Zwitterion Polymerization of Tetrahydro-1-[4-hydroxy-3-(2-hydroxyethoxy)phenyl]thiophenium Hydroxide Inner Salt

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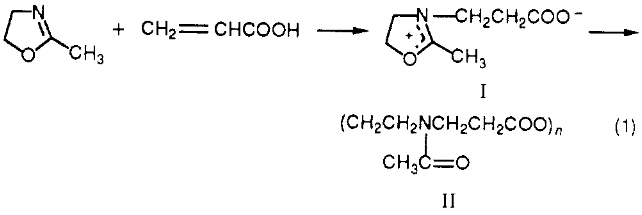
ABSTRACT: Tetrahydro-1-[4-hydroxy-3-(2-hydroxyethoxy)phenyl]thiophenium hydroxide inner salt was synthesized and then polymerized in bulk and solution over the temperature range 65–140 °C. Bulk polymerization gave linear polymer in 88.3–90.6% yield. The polymer was identified as poly[oxytetramethylenethio[3-(2-hydroxyethoxy)-1,4-phenylene]] by elemental analysis, IR, and NMR. Size-exclusion chromatography showed the number-average molecular weight to be in the range 51 300–67 800, depending on the reaction temperature. These are the highest polymer molecular weights ever reported for a zwitterion polymerization. Cyclic oligomers from dimer to hexamer were identified by mass spectroscopy and NMR as minor products. The polymer yields were no higher than 19.4% in solution polymerization unless the TFA salt of the zwitterion was present as an initiator. The yields increased to 62% in the presence of TFA salt. The polymer molecular weights varied from 4420 to 9730, depending on concentration, temperature, and the presence of TFA salt. The predominant polymer end groups were identified by NMR as vinyl and phenol for bulk polymerization and alcohol and phenol for solution polymerization. Our previously proposed mechanism for this type of zwitterion polymerization is discussed in terms of the present study.

Introduction

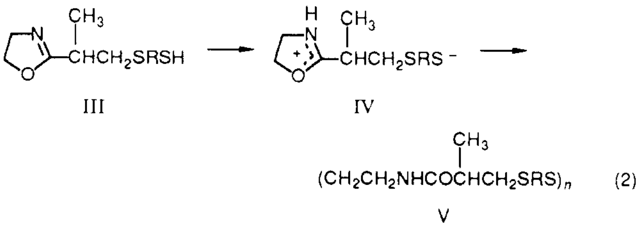
The term zwitterion polymerization has been used to describe polymerizations involving either zwitterion intermediates or isolable (stable)zwitterions.[1–13] We can distinguish three types of zwitterion polymerizations.

(1) A nucleophile and an electrophile polymerize via a zwitterion intermediate, e.g., 2-methyl-2-oxazoline plus acrylic acid.[1–3,5–10]



(1)

(2) A molecule containing both nucleophilic and electrophilic groups polymerizes via a zwitterion intermediate, e.g., a 2-(mercaptoalkyl)-2-oxazoline (III).[4,11]



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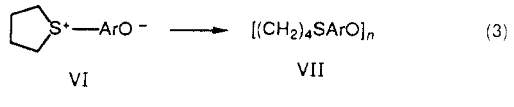
(3) A stable (isolable) zwitterion undergoes polymerization, e.g., a tetrahydrothiophenium–arene oxide (VI).[12,13]



(3)

A wide variety of type 1 zwitterion polymerization systems have been reported.[1–3,5–10] More than two dozen systems have been studied. The nucleophiles studied included 2-methyl-2-oxazoline, ethylenimine, ethylene phenylphosphonite, and 5,6-dihydro-4*H*-1,3-oxazine; the electrophiles included 4-phenyl-1,2,4-triazoline-3,5-dione, propanesultone, α,β-unsaturated acids, *N*-phenylmaleimide, tetracyanoethylene, β-lactones, dicarboxylic anhydrides, and carbonyl sulfide. The polymer molecular weights were very low in almost all systems studied. Very few systems yielded molecular weights above a few thousand. We reinvestigated the most-studied system, 2-methyl-2-oxazoline + acrylic acid (MeOXO–AA), with a view to understanding the mechanism responsible for the low product molecular weight. Our results[9] indicated that the MeOXO–AA system carries the seeds of its own destruction. The reactants MeOXO and AA are themselves responsible for termination of polymer growth both directly and indirectly. AA directly reacts with and terminates growth of the propagating zwitterion intermediate. In addition, AA and MeOXO form a protonated MeOXO–acrylate salt (by proton transfer from AA to MeOXO), which also terminates the propagating species. Termination is highly favored since the propagating species is present in much lower concentrations than MeOXO and AA. Similar results were found for the MeOXO–methacrylic acid system.[10] Whether or not the mechanism responsible for low polymer molecular weights in all type 1 systems is the same as that in the two systems we studied is not known.

The general inability to obtain anything other than low molecular weight products in type 1 zwitterion polymerizations led us to focus our efforts on the type 2 and 3 systems. We found[11] the type 2 system 2-(mercaptoalkyl)-2-oxazoline (III) easily produced polymers with number-average molecular weights greater than 40 000.

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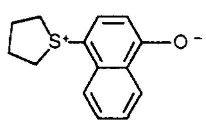
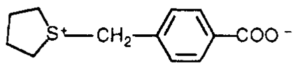
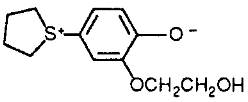
This system overcomes the problem inherent in the type 1 system, since there are no high concentrations of materials such as MeOXO and AA to bring about very facile termination of propagating species. Our results on type 3 zwitterion polymerization systems have also been encouraging. Type 3 polymerizations, originally investigated by Schmidt and co-workers,[12] proceed with high concentrations of zwitterion in addition to the absence of facile terminating reactants. Number-average molecular weights above 25 000 and 40 000 were obtained[13,14] in the thermal polymerizations of VIII and IX, subsequently referred to as the naphthyl and carboxylate zwitterions.



VIII



IX



Xa

The present paper reports the polymerization of tetrahydro-1-[4-hydroxy-3-(2-hydroxyethoxy)phenyl]thiophenium hydroxide inner salt (X), subsequently referred to as the hydroxyethoxy zwitterion or simply zwitterion. Our interest in the hydroxyethoxy zwitterion stems from the presence of common solvents (e.g., dimethyl sulfoxide) for both the zwitterion and the polymer produced from it. This allows various polymerization studies under homogeneous solution (as well as solid-state or melt) conditions, which is not the case for the other tetrahydrothiophenium–arene oxide (VIII).

Experimental Section

Materials. Various Aldrich and Fisher ACS Certified grade or better chemicals were used as received unless otherwise noted.

