other end. HPLC fractionation coupled with NMR and mass spectroscopy identified the oligomer fraction as consisting of 91% cyclic oligomers (dimer to pentamer) and 9% linear oligomers. A mechanism is proposed to describe this polymerization. Initiation and propagation proceed by ring-opening nucleophilic attack by the arene oxide anionic center of one zwitterion on the α-carbon of the tetrahydrothiophenium ring of a second zwitterion. Termination occurs by cyclization, β-elimination, and substitution.

Introduction

The zwitterion polymerization of many different pairs of electrophilic (E) and nucleophilic (N) reactants, e.g., acrylic acid and 2-methyl-2-oxazoline, have been studied.[1,2] The generally accepted reaction mechanism involves the initial formation of a genetic zwitterion intermediate $^+NE^-$ from reaction of the electrophile and nucleophile followed by polymerization of the zwitterion. Only low molecular weight (typically 1000–3000) polymers were obtained in all zwitterion polymerizations with one notable exception. The exception was the thermal polymerization of various tetrahydrothiophenium–arene oxides studied by Hatch and Schmidt and co-workers.[3-7] In addition to higher molecular weights (>10 000), the tetrahydrothiophenium–arene oxides differed from the other zwitterion polymerizations in that the genetic zwitterion was sufficiently stable to be isolated. Although the polymerization of a number of tetrahydrothiophenium–arene oxides have been studied, there have been no detailed studies of the reaction mechanism. We have recently initiated an effort to elucidate the polymerization mechanism in these systems.[8] The present paper describes our studies on the synthesis of the zwitterion tetrahydro-1-(4-hydroxy-1-naphthyl)-thiophenium hydroxide inner salt (I) and its polymerization to poly(oxytetramethylenethio-1,4-naphthylene) (II). Ia and IIa will be referred to as the naphthyl zwitterion (or monomer) and naphthyl polymer, respectively, throughout the remainder of this paper.

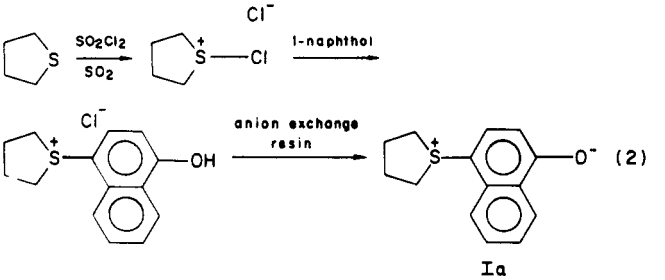


(1)

Ia IIa

Experimental Section

Synthesis of Naphthyl Zwitterion. The naphthyl zwitterion is most conveniently formed by reaction of 1-naphthol with the 1:1 complex of tetrahydrothiophene and chlorine according to the scheme



(2)

Ia

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A solution of 92.6 g (1.05 mol) of tetrahydrothiophene and 0.01 g iodine over dry nitrogen was cooled to −40 °C with dry ice–methylene chloride and then 300 g of sulfur dioxide was condensed into the solution through a dry ice–methylene chloride cooled condenser. About 20 g of gaseous HCl was dissolved in the solution followed by the addition of 135.0 g (1.00 mol) of sulfuryl chloride at a rate to maintain the temperature below −15 °C. 1-Naphthol (144.2 g, 1.00 mol) was added to this solution, which was then allowed to warm to reflux. After refluxing for 3 h, water (5 mL) was added and then about 200 mL of sulfur dioxide removed under vacuum. Acetone (1 L) was added, the precipitated solid was isolated and dissolved in methanol (1.2 L). The methanol solution was treated with Dowex-2 anion exchange resin (hydroxide form) to increase its pH to 10.5 and about 1 L of solvent removed under vacuum. The addition of acetone gave 95.4 g (33.6% yield) of the crystalline naphthyl zwitterion as a trihydrate.

The crude naphthyl zwitterion, a pale yellow solid, was recrystallized from ethanol and diethyl ether. To a 25% solution of the naphthyl zwitterion in ethanol, diethyl ether was added at ambient temperature until the solution turned slightly cloudy and then the solution was maintained overnight at 0 °C. Needle-shaped, white crystals were filtered and more ether was added to the filtrate, which was again maintained overnight at 0 °C. Three crops of crystalline zwitterion were obtained in this manner. The second crop was used in our experiments after drying overnight in a desiccator in the dark at atmospheric pressure at ambient temperature. The purified naphthyl zwitterion, which is sensitive to heat and light, was stored in the dark in the refrigerator.

Polymerization. Polymerization of the naphthyl zwitterion was studied over the temperature range 60–200 °C under both sealed-tube and continuous-vacuum conditions. In the sealed-tube method, the naphthyl zwitterion (0.2 g) was placed in a polymerization tube, evacuated at about 1 torr for 15 min, and sealed under vacuum. The polymerization tube was covered with aluminum foil (to keep out light) and then heated at the reaction temperature for the specified time. Water condensed at the top of the polymerization tube as the zwitterion lost its water of hydration upon reaction. The polymerization tube was broken and the light yellow reaction mixture stirred for 4 hours with methylene chloride. The naphthyl polymer, which precipitated as a white solid, was filtered and then washed with methylene chloride followed by methanol. The oligomeric methylene chloride soluble products were recovered by evaporation of the solvent. Both products were dried overnight in a vacuum oven (ca. 1 torr) at 40 °C. The experimental procedure was the same in the continuous-vacuum method except that the polymerization tube was not sealed but was under continuous vacuum (ca. 1 torr) throughout the reaction to continuously remove the water of hydration from the reaction mixture. There was a quantitative conversion of zwitterion to polymer plus oligomer in all instances except for reaction at 60 °C under continuous vacuum.

Acetylation of Naphthyl Polymer. The naphthyl polymer (0.2 g) was dissolved in 1,1,2,2-tetrachloroethane (2 mL) and pyridine (0.06 g) added with stirring. Acetyl chloride (0.06 g) in 1,1,2,2-tetrachloroethane (1 mL) was added with stirring to the polymer solution at ambient temperature. After the reaction mixture was stirred for 4 h, it was added to diethyl ether and the resulting precipitate filtered off, washed with water followed by acetone, and dried overnight in a vacuum oven (ca. 1 torr) at 45 °C.

High-Performance Liquid Chromatography (HPLC). Analytical HPLC of the CH_2Cl_2-soluble products was performed at ambient temperature with a Waters system consisting of a μ-Porasil column, an M-6000 solvent delivery unit, a U6K universal chromatography injector, and a 450 variable-wavelength UV monitor with an 8-μL flow-through cell. The mobile phase was cyclohexane–CH_2Cl_2 (70:30) at a flow rate of 2 mL/min maintained by a pressure of 500–1000 psi. All solvents (HPLC grade, Fisher) were filtered (Millipore) prior to use. The recorder chart paper speed was 0.5 in./min. Sample size was in the range 1–10 μg of material injected in volumes of 1–25 μL of mobile phase. The UV detector was set at 254 nm at 0.1 AUFS (absorbance units for full scale) for detection of the aromatic moiety.

The CH_2Cl_2-soluble products were fractionated by preparative HPLC with a Waters Prep LC system 500 using a PrePack-500 silica column with cyclohexane–CH_2Cl_2 (75:25) as the mobile phase. A solution of the products, 0.85 g in 15 mL of mobile phase, was injected into the column and eluted at a flow rate of 50 mL/min. Fractions of 75 mL were collected, and every other fraction was analyzed for purity by analytical HPLC. With the elution of successive components, the polarity of the mobile phase was gradually increased by increasing the CH_2Cl_2 content in 5% increments. Pure fractions (i.e., fractions containing one component as determined by HPLC) of the same component were combined, concentrated with a rotary evaporator under reduced pressure, and dried in a vacuum oven at 40 °C overnight.

Spectroscopic Analysis. IR spectra of the naphthyl zwitterion and polymer were recorded on a Beckman 4260 IR spectrometer using thin-film samples on NaCl plates. The zwitterion was deposited as a thin film on the NaCl plate from a methanol solution; the solvent was evaporated in a vacuum desiccator (ca. 5 torr) at ambient temperature for 1 h. The polymer was deposited from bromobenzene with solvent evaporation in a vacuum oven (ca. 1 torr) at 50 °C overnight. ^1H (200.1 MHz) and ^{13}C (50.3 MHz) NMR spectra were recorded on an IBM WP 200SY FTNMR spectrometer using a 5-mm dual $^{13}C/^1H$ probe. ^1H NMR of the monomer was obtained at 27 °C with a 5% (w/v) solution in Me_2SO-d_6 with Me_4Si as an internal standard. ^1H NMR of the polymer was obtained at 60 °C with a 5% (w/v) solution in 1,1,2,2-tetrachloroethane-d_2 (TCE). ^1H NMR spectra of the oligomer samples were obtained at 25 °C with 2–8% (w/v) solutions in $CDCl_3$. ^{13}C NMR spectra were obtained with more concentrated solutions (10%) for most samples. Me_4Si was present as an internal standard for both ^1H and ^{13}C NMR. The acquisition parameters for ^1H NMR were 30° pulse angle, 10-s total delay between pulses, and 128–4000 total acquisitions. The acquisition parameters for ^{13}C NMR were 30° pulse angle, 2.65-s total delay between pulses, and 16 400–36 270 total acquisitions. Data were acquired and Fourier transformed in 16K. Mass spectroscopic analysis of the oligomer fractions was performed on a ZAB-HF instrument.

