on polystyrene standards) M_n is 4400 g/mol while M_w is 4800 g/mol.

Acknowledgment. I would like to acknowledge E. Gurnee, S. Babinec, and A. Gatzke for much helpful advice and discussion and S. Konoponicki, P. Kirchhoff, R. Newman, and D. Hawn of the Dow Analytical Laboratory for their help in characterization and to G. Eastland of Saginaw Valley State College for running the ESR spectra.

Registry No. III, 107259-31-4; HO-*p*-C_4H_4-CH_2CH_2OH, 501-94-0; 2-chloro-1,4-diaminoanthraquinone, 54841-24-6; 2,6-dimethylphenol, 576-26-1; poly(2,6-dimethylphenylene oxide), 24938-67-8; ethylene, 74-85-1.

References and Notes

(1) Acker, D. S.; Harder, R. J.; Hertler, W. R.; Maher, W.; Melby, L. R.; Benson, R. E.; Mochel, W. E. *J. Am. Chem. Soc.* **1960**, *82*, 6408.
(2) Little, W. A. *Phys. Rev.* **1964**, *134*(6A), A1416.
(3) Shirakawa, H.; Ito, T.; Ikeda, S. *Polym. J.* **1973**, *4*, 460.
(4) Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 578.
(5) Shacklette, L. W.; Chance, R. R.; Ivory, D. M.; Miller, G. G.; Baughman, R. H. *Synth. Met.* **1980**, *1*, 307.
(6) Shacklette, L. W.; Elsenbaumer, R. L.; Chance, R. R.; Eckhardt, H.; Frommer, J. E.; Baughman, R. H. *J. Chem. Phys.* **1981**, *75*(4), 1919.
(7) Kanazawa, K. K.; Diaz, A. T.; Gill, W. D.; Grant, P. M.; Street, G. B.; Gardini, G. P.; Kwak, J. F. *Synth. Met.* **1980**, *1*, 329.
(8) Wohrle, D. *Adv. Polym. Sci.* **1983**, *50*, 47.
(9) Nohr, R. S.; Kuznesof, P. M.; Wynne, K. J.; Kenney, M. E.; Srebenmann, P. G. *J. Am. Chem. Soc.* **1981**, *103*, 4371.
(10) Schoch, K. F.; Kundalkar, B. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 7071.
(11) Wegner, G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 361.
(12) Frommer, J. E. *Acc. Chem. Res.* **1986**, *19*, 2.
(13) Block, B. P. In *Encyclopedia of Polymer Science and Technology*; Conrad, J., Ed.; Interscience: New York, 1966; Vol. 4; pp 150-165.
(14) Prakash, H. *Indian J. Chem.* **1981**, *20A*, 708.
(15) Kim, O. K.; McDermott, D.; Tsai, T. Presented at the 193rd National Meeting of the American Chemical Society, Denver, CO, April 1987; PHYS 209.
(16) Reynolds, J. R.; Lillya, C. P.; Chien, J. C. W. *Macromolecules* **1987**, *20*, 1184.
(17) Hoph, F. R.; Rogic M. M.; Wolf, J. F. *J. Phys. Chem.* **1983**, *87*(23), 4681.
(18) Praliaud, H.; Kodratoff, Y.; Coudurier, G.; Mathieu, M. V. *Spectrochim. Acta, Part A* **1974**, *30A*, 1389.
(19) Bodek, I.; Davies, G. *Inorg. Chem.* **1978**, *17*, 1814.
(20) Rogic, M. M.; Demmin, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 5472.
(21) Demmin, T. R.; Swerdloff, M. D.; Rogic, M. M. *J. Am. Chem. Soc.* **1981**, *103*, 5795.
(22) Davies, G.; El-Sayed, M. A. In *Copper Coordination Chemistry: Biochemical & Inorganic Perspectives*; Karlin, K. D., Zubieta, J. Eds.; Adenine: New York, 1983; p 297.
(23) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Interscience: New York, 1972; p 921.
(24) Diel, B. N.; Inabe, T.; Lyding, K. F.; Schoch, K. F.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1551.
(25) Alexander, L. E. *X-Ray Diffraction Methods in Polymer Science*; Krieger: Huntington, 1979; p 335.
(26) Teh, F. Y.; Erdman, J. G.; Pollack, S. S. *Anal. Chem.* **1961**, *33*(11), 1587.
(27) Solomon, E. I. *Pure Appl. Chem.* **1983**, *55*(7), 1069.
(28) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.
(29) Schoch, K. F.; Kundalkar, B. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 7071.
(30) Van Krevelen, D. W.; Goedhart, D. J.; Hoftijzer, P. J. *Polymer* **1977**, *18*, 751.
(31) Babinec, S. J. The Dow Chemical Company, unpublished results.
(32) Stathis, E. C. *Chem. Ind.* **1958**, 633.
(33) Phillips, D. A. Br. Patent 1 373 356.