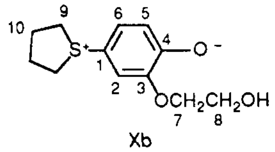
Hydroxyethoxy Zwitterion (X). The hydroxyethoxy zwitterion was synthesized by electrophilic substitution of tetrahydrothiophene on 2-(2-hydroxyethoxy)phenol using the general procedure developed for the naphthyl zwitterion.[13] A solution of 68.7 g (0.779 mol) of tetrahydrothiophene and 0.01 g of iodine in a dry nitrogen atmosphere was cooled to −40 °C by using dry ice–methylene chloride and then 300 g of sulfur dioxide condensed into the solution through a dry ice–methylene chloride condenser. About 20 g of gaseous hydrogen chloride was dissolved in the solution followed by the addition of 100.7 g (0.746 mol) of sulfuryl chloride at a rate to maintain the reaction temperature below −15 °C. 2-(2-Hydroxyethoxy)phenol, 100.0 g (0.649 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 about 200 mL of sulfur dioxide removed under vacuum. The resulting solution was extracted three times with 100-mL portions of 1-hexanol and then twice with 100-mL portions of methylene chloride. The aqueous solution was treated with Dowex-2 anion exchange resin (hydroxide form) to increase its pH to between 10.5 and 10.7 and the solvent was then removed under vacuum. The resulting product was washed with acetone and dried in a vacuum oven (ca. 1 Torr) at 40 °C to yield 144 g (84%) of the dihydrate of the hydroxyethoxy zwitterion.

The crude zwitterion was purified by dissolving it in a mixture of 2-propanol and methanol (5:1 by volume), adding a small amount of water, filtering off a small amount of insoluble tar, and then precipitating the zwitterion by the addition of diethyl ether. The product, a white solid, was filtered, suction-dried, and stored in a refrigerator. We limited this purification process to small batches (< (1/2)–1 g) of crude zwitterion. Purification on a large scale (>5 g) sometimes resulted in purified zwitterion, which subsequently produced insoluble product. Insoluble product was observed during some bulk polymerizations—either directly upon polymerization or when polymer was allowed to stand for long periods (1–2 months). Insoluble product was never observed directly upon solution polymerization but was observed when the polymers from some solution polymerizations were allowed to stand. The insolubility phenomenon was most likely caused by the presence of a polyfunctional impurity that was not excluded during purification on a large scale.

Table I
^{13}C NMR Spectral Assignments (ppm)

carbon	zwitterion	polymer	phenol diol	vinyl phenol
1	94.2	127.0	124.6	124.4
2	119.3	115.0	115.9	124.4
3	151.6	148.7	146.8	146.8
4	169.8	147.4	146.1	146.2
5	120.4	116.9	116.9	117.1
6	128.9	122.9	124.1	124.1
7	74.0	70.7	70.8	70.7
8	60.1	59.4	59.6	59.5
9	48.7	33.5	34.6	33.9
10	28.1	25.1	25.4	32.7
11		27.5	31.3	136.5
12		68.3	60.2	115.9

The hydroxyethoxy zwitterion was identified as the dihydrate of X by a combination of IR and NMR spectroscopy, TGA, and Karl-Fisher titration. The ^{1}H NMR spectrum showed signals at δ 2.11 and 2.39 (two m, 4 H, CH_2CH_2S), 3.33 and 3.76 (two m, CH_2S), 3.51 (br t, CH_2OH), 3.85 (m, OCH_2CH_2OH), 6.27 (d, J = 8.5 Hz, 1 H, aromatic H-5), 7.00 (d, J = 2.9 Hz, 1 H, aromatic H-2), and 7.06 (two d, J = 3.0, 8.4 Hz, 1 H, aromatic H-6). The signal for the hydrate protons was superimposed mostly on (and exchanged with) the alcohol signal but it also spread over the entire region of the CH_2S and OCH_2CH_2OH signals. The individual intergrals for these signals could not be determined but the total integral for the region was 13 H, corresponding to the dihydrate of structure X. Both the alcohol and water protons exchanged with D_2O. Signal assignments were aided by homodecoupling experiments. Thermogravimetric analysis and Karl Fisher titration both indicated the presence of 2.0 mol of water per mol of zwitterion.

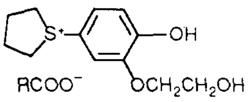


Xb

The proton-decoupled ^{13}C NMR spectrum supported structure X. The carbon signals were assigned as shown in Xb and Table I. Signal assignments were aided by selective heterodecoupling and INEPT experiments, as well as long-range heterodecoupling of the corresponding zwitterion containing a methyl group at the 3-position instead of the 2-hydroxyethoxy group, and reference to previous spectral results on other zwitterions.[13,15]

The IR spectrum showed absorption peaks at 3500–2500 (O—H and H_2O), 3026 (aromatic C—H), 2984, 2951, 2912, 2855 (aliphatic C—H), 1566, 1506 (aromatic C═C), and 895, 823 (1,2,4-trisubstituted benzene C—H) cm^{-1}. Absorptions at 1422, 1342, 1305, 1252, 1218, 1094, 1081, 1057, 939, 720, and 625 cm^{-1} were compatible with a combination of various C—O, methylene, aromatic, and C—S vibrations. A strong absorption at 1680 cm^{-1} together with the abnormally upfield-shifted (by 20 ppm) ^{13}C signal for C-1 indicates the significant contribution of the quinoid resonance form to the structure of the zwitterion as previously observed for other tetrahydrothiophenium–arene oxide zwitterions.