Gel Permeation Chromatography (GPC). GPC of the reaction mixture obtained by heating the naphthyl zwitterion was carried out on a Waters 150C instrument using 1,2,4-trichlorobenzene at 135 °C as the mobile phase. The stationary phase consisted of a set of two Shodex A80M/S and one Shodex A802S cross-linked polystyrene columns covering the molecular weight range 10^2–10^7. Butylated hydroxytoluene (2,6-di-*tert*-butyl-4-methylphenol) (BHT) was added to the samples at 0.1% concentration prior to injection to avoid the possibility of vinyl polymerization since the polymer contained olefinic end groups. The GPC calibration was based on polystyrene standards.

Thermal Analysis. The water of hydration of the naphthyl zwitterion was determined by carrying out its polymerization in a thermogravimetric analysis (TGA) experiment using a Dupont 990 thermal analyzer coupled to a 950 thermogravimetric analyzer module. The zwitterion (10–15 mg) was weighed to the nearest 0.01 mg at ambient temperature in an aluminum cup in the TGA module, heated to 175 °C at a rate of 5 °C/min, held at 175 °C until a constant weight was observed, cooled, and weighed at ambient temperature to obtain the water loss due to polymerization. The water of hydration values obtained in this manner were precise to within ±0.02 mol water. Differential scanning calorimetry of the naphthyl polymer was carried out with the Dupont 990 coupled with a 910 differential scanning calorimeter module. The polymer sample (7 mg) was compression sealed in an aluminum pan and heated at 10 °C/min. The TGA and DSC results were independent of whether an air or nitrogen atmosphere was used.

Results and Discussion

Identification of Naphthyl Zwitterion. The structure of the naphthyl zwitterion was established by IR and NMR (^1H and ^{13}C) spectroscopy and TGA. The zwitterion, like many other tetrahydrothiophenium–arene oxides,[3] is formed as a hydrate with the water of hydration stabilizing the ionic center(s). The only tetrahydrothiophenium–arene oxides that are anhydrous are those that are sufficiently stabilized by electron-withdrawing substituents, e.g., the zwitterion derived from 2,6-dichlorophenol.[5] TGA

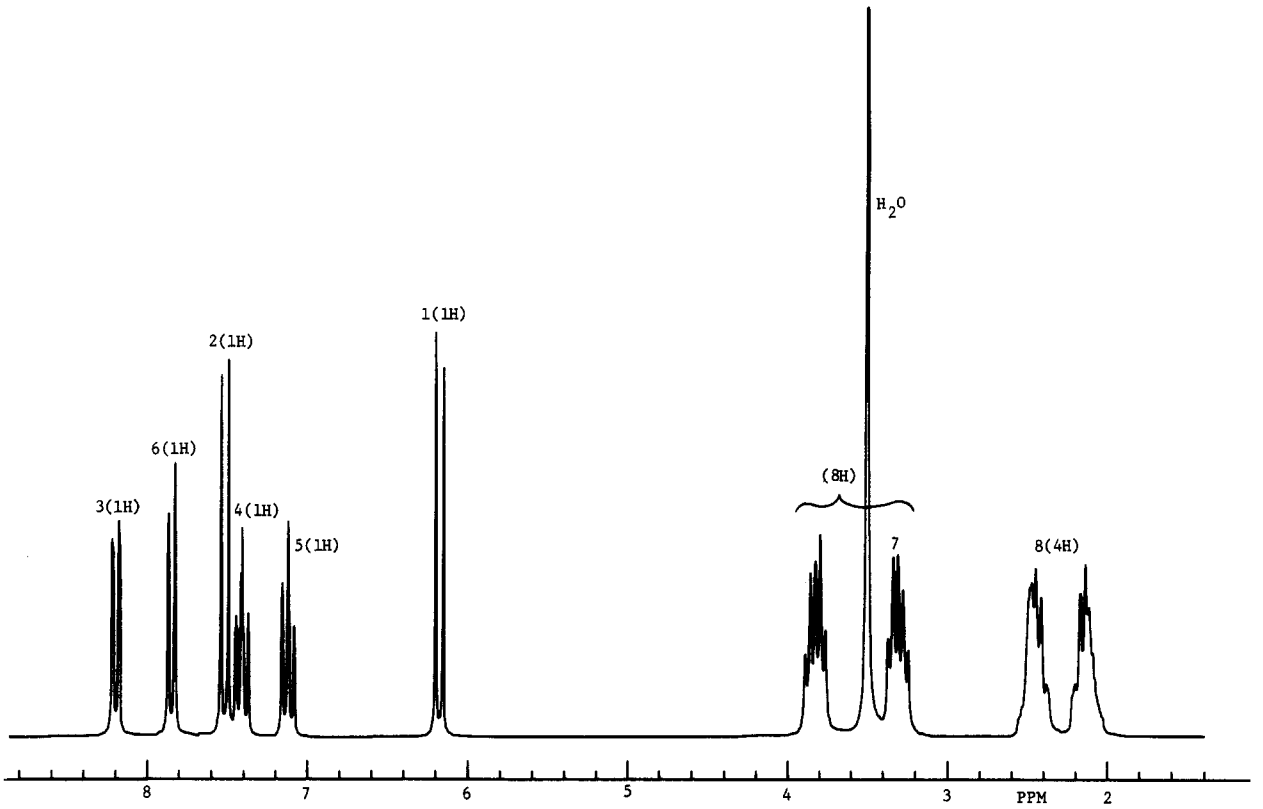
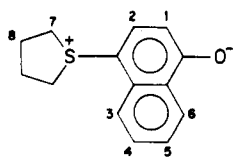


Figure 1. 200.1-MHz ^1H NMR spectrum of naphthyl zwitterion.

showed the crude naphthyl monomer to contain 3.00 (mol water)/(mol zwitterion) whereas the first and second crops obtained by recrystallization contain 2.50 and 2.00 mol water, respectively. The second crop, the zwitterion dihydrate, was used in all polymerization studies. We observed that recrystallizations of the crude zwitterion consistently yielded the dihydrate as the second crop. Further, the zwitterion dihydrate was stable as a dihydrate when stored in the refrigerator over a period of at least several months. The recrystallized zwitterion was dried (5 h at ca. 1 torr at ambient temperature) to yield a very pale yellow crystalline solid containing 0.50 mol water without causing the zwitterion to polymerize. The hemihydrate had the same ^1H NMR spectrum as the zwitterion dihydrate except for the signal area for water. However, the completely dehydrated zwitterion cannot be obtained. Drying a sample of the dihydrate in a vacuum desiccator (ca. 1 torr) at ambient temperature for 40 h resulted in quantitative removal of water with 10% conversion of zwitterion to polymer.

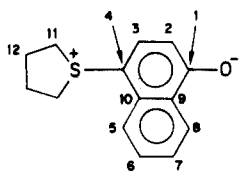
The ^1H NMR spectrum of the naphthyl zwitterion is shown in Figure 1. The signal assignments shown in Ib were based on the chemical shift values in relation to those for protons in analogous environments,[9,10] the observed



Ib

splitting patterns, signal areas, and the effect of added D_2O on ^1H NMR signals. The ^1H NMR spectrum, consistent with structure I, showed some interesting features. The chemical shifts of the α- and β-protons of the tetrahydrothiophenium ring (protons 7 and 8, respectively) were similar to those observed by Schmidt and co-workers[11] for other S-substituted tetrahydrothiophenium salts. Geminal protons at both the α- and β-positions were not equivalent due to noninversion at sulfur, i.e., geminal α- and β-protons were either cis or trans to the naphthalene ring. Thus, the geminal α-protons had different chemical shifts and coupled with each other. Each was coupled separately with the two different geminal β-protons and vice versa for the β-protons. The signal for the water of hydration, observed as a singlet at 3.5 ppm, was not base line resolved from the signals for protons 7. Integration yielded a signal area of 8 for the 3–4 ppm region, consistent with the dihydrate structure for the naphthyl zwitterion obtained from TGA measurements. This interpretation was verified by the addition of sufficient D_2O to the NMR sample to exchange the hydrate protons and move the resulting free H_2O signal downfield to 4.4 ppm (resolved from the signals for protons 7). The signal area for the 3–4 ppm region decreased from 8 to 4 under these conditions.