Zwitterion Polymerization of 1-[(4-Carboxyphenyl)methyl]tetrahydrothiophenium Hydroxide Inner Salt

P. Gunatillake and G. Odian*

College of Staten Island, City University of New York, Staten Island, New York 10301

D. L. Schmidt

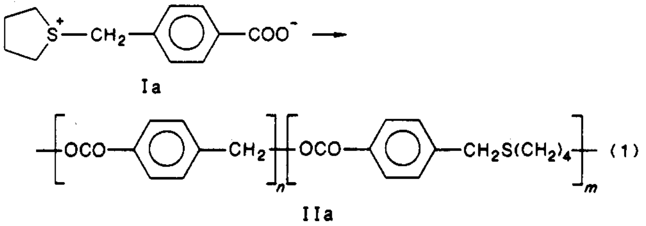
Central Research—Specialty Products, Dow Chemical Company, Midland, Michigan 48640.

Received February 18, 1988

ABSTRACT: The zwitterion 1-[(4-carboxyphenyl)methyl]tetrahydrothiophenium hydroxide inner salt was synthesized from tetrahydrothiophene (thiolane) and 4-(chloromethyl)benzoic acid and characterized by NMR and IR spectroscopy. Bulk polymerization of the zwitterion over the temperature range 70-200 °C gave linear polymer in 88-96% yield. The polymer was identified as a random copolymer containing oxycarbonyl-1,4-phenylenemethylene and oxycarbonyl-1,4-phenylenemethylenethiotetramethylene repeat units based on NMR, IR, and elemental analysis. Size-exclusion chromatography showed the number-average molecular weight to vary with temperature in the range 5100-41 000. Solution polymerization in DMF gave lower polymer yields (38-69%), lower polymer molecular weights (3000-7400), and higher oligomer yields (31-62%). HPLC fractionation coupled with NMR identified the oligomer fraction as consisting of a range of linear and cyclic oligomers of varying molecular size. The polymer end groups were identified by ^1H NMR as OH and COOH. When methanol was present during polymerization, the COOH end group was replaced by $COOCH_3$. Polymerization proceeded by ring-opening nucleophilic attack of carboxylate anion on the benzylic carbon and α-carbon of the tetrahydrothiophenium (thiolanium) ring to incorporate the two different types of repeat units into the polymer. Termination involved cyclization and reaction of propagating centers with water (and methanol, when present).

Introduction

Zwitterions have been proposed as reactive intermediates in polymerizations involving various pairs of electrophilic and nucleophilic reactants (e.g., β-propiolactone or acrylic acid with 2-methyl-2-oxazoline).[1,2] Zwitterion polymerizations involving stable (isolable) zwitterions have received relatively less attention. We recently reported the thermally initiated zwitterion polymerization of tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide inner salt which proceeds via ring-opening nucleophilic attack of ArO^- on the CH_2–S^+ bond of the tetrahydrothiophenium ring.[3] This paper reports the synthesis of 1-[4-carboxyphenyl)methyl]tetrahydrothiophenium hydroxide inner salt (I) and its thermal polymerization to a random copolymer II containing oxycarbonyl-1,4-phenylenemethylene and oxycarbonyl-1,4-phenylenemethylenethiotetramethylene repeat units. The two repeat units will be referred to as A and B repeat units, respectively, throughout this paper. I and II will be referred to as the thiolanium benzoate zwitterion (or monomer) and polymer, respectively. Although structure II is written as a block copolymer, II is not a block copolymer. II is a random copolymer with an overall composition given by the values of n and m.