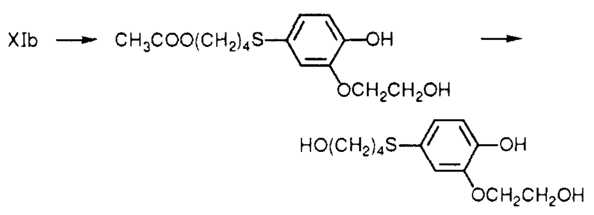
Trifluoroacetic Acid Salt of X (TFA Salt). Tetrahydro-1-[4-hydroxy-3-(2-hydroxyethoxy)-1-phenyl]thiophenium trifluoroacetate (XIa, R = CF_3) was prepared by dissolving the hydroxyethoxy zwitterion (2.0 g) in 10 mL of a mixture of 2-propanol and methanol (5:1 by volume) at ambient temperature, adding an excess of trifluoroacetic acid (4.0 g) followed by diethyl ether to precipitate the product as a white solid. The product, subsequently referred to as the zwitterion trifluoroacetate or TFA salt, was air-dried to constant weight, mp 127–128 °C, 78% yield. IR: 1690 (COO^-), 1290 (aromatic OH) cm^1. ^{1}H NMR: δ 2.31 (complex m, 4 H, CH_2CH_2S), 3.76 (t, 2 H, CH_2OH), 3.70 and 3.89 (two m, 2 H, CH_2S), 4.12 (t, 2 H, $ArOCH_2$), 5.09 (br, exchange with D_2O, CH_2OH), 7.05 (d, J = 8.1 Hz, 1 H, aromatic H-5), 7.37 (two d, J = 2.2, 8.8 Hz, 1 H, aromatic H-6), 7.40 (d, J = 1.9 Hz, 1 H, aromatic H-2), 10.59 (br, exchange with D_2O, ArOH). ^{13}C NMR (CD_3OD): δ 29.9 (CH_2CH_2S), 49.7 (CH_2S), 61.3 (CH_2OH), 72.0 (CH_2OAr), 115.1 (aromatic C-2), 118.2 (q, J = 294 Hz, CF_3), 115.8 (aromatic C-1), 118.3 (aromatic C-6), 125.7 (aromatic C-5), 149.7 (aromatic C-3), 153.6 (aromatic C-4), 162.6 (J = 34 Hz, COO^-).


XI

Anal. Calcd for $C_{14}H_{17}F_3O_5S$: C, 47.43; H, 4.80; F, 16.09; S, 9.03. Found: C, 47.33; H, 4.87; F, 15.82; S, 9.05.

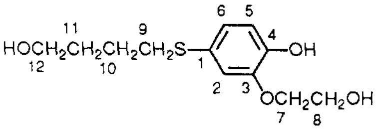
The corresponding zwitterion acetate (XIb, R = CH_3), mp 115–116 °C, was synthesized in a similar manner to the trifluoroacetate by adding acetic acid to a solution of the hydroxyethoxy zwitterion in methanol. IR, NMR, and elemental analysis verified the structure as XIb.

Model Compounds for Polymer End Group Analysis. 2-(2-Hydroxyethoxy)-4-((4-hydroxybutyl)thio)phenol (XII). XII, subsequently referred to as the phenol diol, was synthesized according to eq 4 by heating the zwitterion acetate (2.0 g) at 80 °C for 3 h followed by dissolution in 3 M sodium hydroxide (15 mL) and refluxing overnight. Acidification of the reaction mixture, extraction with chloroform, and solvent stripping from the chloroform solution yielded the product as a white solid, mp 89–91 °C. ^{1}H NMR: δ 1.55 (complex m, 4 H, $CH_2CH_2CH_2S$), 2.83 (t, 2 H, CH_2S), 3.41 (t, 2 H, $HOCH_2CH_2CH_2$), 3.73 (t, 2 H, $HOCH_2CH_2O$), 4.00 (t, 2 H, $ArOCH_2$), 4.34 (br s, exchange with D_2O, $HOCH_2$), 6.74 (d, J = 8.2 Hz, 1 H, aromatic H-5), 6.84 (two d, J = 1.8, 8.2 Hz, 1 H, aromatic H-6), 6.95 (d, J = 1.8 Hz, aromatic H-1), 8.65 (br s, exchange with D_2O, ArOH). The ^{13}C NMR spectral assignments are shown in Table I and structure XIIb.



(4)

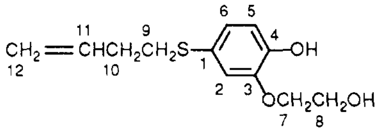
XIIa



XIIb

Anal. Calcd for $C_{12}H_{18}O_4S$: C, 55.80; H, 7.03; S, 12.39. Found: C, 55.36; H, 7.18; S, 12.41.

2-(2-Hydroxyethoxy)-4-(4-butenylthio)phenol (XIII). XIII, subsequently referred to as the vinyl phenol, was synthesized by adding 3 M sodium hydroxide (15 mL) to a solution of the hydroxyethoxy zwitterion (1.5 g) in water (15 mL) followed by refluxing for 3 h. The reaction mixture was neutralized with 6 N HCl, buffered with 5% sodium bicarbonate (15 mL), and extracted twice with 25-mL portions of methylene chloride. The methylene chloride solution was subjected to column chromatography on silica gel from which the vinyl phenol was eluted by using a 50/50 (v/v) mixture of 2-butanone and cyclohexane. Solvent stripping of the eluate yielded the product as a white solid, mp 79–82 °C. ^{1}H NMR: δ 2.26 (q, 2 H, CH_2CH_2S), 2.87 (t, 2 H, CH_2S), 3.18 (br s, exchange with D_2O, CH_2OH), 3.71 (t, 2 H, CH_2OH), 3.99 (t, 2 H, $ArOCH_2$), 5.00, 5.09 (two complex m, 2 H, CH_2=CH), 5.82 (complex m, 1 H, CH=CH_2), 6.75 (d, J = 8.2 Hz, 1 H, aromatic H-5), 6.84 (two d, J = 2.0, 8.2 Hz, 1 H, aromatic H-6), 6.96 (d, J = 2.0 Hz, 1 H, aromatic H-2), 8.5 (br s, exchange with D_2O, ArOH). The ^{13}C NMR spectral assignments are shown in Table I and structure XIII.



XIII

Anal. Calcd for $C_{12}H_{16}O_3S$: C, 59.99; H, 6.71; S, 13.32. Found: C, 59.58; H, 7.08; S, 13.61.

Polymerization. Bulk polymerization of the hydroxyethoxy zwitterion was studied over the temperature range 70–140 °C. Samples were heated in open test tubes in an oil bath for periods of up to 24 h. The reaction mixtures were worked up in several ways: some were dissolved in dimethylformamide (DMF) and analyzed by size-exclusion chromatography (SEC); some were dissolved in Me_2SO-d_6 and analyzed by ^{1}H NMR; some were extracted with methylene chloride to isolate the low molecular weight (<2000) oligomer fraction; others were dissolved in DMF and the polymer fraction isolated via precipitation with diethyl ether followed by drying and analysis by SEC, IR, and NMR. The effect of various additives on bulk polymerization was studied by dissolving the zwitterion and additive in methanol and stripping the methanol at room temperature under aspirator vacuum to yield a film of monomer plus additive, which was then heated at 100 °C for 2 h followed by SEC analysis.

Solution polymerization of the zwitterion in Me_2SO and DMF was studied over the temperature range 60–140 °C at concentrations of 0.02–0.2 mol/L with and without various additives present. Most reaction mixtures were directly analyzed by SEC and NMR. The polymer and oligomer fractions were separated and isolated in some experiments by stripping off the solvent in a rotary evaporator at 80 °C under vacuum followed by extraction of the resulting solid with methylene chloride. The polymer and oligomer were insoluble and soluble, respectively, in methylene chloride.