The proton-decoupled ^{13}C NMR spectrum of the naphthyl zwitterion also supported structure I. The carbon signals were assigned as shown in Ic based on the



Ic

chemical shift values for similar carbons,[10,12] single-frequency off-resonance decoupling (SFOR) experiments, and data for several other tetrahydrothiophenium–arene oxides (those based on phenol and 3,5-dichloro-, 2-methyl-, 3-methyl-, 4-methyl- and 2-(2-hydroxyethoxy)phenols).[8,13] The ^{13}C NMR of all of these zwitterions showed a large upfield shift (>10–15 ppm) for C-4 relative to the expected value based on the additive effects of substituents on the aromatic ring.[10,12] Some of the zwitterions also showed a

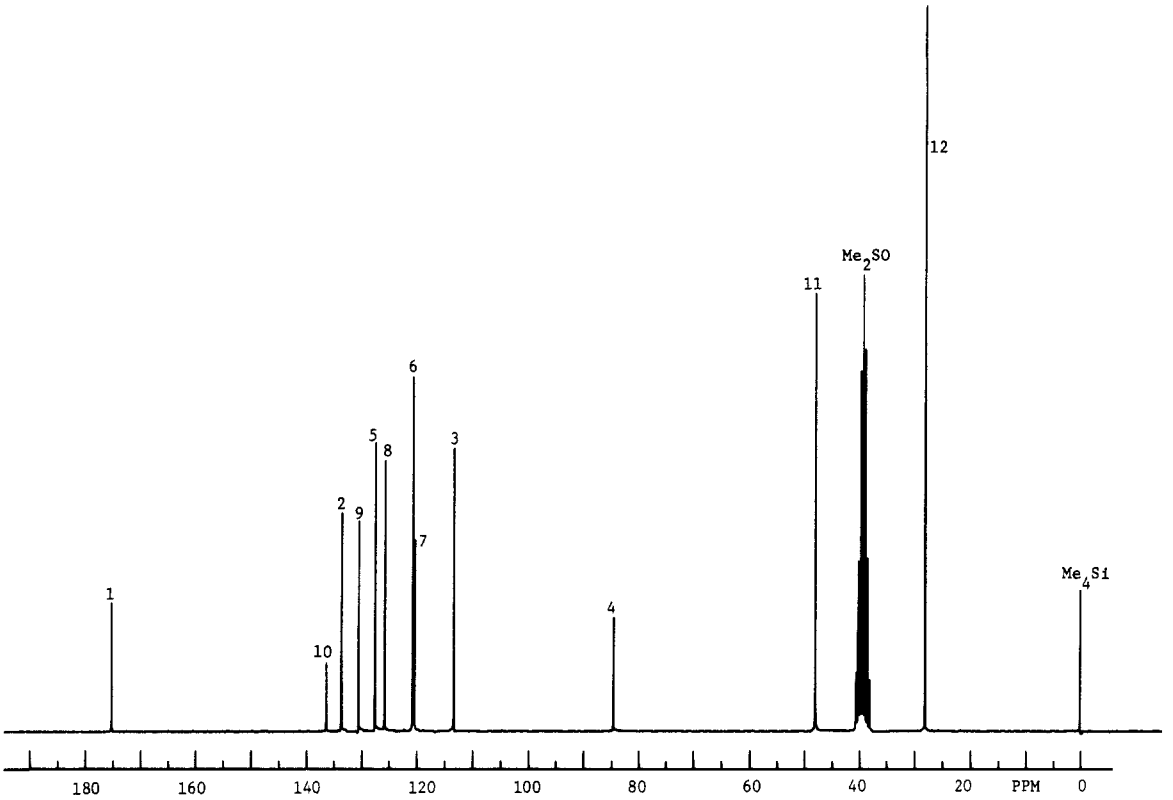
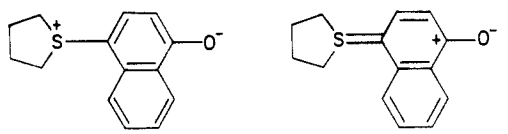


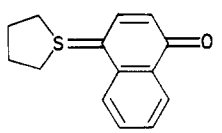
Figure 2. 50.3-MHz ^{13}C NMR spectrum of naphthyl zwitterion.

downfield shift for C-1 but that effect was much smaller than for C-4. Direct calculation of the chemical shift for C-1 and C-4 of the naphthyl zwitterion could not be made since the appropriate substituent chemical shift parameters were not available. However, chemical shifts of 174.0 and 113.5 ppm were calculated for C-1 and C-4, respectively, assuming that the substituent parameters for substituted benzenes were applicable to substituted naphthalenes and the substituent parameters for Me_2S^+ and ONa simulate those for the tetrahydrothiophenium ring and O^-, respectively. The observed chemical shifts for C-1 and C-4 were 175.3 and 84.6 ppm, respectively. Thus, C-4 exhibited an upfield shift of 28.9 ppm while C-1 exhibited no significant shift. The very large shift of the C-4 signal from the calculated value may indicate a considerable contribution of quinoid-type resonance forms Id and/or Ie to



Ia

Id



Ie

the structure of the zwitterion. The lack of a shift in the C-1 signal may indicate that the water of hydration is primarily associated more with one of the charged centers (O^-?) than both.

The IR spectrum of the naphthyl zwitterion showed many absorption peaks. Some of the peaks were easily assigned:[10,16] 3600–2800 (H_2O), 3050 (aromatic C–H), 3010, 2950, 2880 (aliphatic C–H), 1555, 1505 (aromatic C–H), 880, 830, 780, 765 cm^{-1} (aromatic C–H). Absorptions at 1460, 1421, 1360, 1329, 1276, 1190, 1160, 1134, 1028, and 955 cm^{-1} were compatible with structure I and attributed to aromatic C–C, C–O, methylene twisting and wagging vibrations, aromatic C–H in-plane bending vibrations, S–CH_2, and CH_2 ring bending vibrations. A strong absorption at 1614 cm^{-1} was more difficult to assign. It could be assigned as an aromatic overtone peak were it not a lone, strong peak. Overtone peaks typically occur as a group of several weak absorption peaks, considerably weaker than the observed peak at 1614 cm^{-1}. The strong absorption at 1614 cm^{-1}, in the carbonyl region, is compatible with resonance forms Id and Ie contributing to the structure of the naphthyl zwitterion. (We have observed a corresponding absorption in the carbonyl region for other tetrahydrothiophenium–arene oxides.) Thus, both ^{13}C NMR and IR data support the importance of the quinoid structure. There are literature references to the importance of similar quinoid-type resonance; e.g., (*p*-hydroxyphenyl)dimethylsulfonium salts had enhanced stability toward nucleophilic attack and were more acidic than the meta isomer.[14,15] However, the existence of the naphthyl zwitterion as a stable dihydrate indicates that the charged structure Ia probably contributes as much if not more than Id and Ie.

Characterization of the Polymer Fraction. Heating the white crystalline naphthyl zwitterion either under continuous vacuum or in a sealed tube yielded a light yellow reaction mixture that was insoluble in DMF, Me_2SO, and methanol (which are good solvents for the zwitterion), partially soluble in methylene chloride, and completely soluble in hot bromobenzene, 1,2,4-trichlorobenzene, and 1,1,2,2-tetrachloroethane. The absence of any methanol-soluble fraction indicated the complete conversion of zwitterion. The reaction products were extracted with methylene chloride to yield CH_2Cl_2-insoluble polymer and CH_2Cl_2-soluble oligomer fractions. Comparison of the gel permeation chromatograms of the original mixture of reaction products and the isolated