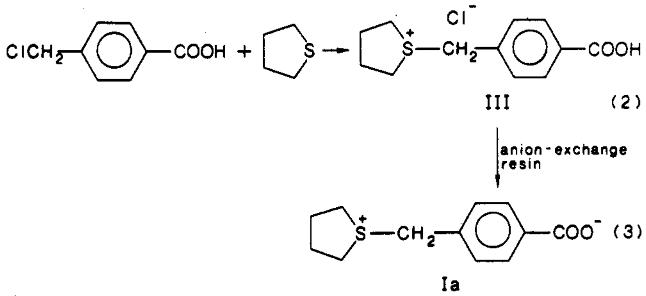

Ia

IIa (1)

Experimental Section

Materials. 4-(Chloromethyl)benzoic acid, tetrahydrothiophene (thiolane), tetrahydrofuran (Aldrich), DMF, methanol, acetonitrile, methylene chloride, and diethyl ether (Fisher) were used as received unless otherwise indicated.

Synthesis of Thiolanium Benzoate Zwitterion. The thiolanium benzoate zwitterion was synthesized according to eq 2 and 3. Tetrahydrothiophene (thiolane) (31.0 g, 0.352 mol) was added with stirring to a solution of 4-(chloromethyl)benzoic acid (10.0 g, 0.0586 mol) in tetrahydrofuran (45.0 g) to yield a clear solution. The reaction vessel was sealed and heated at 35 °C with stirring for 7 days. The insoluble product III, 1-[(4-carboxyphenyl)methyl]tetrahydrothiophenium chloride was filtered, washed twice with anhydrous diethyl ether, and dried under suction. The dry powder was purified twice by dissolving in a mixture of methanol (30 mL) and water (2 mL) and then precipitated by pouring into diethyl ether (100 mL). A yield of 5.0 g (35%) of white crystals was obtained after filtering, washing with diethyl ether, and drying for 2 h in the funnel with nitrogen pressure.



III (2)

Ia (3)

1-[(4-Carboxyphenyl)methyl]tetrahydrothiophenium chloride (2.0 g, 0.0077 mol) was dissolved in methanol (20 mL) and treated with Dowex-2 anion-exchange resin (hydroxide form) to increase its pH to 10. The methanol solution was concentrated in a rotary evaporator at 30 °C, diethyl ether added until the solution turned cloudy, and then the mixture cooled in a refrigerator to precipitate white crystalline thiolanium benzoate zwitterion. Purification by redissolution in methanol, addition of diethyl ether, and cooling yielded 1.3 g (76%) of thiolanium benzoate zwitterion after the mixture was dried for 2 h under pressurized nitrogen. The zwitterion obtained in this manner contained 0.4 mol of methanol/mol of zwitterion as determined by ^1H NMR. Thiolanium benzoate zwitterion free of methanol was prepared by dropwise addition of a 20% solution of the zwitterion in methanol into a 15-fold excess of anhydrous diethyl ether. The resulting solution was stirred for 1 h, filtered under suction, washed three times with diethyl ether, and then dried under nitrogen pressure for 2 h. Polymerization studies were carried with both the methanol-containing and methanol-free thiolanium benzoate zwitterion.

Polymerization. For bulk polymerization experiments, thiolanium benzoate zwitterion was placed in a polymerization tube, sealed under vacuum (1 Torr), and heated at the desired temperature. Some bulk polymerizations were carried out under continuous vacuum (1 Torr). Solution polymerization was carried out in DMF at 30% (w/v) monomer concentration in a sealed tube. The reaction mixture in bulk polymerization was dissolved in hot DMF and the resulting solution poured into a 15-fold excess of diethyl ether to precipitate the thiolanium benzoate polymer. For solution polymerizations, the reaction mixture was directly precipitated into diethyl ether. (The ether solutions were separately worked up to examine the nonpolymeric products. These products are referred to as ether-soluble products.) The precipitated white solid polymers were isolated by filtration, washed with ether, and dried overnight in a vacuum oven (1 Torr) at 40 °C.