Spectroscopy. Infrared spectra were recorded on a Beckman 4260 IR spectrometer using KBr pellet samples. ^{1}H (200.1 MHz) and ^{13}C NMR were recorded on an IBM WP 200SY FTNMR spectrometer using a 5-mm dual ^{13}C/^{1}H probe. NMR spectra were obtained at 25 °C for the hydroxyethoxy zwitterion and its acetate and TFA salts and 65 °C for all other compounds. The spectra were acquired by using samples dissolved in Me_2SO-d_6 at concentrations (w/v) of 2–10% and 10–25% for ^{1}H and ^{13}C NMR, respectively, with Me_4Si added as an internal standard. Some ^{13}C NMR spectra of the polymer from bulk polymerization of the hydroxyethoxy zwitterion were recorded with 35–40% sample concentrations at 100 °C by using a 10-mm broad-band probe. The acquisition parameters for ^{1}H NMR were 30–45° pulse angle, 3–8-s total delay between pulses, and 100–10 000 total acquisitions. The acquisition parameters for ^{13}C NMR were 30–45° pulse angle, 2–6-s total delay between pulses, and 1000–30 000 total acquisitions; some spectra were obtained under quantitative conditions [25 mg of $Cr(acac)_3$ added per mL, inverse gated decoupling]. Most spectra were acquired and worked up in 16K; some were acquired and/or worked up in 32K.

Size-Exclusion Chromatography (SEC). SEC of reaction mixtures and isolated polymer or oligomer samples was carried out at 80 or 100 °C on a Waters 150C instrument with a 840 work station for purposes of analyzing the relative amounts of polymer and oligomer fractions and determining the molecular weight of the polymer fraction. DMF (dried over 3-Å molecular sieves) was used as the mobile phase at a flow rate of 1.0 mL/min. The stationary phase consisted of four Ultrastyragel columns (10^5, 10^4, 10^3, 500 Å and one 100-Å Shodex column. LiBr (0.05 N) was present in the mobile phase to prevent selective absorption between polymer and stationary phase when SEC was used for molecular weight analysis. LiBr was absent when SEC was used for determining the relative amounts of polymer and cyclic oligomer, since the presence of LiBr obscured the region for cyclic dimer and trimer. The SEC analysis was calibrated with polystyrene standards from Pressure Chemical and cyclic oligomers synthesized from the hydroxyethoxy zwitterion.

High-Performance Liquid Chromatography (HPLC). Analytical HPLC of the methylene chloride soluble polymerization reaction products was performed at ambient temperature with a Waters system consisting of a μ-porasil column, an M-600 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 methylene chloride/methanol (100/2) at a flow rate of 1 mL/min. The sample size was 1–10 μg of material injected in a volume of 5–25 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.

Preparative HPLC was performed at ambient temperature with a Waters Prep LC system 500 by using a Prep-Pak-500 silica column with methylene chloride/methanol (100/1.5) as the mobile phase. A solution of the products, 0.3 g in 10 mL of mobile phase, was injected into the column and eluted at a flow rate of 50 mL/min. Fractions of 100 mL were collected and analyzed for purity by analytical HPLC. After the first two components eluted from the column, the polarity of the mobile phase was increased by increasing the methanol content to 2.5 parts. Pure fractions (i.e., fractions containing one component as determined by analytical HPLC) of the same component were combined. Fractions containing the same major and one or two minor components were also combined. Each combined solution was concentrated in a rotary evaporator under reduced pressure at 35 °C and then dried in a vacuum oven at 40 °C.

Thermogravimetric Analysis (TGA). TGA of the hydroxyethoxy zwitterion was performed with a Du Pont 990 thermal analyzer coupled to a 950 TGA module. The zwitterion (10–15 mg) was weighed to the nearest 0.01 mg in an aluminum cup in the TGA module at ambient temperature, heated to 175 °C at a rate of 5 °C/min, held at 175 °C until a constant weight was observed, cooled to ambient temperature, and weighed.

Other Analyses. Karl Fischer titration for water of hydration of the hydroxyethoxy zwitterion was carried out by using a Labindustries 1003 Aquametry II meter–electrode. Elemental analysis was performed by Schwartzkopf and Desert Analytics. Mass spectroscopy was carried out on an a VG-ZAB mass spectrometer operating at medium resolution in the fast-atom bombardment ionization mode, using 8-keV xenon bombardment. Low-angle laser light scattering (LALLS) determination of the weight-average molecular weight was performed in DMF at 25 °C by using a Chromatix KMX-6 photometer and a Chromatix KMX-16 laser differential refractometer (λ = 6328 Å).

Results and Discussion

Thermal polymerization of the hydroxyethoxy zwitterion was studied in bulk and solution over the temperature range 70–140 °C. The bulk polymerization had the appearance of a melt polymerization at reaction temperatures above 80 °C as the hydroxyethoxy zwitterion melted and became a glassy polymer. Below 80 °C, there was no apparent melting as the powdery zwitterion slowly decreased in volume with formation of an opaque glassy polymer. The polymer showed an initial melting point of 98 °C by DSC. After it was cooled (either fast or slow) and reheated no melting transition was observed.

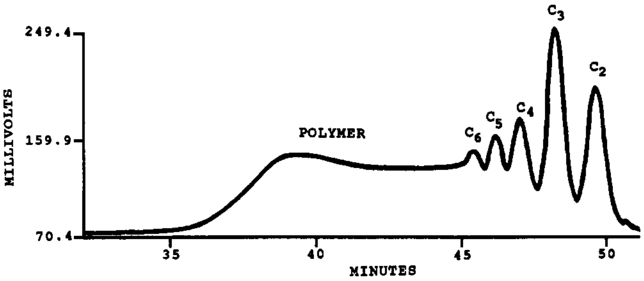
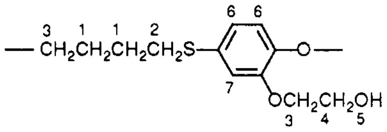


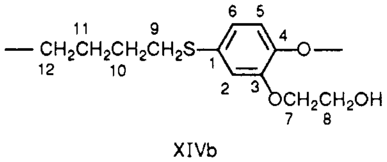
Figure 1. SEC of reaction mixture from solution polymerization (0.145 M in Me_2SO) at 65 °C in the presence of 4.6 mol % TFA salt. C_2–C_6 represent cyclic dimer through hexamer.