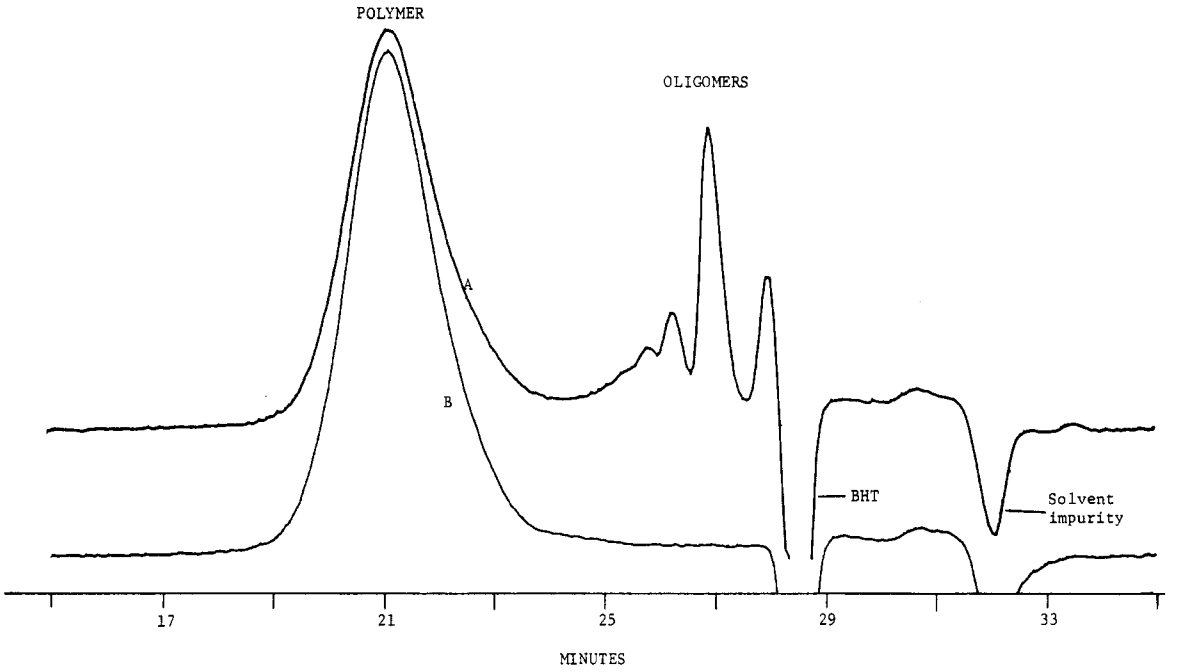
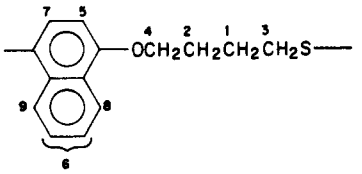


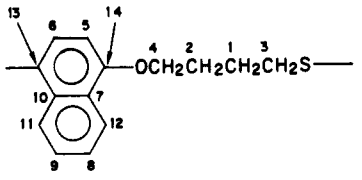
Figure 3. GPC of naphthyl polymer prepared at 135 °C: (A) polymerized reaction mixture; (B) polymer fraction (CH_2Cl_2-insoluble fraction).

CH_2Cl_2-insoluble fraction indicated that the extraction procedure separated oligomer from polymer.

In a typical polymerization, the polymer fraction accounted for about two-thirds to four-fifths of the total products as shown by GPC as well as methylene chloride extractions (Table I). The polymer fraction had $\bar{M}_n$ values as high as 21 160 depending on reaction temperature. $\bar{M}_n$ for the oligomer was in the range 335–460 (Table I). The polymer was characterized as structure II by elemental analysis, IR, and NMR. The elemental analysis (Found: C, 73.27; H, 6.01; S, 13.99) was in good agreement with that calculated for II (Theory: C, 73.01; H, 6.12; S, 13.92). Figure 4 shows the ^1H NMR spectrum of the naphthyl polymer synthesized at 135 °C with various signals for the repeat unit assigned as shown in IIb based on chemical



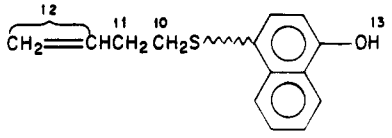
IIb



IIc

shift values,[10,14] splitting patterns, and signal areas. The ^{13}C NMR (Figure 5) signal assignments shown in IIc were based on chemical shift values and SFOR experiments.[8,10,13,17] The signals at 73.8, 79.5, and 99.4 ppm were due to impurities in the solvent. The assignments of some signals were somewhat arbitrary—8 and 9 and possibly 11 and 12 might be interchangeable. It is worth noting that the chemical shift for the C–S carbon signal did not deviate from its expected value, as was the case for the zwitterion. The infrared spectrum showed absorptions at 3060 (aromatic C–H), 2940, 2865 (aliphatic C–H), 1585, 1505 (aromatic C–C), 1264, 1083 (C–O), 810, 760 cm^{-1} (aromatic C–H). Additional absorptions at 1453, 1424, 1365, 1319, and 1235 cm^{-1} are consistent with C–O, CH_2, aromatic C–H, S–CH_2, and other moieties of structure II.

Polymer End Groups. The ^1H and ^{13}C NMR spectra provided evidence for the identities of the polymer end groups. Several signals (10–13) in the ^1H NMR spectrum (Figure 4) of the polymer synthesized at 135 °C were assigned to 3-butenylthio and 4-hydroxy-1-naphthyl end groups as shown in IIIa, where ~~~ represents the repeat

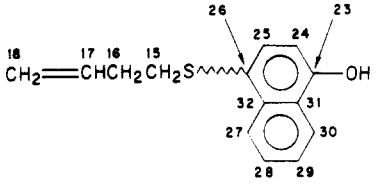


IIIa

unit of the polymer (structure II). The 3-butenylthio and 4-hydroxy-1-naphthyl end groups will subsequently be referred to as olefinic and naphtholic end groups, respectively. The presence of olefinic protons was confirmed by reacting the polymer with bromine. The ^1H NMR of the brominated polymer showed no signals in the olefinic region, with signal 12 being replaced by a multiplet at 3.37 ppm (due presumably to $CH_2BrCHBr$ protons). (The spectrum also showed minor changes indicative of some bromine substitution of the CH_2S and aromatic protons.) The OH signal was difficult to observe unless both the polymer sample and NMR solvent were thoroughly dried. It was sensitive to temperature and exchanged with D_2O. Infrared spectroscopy also identified olefinic end groups as absorption peaks were observed at 1615 (C=C stretching) and 920, 960 cm^{-1} (CH out-of-plane bending). Absorption by OH was not identified, probably due to the high molecular weight of the polymer. HO absorption peaks were observed for the lower molecular weight polymer samples (see below).

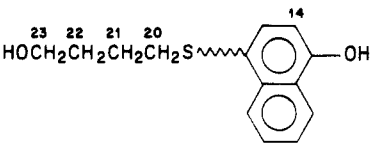
Signals in the ^{13}C NMR spectrum (Figure 5) also supported the olefinic and naphtholic end group assignments as shown in IIIb.

The olefinic and naphtholic end groups were observed as the predominant end groups of the naphthyl polymers



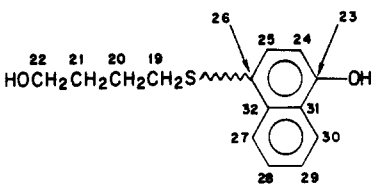
IIIb

synthesized at 135 and 200 °C under sealed-tube conditions and for all polymers synthesized under continuous-vacuum conditions. However, polymers synthesized at 60 and 80 °C under sealed-tube conditions showed NMR signals for (4-hydroxybutyl)thio end groups instead of the olefinic end groups; signals for the repeat unit and naphtholic end groups were the same as in the polymers synthesized at 135 and 200 °C. The 4-(hydroxybutyl)thio end groups will subsequently be referred to as alcoholic end groups. The various end group signals in the ^{1}H NMR spectrum (Figure 6) of the polymer synthesized at 60 °C are shown in IVa.



IVa

The absence of signals for the two OH protons were ascribed to exchange which resulted in a very broad undetected signal. However, subsequent acetylation of IV (see below) supported the presence of alcoholic and naphtholic protons. ^{13}C NMR (Figure 7) gave further evidence for structure IV with the end group signals assigned as shown in IVb. The infrared spectrum of the polymer synthesized



IVb

at 60 °C showed broad absorptions at 3320 and 3560 cm^{-1} that were assigned to alcoholic and phenolic OH groups. The naphthyl polymer synthesized at 100 °C consisted of a mixture of structures III and IV in the approximate ratio 1:2 as determined by the ^{1}H NMR signal areas for olefinic and OCH_2 protons.

To obtain further evidence for naphtholic and alcoholic end groups, polymer samples synthesized at 60 and 200 °C under sealed-tube conditions were acetylated with acetyl chloride and pyridine in 1,1,2,2-tetrachloroethane. NMR analyses of the acetylated products were completely compatible with structures III and IV for the end groups of the 200 and 60 °C polymers, respectively. The ^{1}H NMR spectrum of the acetylated product from the 60 °C polymer showed signals due to main-chain protons similar to those in Figure 6, two singlets (2.43 and 1.98 ppm, respectively) for acetoxyl methyls of naphtholic and alcoholic end groups, multiplets for the OCH_2 (3.99 ppm), CH_2CH_2 (1.70 ppm) and CH_2S (2.85 ppm) protons of the alcoholic end group, and two doublets (7.20 and 7.89 ppm) for aromatic protons ortho and meta to the acetoxyl group. Further support for alcoholic and naphtholic end groups came from ^{13}C NMR data. The ^{13}C NMR spectrum of the acetylated product was similar to that shown in Figure 7 with respect to the main-chain carbon signals although significant chemical shift changes for the carbons of the end groups were observed. The acetoxyl methyl and carbonyl carbons of the naphtholic end group were observed at 20.8 and 169.0 ppm, respectively. The corresponding carbons of the acetylated alcoholic end group appeared at 20.7 and 170.7 ppm.

The ^{1}H NMR spectrum of the acetylated product from the 200 °C polymer showed a singlet (2.43 ppm) for acetoxyl methyl protons, multiplets (5.05 ppm) for CH_2=CH, and two doublets (7.20 and 7.89 ppm) for the aromatic protons ortho and meta to the acetoxyl group. The ^{13}C NMR spectrum was similar to that of the 60 °C acetylated polymer with respect to the main chain and naphtholic end group signals; signals were observed at 115.8 and 136.5 ppm for the CH_2=CH end group carbons.

Characterization of Oligomer Fraction. The methylene chloride soluble oligomer fraction of the reaction products from the polymerization of the naphthyl zwitterion at 135 °C under sealed-tube conditions was characterized by HPLC. The oligomer fraction constituted less than one-third of the reaction products. Figure 8 shows the analytical HPLC with the percentage of each fraction calculated by assuming all components had the same extinction coefficient at 254 nm. Preparative HPLC of the oligomer fraction allowed the isolation of each of the 6 fractions in pure form as shown by analytical HPLC. ^{1}H and ^{13}C NMR and mass spectroscopy were used to characterize each of the isolated fractions. NMR showed that fractions 1–4 were cyclic oligomers since both the ^{1}H and ^{13}C NMR spectra showed signals only for the repeat unit. No signals were observed for any end groups. These products were sufficiently low in molecular weight ($\bar{M}_n$ for the oligomer fraction = 380) that end groups would be observed under the NMR acquisition conditions (6–8% (w/v) sample concentration with 128 and 10 000–32 000 acquisitions for ^{1}H and ^{13}C NMR, respectively). Fractions 1, 2, 3 and 4 were assigned as cyclic dimer, trimer, tetramer, and pentamer, respectively. Mass spectroscopy by both electron-impact and positive chemical ionization verfied this assignment for fractions 1, 2, and 3 by yielding molecular weights of 460, 690, and 920, respectively (calculated values: 460, 690, and 920, respectively, for dimer, trimer, and tetramer). Mass spectroscopy by electron-impact was unsuccessful for fractions 4–6 as volatilization could not be achieved. Positive chemical ionization of fraction 4 gave a molecular weight of 1118 while the cyclic pentamer would have a molecular weight of 1150. The difference in calculated and observed molecular weights corresponded to one sulfur atom and is ascribed to fragmentation at the higher temperature involved in vaporizing fraction 4.

The chemical shifts for the various signals in the ^{1}H NMR spectra of fractions 1–4 were within 0.22 ppm of the corresponding signals of the repeat unit of the linear polymer except for the cyclic dimer, which showed somewhat larger differences, the largest difference being 0.55 ppm for the OCH_2 protons. The chemical shift differences were ascribed to ring-current effects, which would be expected to be greater for smaller sized cyclics. The difference in ^{13}C chemical shifts between cyclic oligomer and polymer repeat unit followed a similar pattern. The differences were less than 0.7 ppm, with the largest differences being for the cyclic dimer.

The two minor products (fractions 5 and 6), constituting only 9.2% of the oligomer fraction and about 2% of the total reaction product, showed complicated NMR spectra. The major signals had chemical shifts similar to those of the polymer repeat unit; the differences in ^{1}H and ^{13}C chemical shifts were less than 0.1 and 0.8 ppm, respec-

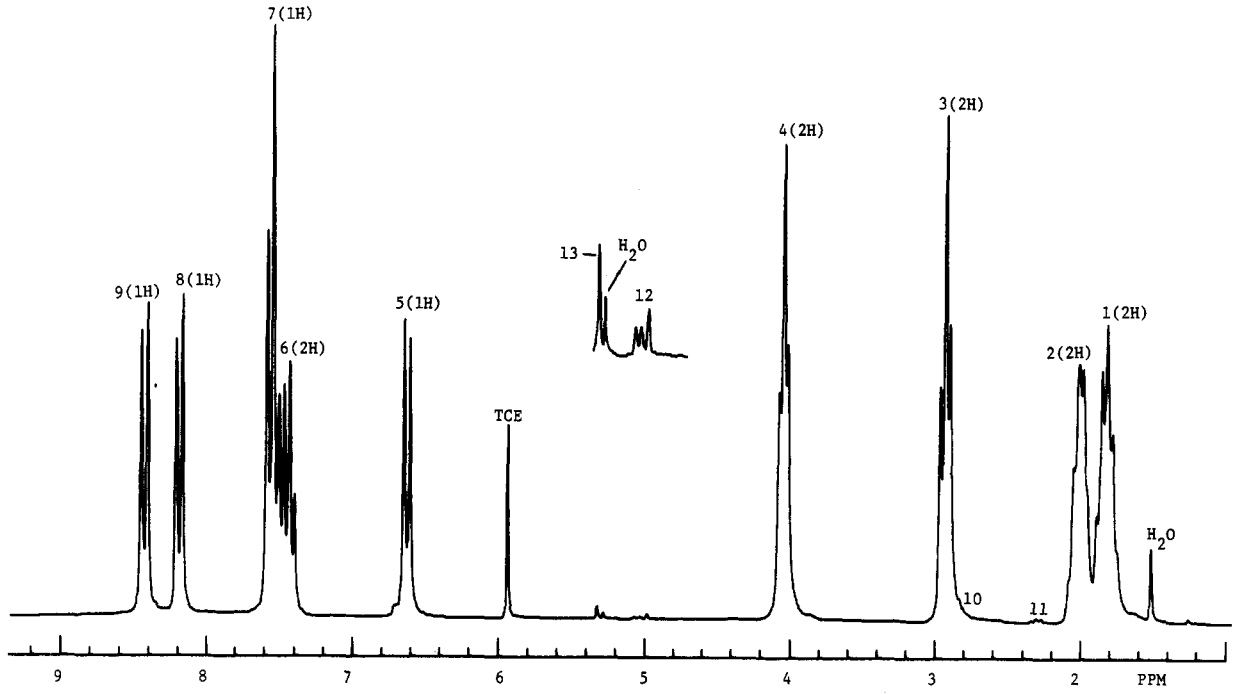


Figure 4. 200.1-MHz ^1H NMR spectrum of naphthyl polymer prepared at 135 °C.

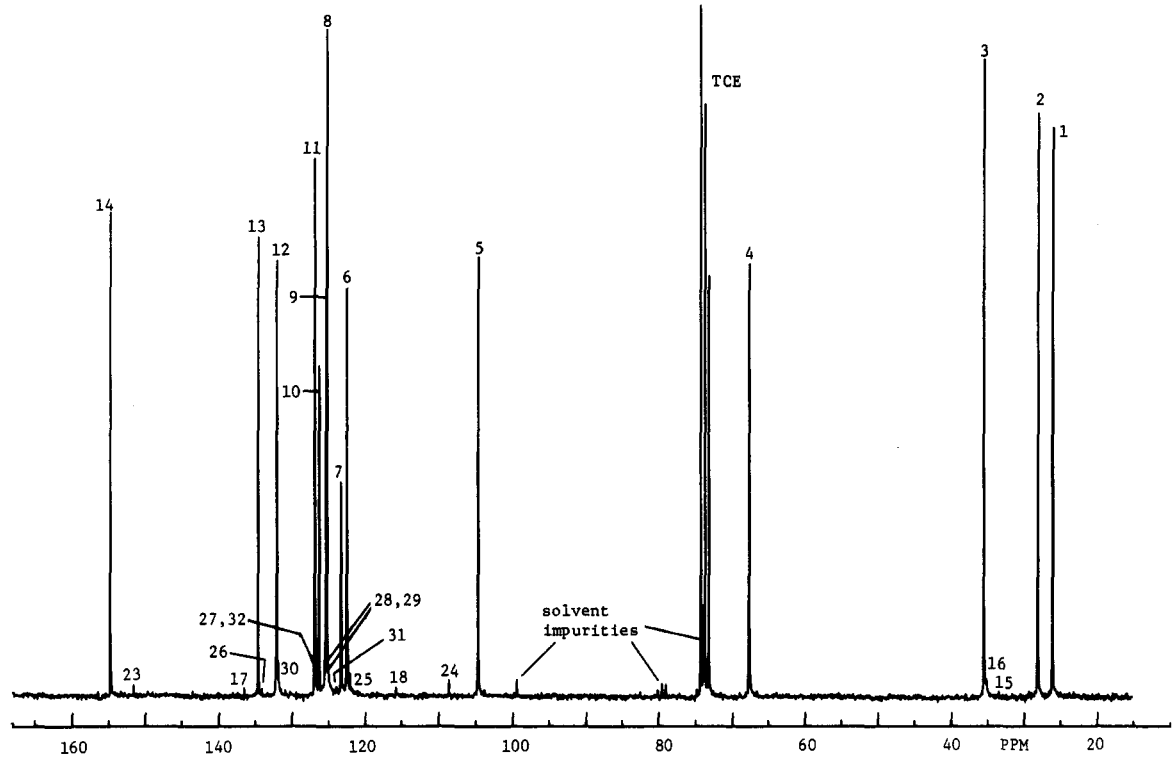


Figure 5. 50.3-MHz ^{13}C NMR spectrum of naphthyl polymer prepared at 135 °C.