Both bulk and solution polymerization yielded a mixture of high molecular weight polymer plus low molecular weight (<2000) oligomer fractions. Figure 1 shows the SEC of the reaction mixture from a solution polymerization. The relative amounts and molecular weights of the polymer and oligomer fractions varied depending on reaction conditions and were directly analyzed by a combination of HPLC and SEC. The two fractions were separated prior to spectroscopic analysis either by methylene chloride extraction of the oligomer from a solid mixture of polymer and oligomer or precipitation of the polymer fraction by addition of diethyl ether to a DMF or Me_2SO solution of the two fractions. SEC analysis before and after these separations verified the two procedures resulted in the same separation of the reaction mixture into polymer and oligomer fractions.

Characterization of the Polymer Fraction. The polymer fraction, consisting of a white powder was insoluble in most solvents (e.g., benzene, chloroform, tetrachloroethane, methylene chloride, methanol, diethyl ether) but was soluble in DMF and Me_2SO. The polymer was identified as poly[oxytetramethylenethio[3-(2-hydroxyethoxy)-1,4-phenylene]] (structure XIV) by elemental analysis, IR, and NMR. The main (lower) plot in Figure 2 shows the ^1H NMR spectrum of the polymer obtained from a bulk polymerization. The various signals for the repeat unit are assigned as shown by structure XIVa on the basis of chemical shift values,[13-16] splitting patterns, signal areas, decoupling experiments, and the effect of added D_2O on signal 5. The ^{13}C NMR spectrum (Table I) signal assignments shown in XIVb were based on chemical shift values,[13-16] INEPT, SFOR, and selective heterodecoupling experiments. The infrared spectrum of the polymer showed absorption bands at 3060 (aromatic C—H), 2930, 2870 (aliphatic C═H), 1580, 1500 (aromatic C═C), 1300 (O—H), 1255, 1215 (aryl alkyl ether), 1040 (alcohol C—O), 895, and 800 (1,2,4-trisubstituted benzene) cm^{-1}.



XIVa



XIVb

The elemental analysis (found: C, 60.17; H, 6.82; S, 13.58) was in good agreement with that for structure XIV (calcd: C, 59.99; H, 6.71; S, 13.32).

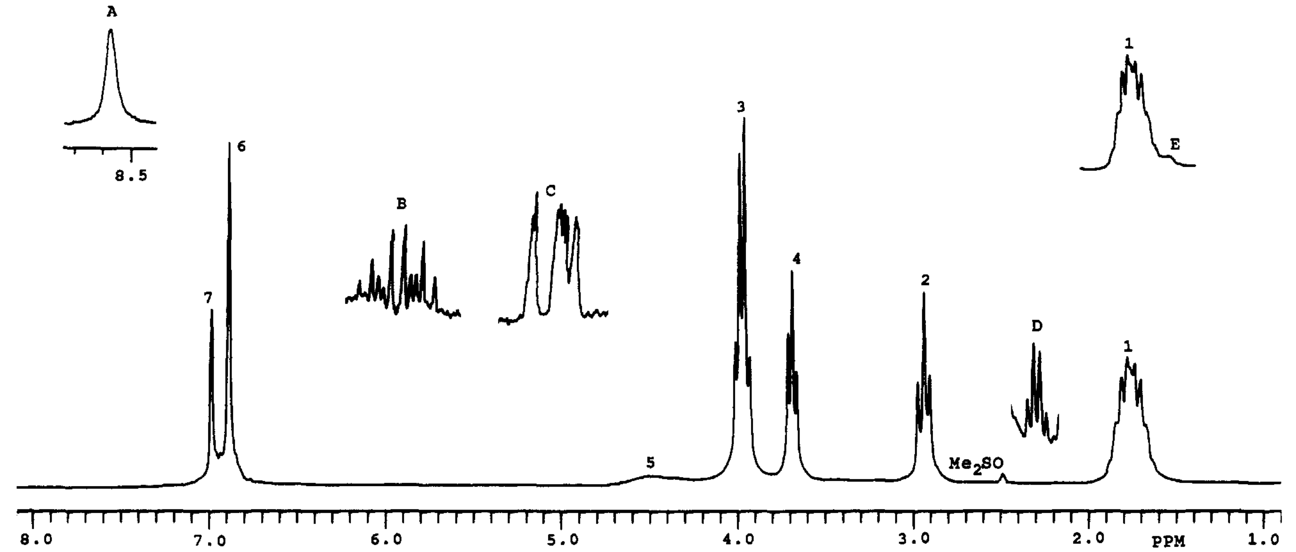


Figure 2. 200-MHz ^{1}H NMR of polymer in Me$_2$SO-d_6.

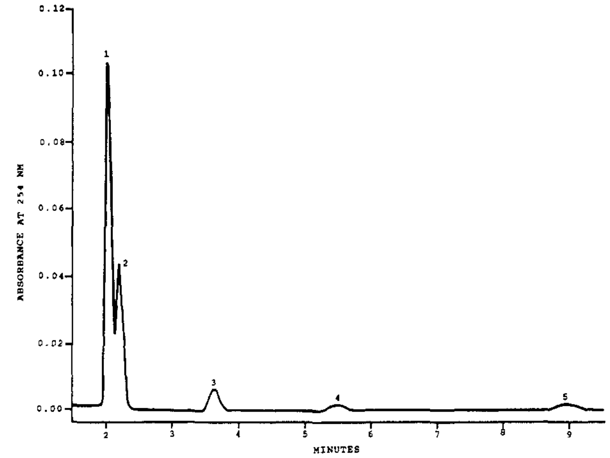
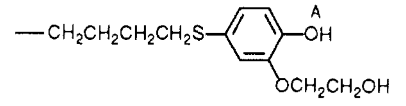
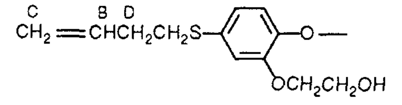


Figure 3. HPLC of the CH_2Cl_2-soluble oligomer fraction from solution polymerization at 80 °C.

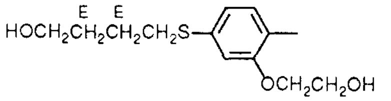
Polymer End Groups. ^{1}H NMR spectra indicated the presence of two types of polymer molecules. One type contains phenol (XV) and vinyl (XVI) end groups. The other contains phenol and alcohol (XVII) end groups. Phenol (XV) end groups were detected by the presence of a signal at 8.6 ppm for the phenolic OH hydrogen (see signal A in the inset in Figure 2). This signal exchanged with D_2O and its position varied with temperature. Vinyl (XVI) end groups were detected by signals B (complex multiplex, 5.81 ppm, $\mathrm{CH_2{=}C}\mathit{H}$), C (complex multiplets, 4.98–5.10 ppm, $\mathit{CH_2}\mathrm{{=}CH}$), and D (q, 2.28 ppm, $\mathit{CH_2}\mathrm{CH{=}CH_2}$). Signals B–D, shown at high magnification as inserts in Figure 2, disappeared as expected upon addition of bromine to the polymer sample solution. Alcohol (XVII) end groups were detected by signal E for $\mathrm{HOCH_2}\mathit{CH_2CH_2}\mathrm{CH_2S}$ protons. The insert at the top of the 1.5 ppm region of Figure 2 shows that the appearance of signal E is observed as a shoulder on the upfield side of signal 1 for the polymer repeat unit. The various end group assignments were aided by spectra obtained on the two model compounds—phenol diol (XII) and vinyl phenol (XIII). The vinyl phenol and phenol diol served as models for vinyl and alcohol end groups, respectively, and both served as models for phenol end groups.