tively. However, a large number of minor signals were observed, due presumably to end groups. Most of these signals had chemical shifts different from those observed for the polymer. Thus, fractions 5 and 6 were identified as linear oligomers with different end groups than found in the polymer. The molecular weights of the linear oligomers were inferred to be higher than those of the cyclic oligomers based on the mass spectroscopic experiments. Under positive chemical ionization, the largest sized ion produced from fraction 5 was the same size as that from fraction 3 (cyclic tetramer) and smaller than that from fraction 4 (cyclic pentamer). However, the temperature required for sample volatilization was higher than for the cyclic oligomer. Volatilization of fraction 6 was not achieved. Since cyclic compounds have higher boiling points than corresponding acyclic compounds, we concluded that fractions 5 and 6 had higher molecular weights than fraction 4. If fraction 5 were the linear pentamer, it would volatilize at a lower temperature than fraction 4 (cyclic pentamer). The observation of the lower mass ion in the mass spectrometer experiment from fraction 5 relative to that from fraction 4 is ascribed to fragmentation at the higher temperature involved in volatilizing fraction 5.

Polymerization Mechanism. Our results are consistent with the polymerization mechanism proposed by Schmidt and co-workers.[4,5] Polymerization is initiated by loss of the water of hydration followed by ring-opening

Table I
Effect of Reaction Temperature on Polymerization

temp,[a] °C	ratio of polymer to oligomer		MW by GPC			
			polymer		oligomer	
	GPC	extraction	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
Polymerization in Sealed Tube						
200	2.6	2.6	15850	2.1	406	1.2
135	2.1	2.3	15700	2.9	380	1.4
100	3.7	2.5	21680	1.9	375	1.5
80	5.8	4.3	8560	1.9	360	1.3
60	5.6	5.2	6300	1.7	460	1.4
Polymerization under Continuous Vacuum						
200	2.8	2.6	14020	2.5	395	1.5
135	2.0	2.8	12660	2.4	400	1.7
100	4.0	4.0	20000	2.6	370	1.8
80	5.6	4.8	18010	2.9	335	1.3
60		0.6[b]	18160			

[a] Reaction times were 20 and 100 h respectively for temperatures 80–200 and 60 °C. [b] Conversion of zwitterion to polymer plus oligomer was low; conversion was quantitative in all other experiments.

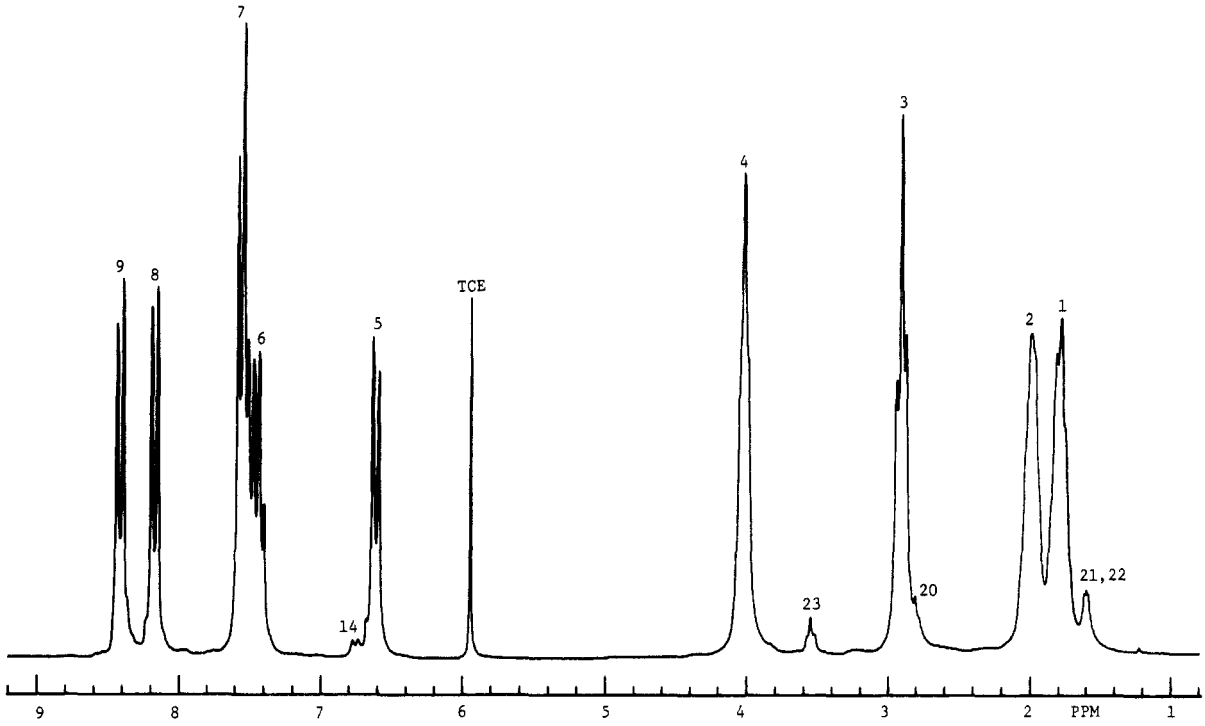
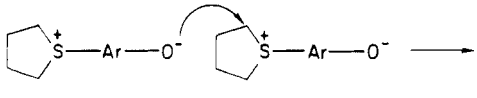
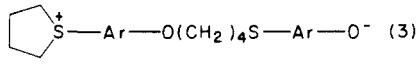


Figure 6. 200.1-MHz ^1H NMR spectrum of naphthyl polymer prepared at 60 °C.

nucleophilic attack of the arene oxide anionic center of one zwitterion on the α-carbon of the tetrahydrothiophenium ring of a second zwitterion (eq 3), where Ar represents the

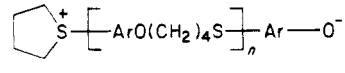


I



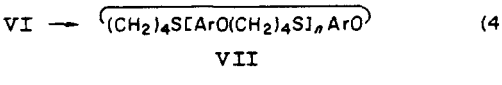
V

naphthalene ring. The resulting linear activated dimer V is a more reactive zwitterion than the original zwitterion I. It has both more highly electrophilic and nucleophilic centers since there can be no quinoid-type resonance interaction between the S^+ and O^- centers. Propagation proceeds by reaction of V with itself and I to produce the linear tetramer and trimer, respectively. The latter can react with themselves, each other, V, and I. Growth continues in a step-reaction manner with the formation of different-sized molecules of type VI.



VI

^1H and ^{13}C NMR and IR identified the polymer fraction as composed of linear molecules containing naphtholic groups at one end and either olefinic or alcoholic at the other end. HPLC fractionation coupled with ^1H and ^{13}C NMR and mass spectrometry identified the major components of the oligomer fraction as cyclic dimer, trimer, tetramer, and pentamer with minor amounts of larger sized linear oligomers. Three types of termination are proposed to explain these results–cyclization, β-elimination, and substitution with water. Cyclization involves intramolecular reaction instead of intermolecular reaction (eq 4).



VII

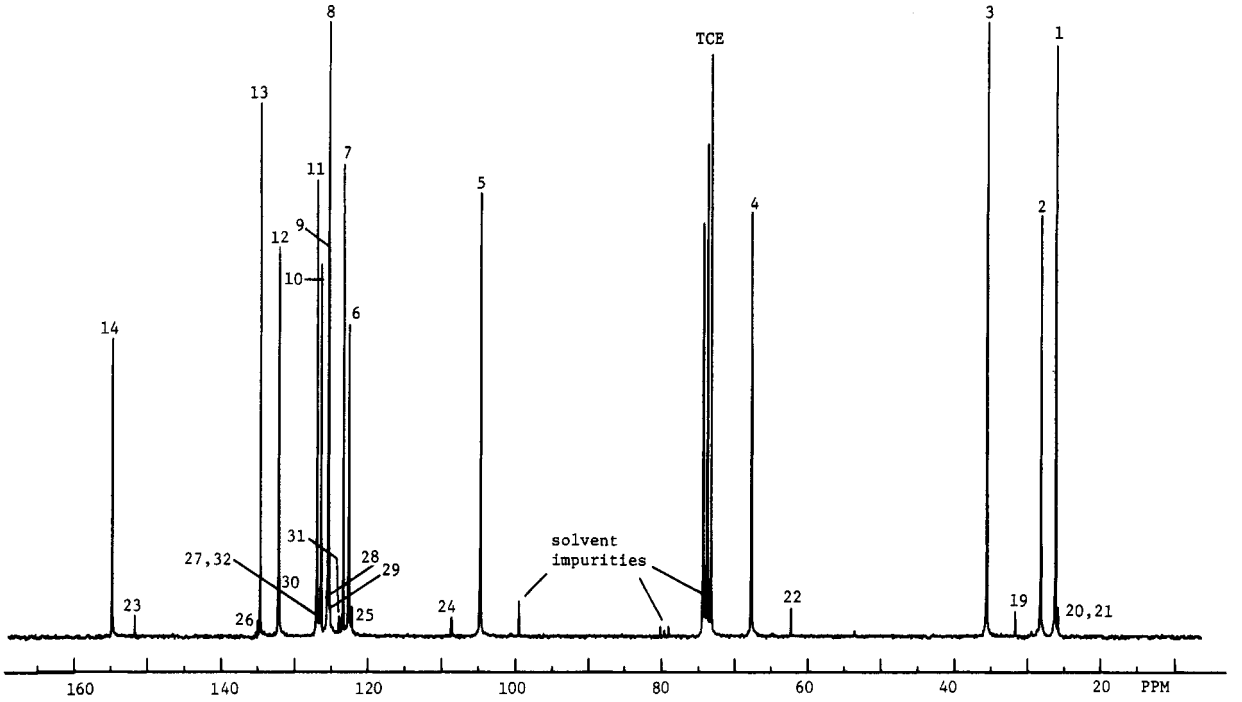


Figure 7. 50.3-MHz ^{13}C NMR spectrum of naphthyl polymer prepared at 60 °C.

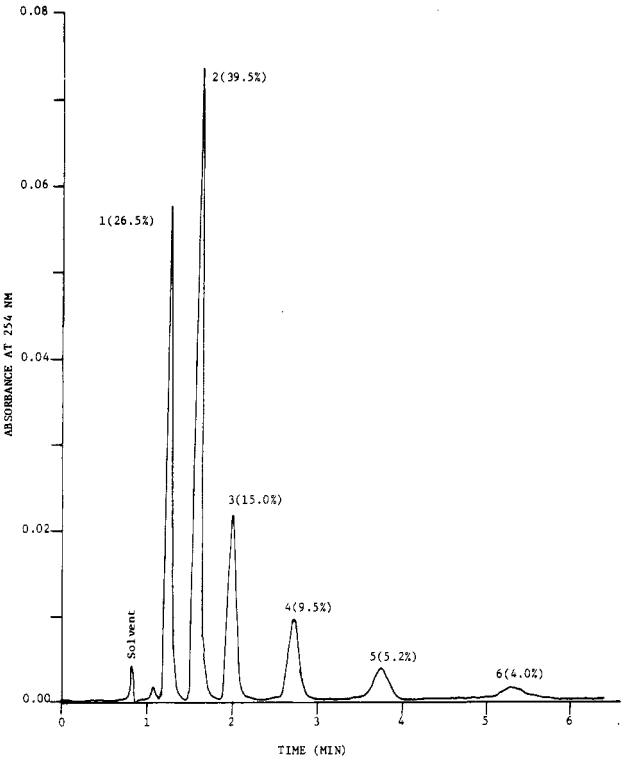


Figure 8. HPLC of CH_2Cl_2-soluble oligomer fraction on a μ-Porasil column. Mobile phase: cyclohexane–CH_2Cl_2 (70:30).

Cyclic dimer and trimer are the main products; larger sized cyclics become progressively more difficult to form, presumably for kinetic reasons.

Termination by β-elimination involves intra- and/or intermolecular abstraction of H^+ from the β-carbon of the tetrahydrothiophenium ring to yield the naphthyl polymer with olefinic and naphtholic end groups (eq 5). β-Elimination most likely involves hydroxide ion as a base as well as the arene oxide anion. A considerable hydroxide ion concentration exists since zwitterion solutions typically have pH values of 10–11.

$$\text{VI} \rightarrow \underset{\text{III}}{CH_2{=}CHCH_2CH_2S[ArO(CH_2)_4S]_nArOH} \quad (5)$$

Reaction of a growing zwitterion with water or hydroxide ion involves ring-opening OH substitution at the α-carbon of the tetrahydrothiophenium ring and yields the naphthyl polymer with alcoholic and naphtholic end groups (eq 6).

$$\text{VI} \rightarrow \underset{\text{IV}}{HOCH_2CH_2CH_2CH_2S[ArO(CH_2)_4S]_nAr\text{-}OH} \quad (6)$$

The relative extents of termination by substitution and β-elimination are strongly affected by temperature and the polymerization method as described below.

Effect of Temperature on Polymerization. Table I shows the molecular weight of the polymer prepared by the sealed-tube and vacuum methods as determined by GPC (based on calibration with polystyrene standards). For sealed-tube polymerizations, the polymer molecular weight increased significantly with increasing temperature in the 60–100 °C range, reached a maximum at 100 °C, and decreased somewhat above 100 °C with no difference observed between 135 and 200 °C. No significant change in $\bar{M}_n$ was observed for polymers obtained by the vacuum method in the 60–100 °C range, and the polymer molecular weight was very close to the 100 °C value in the sealed-tube polymerization. Above 100 °C the polymer molecular weight decreased somewhat, as was the case for polymerization by the sealed-tube method.

The difference observed for polymerizations by the sealed-tube and vacuum methods is attributed to a difference in the rate of removal of the water of hydration. Water is not quickly removed from the zwitterion under sealed-tube conditions until the polymerization temperature reaches 100 °C. Termination by water (and/or OH^-) is extensive below 100 °C and limits the polymer molecular weights to the 6300 and 8560 values. Termination by water is reasonably fast due to the large amount of water present (2 mol/(mol zwitterion)). Above 100 °C water is rapidly expelled from the reaction mixture (and condenses at the top of the polymerization tube), termination by water is negligible, and maximum molecular weights are obtained. For polymerization under vacuum conditions, the water of hydration is quickly removed even at 60–80 °C, termination by water is low, and the polymer molecular weights are high even at the lower reaction temperatures. The decrease in polymer molecular weight for polymeri-

zation above 100 °C under both sealed-tube and vacuum conditions is ascribed to the increased extent of β-elimination. β-Elimination is not important at lower temperatures but becomes predominant at higher temperatures since elimination reactions generally have high activation energies. Superimposed on these considerations, one assumes that the propagation rate constant increases with temperature. The overall balance of the two processes is such that the latter increase does not keep up with β-elimination. The polymer molecular weight is about the same above 100 °C for both the sealed-tube and vacuum methods, indicating that water of hydration is essentially absent and both systems are equivalent. ^{1}H NMR analysis of the various polymers supported these conclusions. None of the end-group signals were sufficiently base line resolved to allow one to obtain the quantitative trends in the amounts of olefinic and alcoholic end groups as a function of temperature. However, the qualitative trends were consistent with the above discussion.

The molecular weight of the oligomer fraction showed no significant change in the 60–200 °C range for both the sealed-tube and vacuum methods. The polymer-to-oligomer ratio was somewhat higher at the lower reaction temperatures except for the 60 °C polymerization under vacuum. Since the oligomer fraction consisted mostly of cyclic oligomers, the decreased oligomer fractions at the lower temperatures indicated that cyclization was more favored at the higher temperatures. The GPC plots for the oligomers from the reactions at 100, 135, and 200 °C showed the same pattern of fractionation into 4 or more components (Figure 3). This was very similar to the pattern observed in the HPLC of the 135 °C polymerization mixture (Figure 8). However, the oligomer fractions from the 60 and 80 °C reactions showed mostly the two lowest molecular weight components (those eluting at approximately 27 and 27.5 min in Figure 3), indicating that predominantly the cyclic dimer and trimer were formed at the lower reaction temperatures. At first glance, the GPC values for $\bar{M}_n$ of the oligomer fractions appeared too low by a factor of 2–3 since the average molecule in the oligomer fractions was a trimer (MW = 690) or tetramer (MW = 920) based on the mass spectroscopic results of the HPLC fractions. We believe this can be accounted for by a consideration of the basis for GPC fractionation—hydrodynamic volume. Cyclic molecules, having smaller hydrodynamic volumes compared to their acyclic analogues, take longer to elute from the GPC columns.