XV



XVI



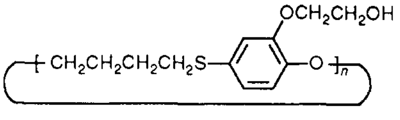
XVII

The detection of alcohol end groups was limited compared to the detection of phenol and vinyl end groups. Signal E could not be observed if the alcohol end group concentration was too low compared to signal 1 for the polymer repeat unit. The 3.41 ppm signal for methylene protons adjacent to the alcohol OH was also not significantly helpful in detecting alcohol end groups at low concentrations since the base line of that region of the spectrum was generally not clean due to the presence of small amounts of water.

^{13}C NMR spectra assisted in the identification of the various end groups. Phenol end groups were detected by polymer signals corresponding to signals 3 and 4 for the two model compounds. Vinyl end groups were detected by signals corresponding to signals 9, 10, and 11 for the vinyl phenol. Alcohol end groups were detected by signals corresponding to signals 9, 11, and 12 for the phenol diol.

Characterization of the Oligomer Fraction. Identification of the methylene chloride soluble oligomer fraction from polymerization of the hydroxyethoxy zwitterion was carried out by a combination of HPLC, SEC, ^{1}H NMR, and mass spectroscopy. Analytical HPLC (Figure 3) showed the presence of five different compounds in the oligomer fraction. The oligomer fraction was fractionated by preparative HPLC and each fraction subsequently subjected to analytical HPLC. Fraction 1 contained compound 1 in pure form. Fractions 2, 3, and 4 contained compounds 2, 3, and 4 in 71, 87, and 70% purities, respectively. Compound 2 was obtained in a mixture with 29% compound 1, compound 3 in a mixture with 6% compound 1 and 7% compound 2, and compound 4 in a mixture with 30% compound 3. Compound 5 was present in the oligomer fraction in too small an amount to be isolated.

Mass spectroscopy of the fractions isolated from preparative HPLC yielded molecular ions of 480, 720, 940, and 1440 for compounds 1, 2, 3, and 4, respectively. One set of structures consistent with these molecular weights are the cyclic dimer, trimer, tetramer, and pentamer, respectively, of structure XVIII (n = 2–5). Another possibility is that compounds 1–4 are linear oligomers isomeric with the cyclic oligomers. NMR established that compounds 1–4 were the cyclic oligomers XVIII. The ^{1}H NMR spectrum of compound 1 showed signals at δ 1.66 (complex m, 4 H, $CH_2CH_2CH_2S$), 2.85 (t, 2 H, CH_2S), 3.66 (q, 2 H, CH_2OH), 3.89 (t, 4H, CH_2OAr), 4.56 (t, 1 H, OH; splitting, ppm, and integral values varied depending on temperature and moisture content of solvent), 6.51 (d, J = 8.4 Hz, 1 H, aromatic H-5), 6.82 (two d, J = 2.0, 8.4 Hz, 1 H, aromatic H-6), and 6.93 (d, J = 2.0 Hz, 1 H, aromatic H-2). This spectrum is consistent only with the repeat unit of structure XVIII. No other signals were observed, i.e., no signals for any end groups. The ^{13}C NMR spectrum of compound 1 also supported the cyclic dimer structure. The δ values of the various signals were within 0–4 ppm of the corresponding signals for the polymer and there were no signals other than for the repeat unit. The ^{1}H NMR spectra of fractions 2–4 were similar to that of the cyclic dimer and supported the assignment of compounds 2–4 as the cyclic trimer, tetramer, and pentamer. Compound 5, not isolated in sufficient quantity for analysis, was assumed to be the cyclic hexamer.



XVIII

Analysis of Product Distribution in Polymerization. SEC was used to obtain the relative amounts of the polymer fraction and various cyclic oligomers as well as the molecular weight of the polymer fraction. Figure 1 shows the SEC of a solution reaction mixture polymerized at 65 °C. The peaks with elution times of 49.67, 48.25, 47.05, 46.17, and 45.42 min were identified as cyclic dimer, trimer, tetramer, pentamer, and hexamer, respectively, by comparison with those of the cyclic oligomer samples isolated by preparative HPLC. The signal areas of SEC peaks were proportional to the amount of each component present. This was verified by experiments in which artificial mixtures of various components (e.g., polymer and cyclic dimer) were analyzed by SEC. The extent of conversion of the hydroxyethoxy zwitterion to polymer and oligomer products was separately analyzed by ^{1}H NMR. The signal (6.25 ppm) for the aromatic proton at position 5 of the zwitterion was sufficiently resolved from the nearest signals for cyclic oligomer (6.51 ppm for the dimer and further downfield for the higher cyclics) or polymer (6.89 ppm) to allow this analysis. The conversion was 100% for all data reported in this paper. The 6.51 ppm signal for the cyclic dimer was sufficiently resolved from signals for higher cyclics and the polymer to give a check on the SEC method for analysis of the cyclic dimer. The individual signals for the polymer and cyclic oligomers larger than dimer were not sufficiently resolved for analytical purposes.

Table II
Effect of Temperature on Bulk Polymerization[a]

temp, °C	product distribution by SEC,[b] %						MW of polym fractn by SEC	
	C_2	C_3	C_4	C_5	C_6	P	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
70	3.5	3.1	2.3	1.2	0.7	89.2	67 800	3.8
100	3.3	3.7	1.7	1.0	1.0	88.3	61 300	2.7
100[c]	2.8	1.9	2.0	2.2	2.1	89.0	30 800	2.4
100[d]							35 600	1.9
140	3.3	2.8	1.4	0.9	0.8	90.6	51 300	2.0

[a] Reaction times: 2–3 days and 5 h respectively for temperatures of 70–100 and 140 °C. [b] C_2–C_6 = cyclic dimer through hexamer, P = polymer. [c] Contained 4 mol % TFA salt. [d] Contained 2 mol % sodium methoxide.

Bulk Polymerization. Bulk polymerization of the hydroxyethoxy zwitterion was studied over the temperature range 70–140 °C and the results are shown in Table II. Polymerization was relatively insensitive to reaction temperature. Cyclic oligomers comprised the minor product. The distribution of different-sized cyclic oligomers followed the order expected from a kinetic viewpoint with progressively decreasing amounts of larger cyclics. The major product was polymer with the polymer fraction accounting for 88.3–90.6% of the total products. The polymer molecular weight was very high at all reaction temperatures. The molecular weights exceeded those of any previously reported zwitterion polymerization of any type. There was a trend toward somewhat higher polymer molecular weights with decreasing temperature. The highest polymer molecular weight $\bar{M}_n$ of 67 000 was achieved at the 70 °C reaction temperature. That the molecular weights obtained by SEC with polystyrene calibration gave molecular weights reasonably close to the real values was shown by measurements of weight-average molecular weights by low-angle laser light scattering (LALLS) on two polymer samples. LALLS gave values that were 20–25% higher than the weight-average molecular weights obtained from SEC.

End group analysis showed the major end groups to be phenol (XV) and vinyl (XVI). The high molecular weight of the polymers was evident in the end group analysis. The end groups were observable only at high magnification of NMR spectra. For example, Figure 2 shows the ^{1}H NMR spectrum of the polymer obtained by bulk polymerization at 140 °C. There is no indication of end group signals at the normal magnification used to observe the signals for the repeat unit. End group signals A, B, C, and D were observed only at a 32-fold magnification.

There was no indication of alcohol (XVII) end groups in the products from bulk polymerization although the limitations of the ^{1}H NMR method (i.e., detection by a shoulder, signal E, on a large signal) precluded ruling out the presence of significant amounts (10–20%) of alcohol end groups. ^{13}C NMR spectroscopy supported the conclusions from ^{1}H NMR but did not remove the ambiguity regarding the presence or absence of minor amounts of alcohol end groups. ^{13}C signals indicative of the alcohol end groups were not observed but their presence in low amounts would be difficult to observe for the high molecular weight polymers obtained in bulk polymerization.

Table II also shows the results of bulk polymerizations carried out in the presence of sodium methoxide or TFA salt. Both additives had essentially the same effect. There was a negligible effect on the relative amounts of polymer and oligomer but the polymer molecular weight was halved.

Solution Polymerization. Tables III and IV show the results of solution polymerization of the hydroxyethoxy zwitterion in Me_2SO in the absence of any additives. Cyclic oligomer was the major product with the

Table III
Effect of Zwitterion Concentration on Solution Polymerization[a,b]

concn,	product distribution by SEC,[c] %						MW of polym fractn by SEC	
mol/L	C_2	C_3	C_4	C_5	C_6	P	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
0.202	50.3	23.7	6.5	3.1	2.8	13.6	6930	1.2
0.145	59.7	20.8	4.9	2.1	1.7	10.7	6300	1.2
0.101	64.5	19.0	4.2	1.9	1.4	9.1	5700	1.2
0.060	70.9	14.7	3.5	1.9	1.6	7.4	5140	1.1
0.040	74.6	12.3	2.9	2.3	1.9	6.0	5100	1.1
0.020	77.3	8.5	3.3	3.1	2.0	5.7	4420	1.1

[a] Reaction times: 2, 3, and 4 days respectively for zwitterion concentrations of 0.202, 0.145, and 0.020–0.101 mol/L. [b] Polymerization temperature: 80 °C. [c] C_2–C_6 = cyclic dimer through hexamer, P = polymer.

Table IV[a,b]
Effect of Temperature on Solution Polymerization

temp,	product distribution by SEC,[c] %						MW of polym fractn by SEC	
°C	C_2	C_3	C_4	C_5	C_6	P	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
65	58.5	23.1	5.5	2.2	1.7	8.9	6240	1.2
80	59.7	20.8	4.9	2.1	1.7	10.7	6300	1.2
100	62.8	15.4	3.7	1.9	1.2	15.1	6540	1.2
140	59.9	12.7	3.6	2.2	2.1	19.4	6590	1.2

[a] Zwitterion concentration: 0.145 mol/L. [b] Reaction times: 2 and 3 days respectively for temperatures of 100–140 and 65–80 °C. [c] C_2–C_6 = cyclic dimer through hexamer, P = polymer.

polymer fraction accounting for only 6.0–19.4%. Within this narrow range the polymer fraction increased with increasing concentration of hydroxyethoxy zwitterion (Table III) and increasing reaction temperature (Table IV). (The 0.208 M concentration was slightly below the saturation concentration of zwitterion in Me_2SO at ambient temperature.) The molecular weight of the polymer fraction was essentially independent of reaction temperature but did show a significant increase with increasing zwitterion concentration.

Various additives and solvents were investigated in an attempt to increase the polymer fraction. DMF gave similar results to Me_2SO. Decreasing the polarity of the solvent (e.g., by adding diglyme) increased the polymer fraction but its molecular weight was lowered by precipitation from the reaction medium. Additives such as (dimethylamino)ethanol, sodium bicarbonate, and pyridine had a negligible effect on the reaction. A quaternary ammonium phenoxide had a small effect on increasing the polymer fraction, the phenol diol had a larger effect, and the TFA salt had an even larger effect. The effect of added TFA salt on solution polymerization was studied in some detail (Table V). Polymer became the major product in the presence of TFA salt. The polymer fraction increased dramatically to a high of 62.0% in the polymerization with 8.6% added TFA salt. The polymer molecular weight also increased but the effect was not as large as the increase in the polymer yield.

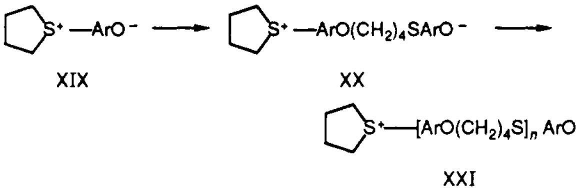
The lower molecular weights in solution polymerization compared to bulk polymerization were evident during the end group analysis. The major end groups were phenol (XV) and alcohol (XVII) and these could be seen in the ^1H NMR spectrum at the same magnification as for the repeat unit signals. End groups were observable in the bulk poymers only at high magnification. A minor amount of vinyl end groups could be observed at high magnification of the spectrum for the polymer obtained by solution polymerization. The alcohol end groups outnumbered the vinyl end groups by about an order of magnitude.