Polymerization at 60 °C by the vacuum method gave very different results from those by the sealed-tube method. Complete conversion of zwitterion with a high yield of polymer relative to oligomer was observed for polymerization by the sealed-tube method. The extent of reaction was low for polymerization by the vacuum method. ^{1}H NMR and the solubility characteristics of the reaction mixture in CD_2Cl_2 and Me_2SO-d_6 showed it contained mostly unreacted zwitterion. The small amount of product contained more oligomer than polymer. (GPC was not carried out on this reaction mixture since the unreacted zwitterion would undergo polymerization during the GPC run at 135 °C. GPC was performed on the polymer plus oligomer fraction extracted from the reaction mixture by CH_2Cl_2.) Increasing the reaction time to 2 weeks resulted in complete conversion and the polymer-to-oligomer ratio was 3.9. Further, reaction at 60 °C under vacuum for 100 h followed by 20 h at 100 °C also resulted in complete conversion; the polymer-to-oligomer ratio was 3.1. All of the 60 °C data indicate that polymerization is much slower by the vacuum method compared to the sealed-tube method. This difference must be viewed in terms of the physical behavior of the crystalline zwitterion during polymerization. Visual observation showed that polymerization at temperatures of 80 °C and higher proceeded with melting of the zwitterion. Melting did not take place for reaction at 60 °C. There was no visual change in the physical state of the crystalline zwitterion during reaction and one concludes that polymerization proceeds within a crystal lattice. Molecular mobility of the zwitterion is needed for reaction to take place. The water of hydration (which leaves slowly) provides the necessary mobility for polymerization by the sealed-tube method. For polymerization by the vacuum method, the water of hydration is quickly removed and the dehydrated zwitterion molecules become "isolated" from each other. Reaction to form both oligomer and polymer is slow due to the low molecular mobility of the zwitterion in the crystal lattice. Apparently the steric requirements for cyclic oligomerization vs. polymerization are such as to favor the former. Polymerizations at 80 °C and higher proceed faster since the necessary molecular mobility is present in the molten zwitterion.

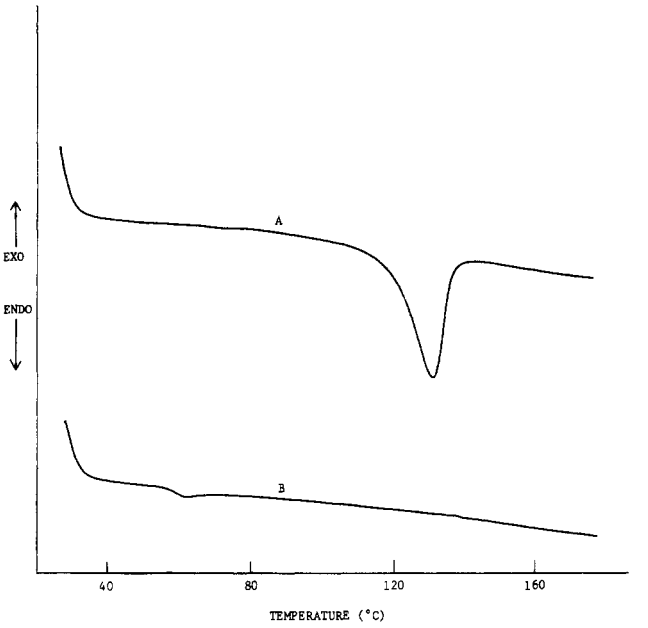


Figure 9. DSC of naphthyl polymer.

Thermal Analysis of Naphthyl Polymer. Figure 9 shows the DSC plot of the 135 °C polymer when subjected to a first heating cycle (curve A) followed by cooling and a second heating cycle (curve B). The 100 °C polymer gave essentially the same DSC. A large endothermic peak, starting at 122 °C with a peak at 132 °C, was observed in the first heating cycle. This endotherm disappeared in the second heating cycle irrespective of the method of cooling, e.g., cooling at the same rate as the heating rate, rapid quenching in dry ice, or annealing at 100 °C for 1 week. During the second heating cycle, a very weak endotherm was observed at 56 °C. This was not observed in the first heating cycle or, perhaps, it was buried in the base line of the large endotherm. The 56 °C phenomenon persisted through a third and fourth cooling–heating cycles. In another experiment, a polymer sample was melted, dissolved in 1,1,2,2-tetrachloroethane, and precipitated into diethyl ether, and the polymer was separated and dried overnight in a vacuum oven at 50 °C. DSC of the dried polymer showed two endotherms (with peak temperatures of 94 and 109 °C) in the first heating cycle. Only the 56 °C phenomenon was observed in the second heating cycle. We do not ascribe the 94, 109, and 132 °C endotherms

observed in the first heating cycles to melting of crystalline polymer. Such first heating cycle endotherms that disappear in subsequent heating cycles have been observed by others. Various mechanisms have been proposed to explain this phenomenon including liquid–liquid transition, loss of a volatile constituent (e.g., solvent) from the sample, and a change in physical contact between sample and sample pan due to liquid flow.[18,19] We tentatively ascribe the 56 °C phenomenon in the DSC curve to the polymer glass transition. This assignment is not made with great certainty since T_g is accompanied by a change in slope of the DSC curve whereas the DSC curve for the naphthyl polymer has what appears to be an endotherm at 56 °C. The 56 °C phenomenon is so weak that it may not be possible to distinguish an endotherm from a change in slope.

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Registry No. **Ia**, 69288-89-7; **Ia** (homopolymer), 69288-90-0; **Ia** (SRU), 101672-00-8; SO_2Cl_2, 7791-25-5; 1-naphthol, 90-15-3; tetrahydrothiophene, 110-01-0.

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Thermotropic Liquid Crystalline Aromatic/Cycloaliphatic Polyesters and Fibers

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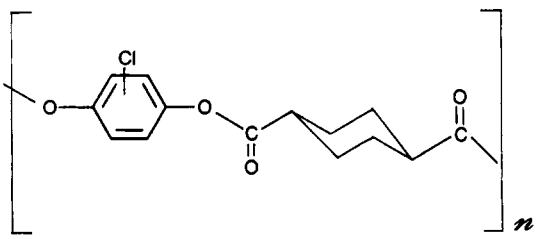
ABSTRACT: Polyesters prepared from chlorohydroquinone diacetate and hexahydroterephthalic acid (1,4-cyclohexanedicarboxylic acid) were extruded from liquid crystalline melts directly into highly oriented fibers with initial moduli as high as 450 g/denier or 57.5 GPa. Heat-treatment in a relaxed state to near the melting point resulted in a 5- to 6-fold increase in tenacity—up to 20 g/denier (2.5 GPa). These polyesters were characterized by X-ray, NMR, IR, DSC, TGA, and optical microscopic methods. Polyesters based on *cis*- and *trans*-hexahydroterephthalic acid were prepared by both melt and low-temperature solution methods. Solution-prepared cis polymer, in which the cis configuration was confirmed by high-resolution NMR, was found to form an isotropic melt at 250 °C that converted to a liquid crystalline melt on heating at 310 °C due to cis–trans isomerization (NMR). The latter indicates the more extended trans form is required for melt anisotropy. All melt-prepared polymers were found by NMR to exist in the trans configuration and formed anisotropic melts and high-strength fibers on spinning and heat treatment.

Introduction

In the past decade a large number of thermotropic polyesters with mesogenic units either in the main chain or in modifying side groups have been prepared and examined for property–structure relationships.[1-12] Unlike the lyotropic mesomorphic polyamides, polyesters with their reduced hydrogen bonding capability are more apt to form melts below their decomposition temperatures. The melting points can be reduced further by the introduction of limited disorder into the polymer chain with substituents, flexible moieties, bent and crankshaft monomers, and copolymerization.

One polyester system that forms liquid crystalline melts is prepared from 2-chlorohydroquinone and *trans*-hexahydroterephthalic acid.[1b]



Poly(chloro-1,4-phenylene *trans*-hexahydroterephthalate)

The chloro substituent produces a certain amount of dissymmetry and reduction of intermolecular forces by its projection from the main chain and by the introduction of an internal copolymer effect depending on whether the chlorohydroquinone is oriented with all chlorines in the

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