Table V[a]
Effect of TFA Salt Concentration on Solution Polymerization

TFA salt,[b]	product distribution by SEC,[c] %						MW of polym fractn by SEC	
mol %	C_2	C_3	C_4	C_5	C_6	P	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
0.41	48.5	28.3	8.0	3.7	1.6	10.0	5970	1.2
0.83	38.5	29.6	10.4	5.6	2.6	13.4	6360	1.2
3.2[d]	10.8	15.0	8.9	6.2	5.5	53.7	9730	1.7
4.0	11.5	16.0	9.8	6.8	5.6	50.4	8130	1.5
4.6	10.3	14.3	8.5	7.0	4.8	55.2	8800	1.5
6.4	7.9	11.7	7.7	6.7	6.0	52.1	8540	1.5
6.1[e]	10.8	14.1	9.0	8.1	5.9	52.1	7740	1.4
8.6	7.7	9.9	7.7	6.7	6.1	62.0	7860	1.4

[a] Reaction temperature: 65 °C. Reaction time: 3 days. [b] Zwitterion concentration: 0.145 mol/L unless otherwise noted. [c] C_2–C_6 = cyclic dimer through hexamer, P = polymer. [d] Zwitterion concentration: 0.208 mol/L. [e] Zwitterion concentration: 0.101 mol/L.

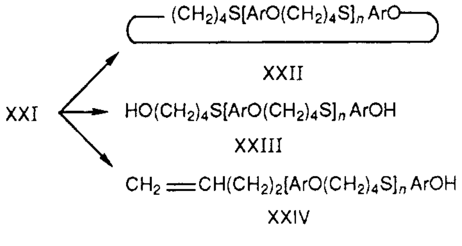
Polymerization Mechanism. The results of the present study are consistent with our previously described mechanism for type 3 zwittion polymerizations.[13,14] The zwitterion XIX becomes destabilized by loss of water of hydration upon heating and undergoes dimerization to XX. The sulfonium and aryloxide centers are more reactive in XX compared to XIX since there is no resonance interaction between the center. Ar in the various structures represents the 2-(hydroxyethoxy)phenyl moiety. XX reacts with itself and with XIX to form tetramer and trimer zwitterion species. Propagation proceeds in a similar manner with the formation of larger zwitterions XXI. Three termination reactions are responsible for stopping polymer growth—intramolecular cyclization to form cyclic oligomer (XXII), substitution by water (of hydration) to yield polymer molecules with alcohol and phenol end groups (XXIII), and β-elimination to yield polymer molecules with vinyl and phenol end groups (XXIV).



(5)

(6)

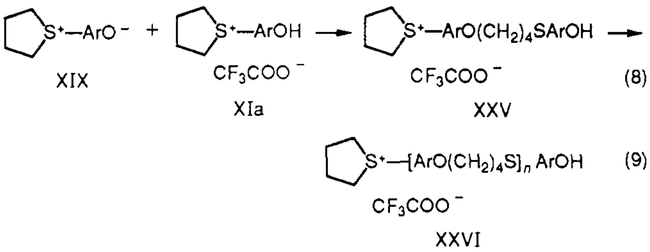
Two of the three termination modes, cyclization and substitution, are relatively unimportant in bulk (solid-state) polymerization of the hydroxyethoxy zwitterion. Cyclization plays a minor role due to the high reactant concentration in bulk polymerization. The cyclic oligomer fraction comprises no more than 11.7% of the reaction products. Substitution by water is negligible (detected by the absence of alcohol end groups) as the water of hydration is expelled from the reaction mixture at the reaction temperatures (70–100 °C) used in bulk polymerization. The decrease in polymer molecular weight with increasing temperature indicates that β-elimination



(7)

becomes progressively more competitive with propagation at higher tempertures but the effect is only moderate.

Bulk polymerization in the presence of sodium methoxide or TFA salt (XIa) results in decreased polymer molecular weights. The addition of TFA salt affects polymer molecular weight by increasing the initiation rate. Initiation in the absence of TFA salt proceeds by self-reaction of zwitterions (XIX) to yield XX (eq 5). Subsequent reactions of XX with itself and the zwitterion are faster than the self-reaction of the zwitterion. Self-reaction is slower since the S^+ and O^- centers of the zwitterion are stabilized by through-resonance interaction with each other. The S^+ and O^- centers of XX and XXI are more reactive since they are not involved in through-resonance interaction. An alternate initiation process is introduced when the TFA salt is present. TFA salt XIa reacts with the zwitterion to form species XXV (eq 8). XXV propagates by reaction of its S^+ center with the O^- center of the zwitterion (eq 9). XXV is formed faster than the corresponding species (XX) responsible for initiation in the absence of TFA salt since the S^+ of the TFA salt is more reactive than the S^+ of the zwitterion. The zwitterion is stabilized by through-resonance while the TFA salt is not. There may be some additional effect of the TFA salt on the polymer molecular weight through termination of O^- centers of XXI by proton transfer. This is probably not the major effect of the TFA salt since the result of that proton transfer is to convert XXI to XXVI and the latter is still a propagating species.



The effect of sodium methoxide in decreasing the polymer molecular weight is analogous to that of TFA salt. The presence of sodium methoxide introduces an alternate and faster route to initiation. Sodium methoxide reacts with zwitterion to form the initiating species XXVII at a rate faster than initiation by the self-reaction of zwitterion. Propagation proceeds by repetitive reaction of XXVI with the zwitterion. In addition, sodium methoxide (and/or sodium hydroxide formed via its reaction with the water of hydration) has a secondary (but less important) effect via termination by β-elimination.

$$CH_3O(CH_2)_4SArO^-Na^+$$

XXVII

Solution polymerization in the absence of TFA salt yields cyclic oligomer as the major product since intramolecular reaction is favored relative to intermolecular reaction by low zwitterion concentrations. The relative amounts of different-sized cyclic oligomers correspond with expectations based on kinetic considerations. There is a decreasing tendency toward cyclization with increasing ring size. Cyclization decreases with increasing reaction temperature pesumably due to a decrease in the conformations favorable to cyclization and/or an increase in propagation relative to cyclization. The lower polymer molecular weights compared to bulk polymerization are ascribed to the high cyclization rate combined with the decreased tendency for expulsion of water from the reaction system. The presence of TFA salt alters the course of the reaction with a 3-fold increase in the polymer fraction. Cyclization becomes the minor product since the one-ended ions (XXV and its larger homolgues) would have a decreased tendency toward cyclization compared to zwitterion species (because ArOH is less nucleophilic than ArO^-). The decreased cyclization rate also results in an increase in polymer molecular weight as there is more zwitterion available for linear growth.

Summary. The hydroxyethoxy zwitterion is the first example of a type III system that can be polymerized both in bulk and solution. Bulk polymerization gave a very high yield (88.3–90.6%) of the highest molecular weight polymer ever reported in any type of zwitterion polymerization. Solution polymerization gave much lower polymer molecular weights but still higher than almost all previously reported type 1 zwitterion polymerization.

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