Size-Exclusion Chromatography (SEC). SEC of reaction mixtures and purified polymer products was carried out at 100 °C on a Waters 150C instrument with 840 Work Station using DMF (dried over 3-Å molecular sieves) containing 0.05 N LiBr as the mobile phase at a flow rate of 1.0 mL/min. The stationary phase consisted of a set of four Ultrastyragel columns of 10^5, 10^4, 10^3, and 500 Å and one 100 Å Shodex column. The SEC calibration was based on polystyrene standards.

Vapor Pressure Osmometry (VPO). The number-average molecular weights of purified polymer samples were determined with a Knauer vapor pressure osmometer using DMF (HPLC grade) at 105 °C. The instrument was calibrated with benzil (MW 210.13). Four concentrations in the 1–6% (w/w) range were used for analysis.

Spectroscopic Analysis. IR spectra of the thiolanium benzoate zwitterion and polymer were recorded on a Beckman 4260 IR spectrometer using KBr pellet and thin film samples, respectively. The thin film sample was deposited on a NaCl plate from 1,1,2,2-tetrachloroethane solution; the solvent was evaporated overnight in a vacuum oven at 50 °C. Mass spectroscopy was performed on a V.G. ZAB instrument operating at medium resolution in the fast-atom (8 KV Xenon) bombardment ionization mode. ^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 zwitterion was obtained at 25 °C by using a 5% (w/v) solution in D_2O. ^1H NMR of the polymer was obtained at 25 °C by using 1–4% (w/v) solution in 1,1,2,2-tetrachloroethane-d_2 (TCE-d_2). ^{13}C NMR spectra of the zwitterion and polymer were obtained by using 10% (w/v) solutions in D_2O and TCE-d_2, respectively. Me_4Si and sodium 4,4-dimethyl-4-silapentane-1-sulfonate (DSS) were used as internal standards in TCE-d_2 and D_2O, respectively. The acquisition parameters for ^1H NMR were 30° pulse angle, 6-s total delay between pulses, and 128-256 total acquisitions. The acquisition parameters for ^{13}C NMR were 30° pulse angle, 2.5-s total delay between pulses, and 10 000–20 000 total acquisitions. Data were acquired and Fourier transformed in 16K.

High-Performance Liquid Chromatography. Analytical HPLC of the ether-soluble reaction 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 methylene chloride–acetonitrile (100:5) at a flow rate of 1 mL/min maintained at 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 sample injected in volumes of 5–25 μL of mobile phase. The UV detector was set at 254 nm at 0.04 AUFS (absorbance units for full scale) for detection of the aromatic moiety.

The ether-soluble products were fractionated by preparative HPLC with a Waters Prep LC system 500 using a PrePack-500 silica column with methylene chloride–acetonitrile (100:2) as the mobile phase. A solution of the products 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. With the elution of successive components, the polarity of the mobile phase was gradually increased by increasing the acetonitrile

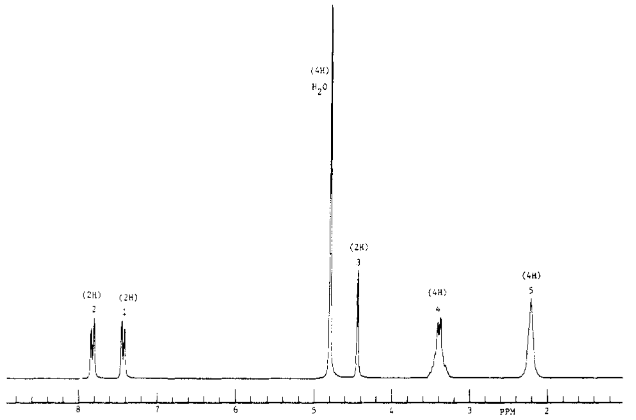


Figure 1. 200.1-MHz ^1H NMR spectrum of thiolanium benzoate zwitterion.

content in 2% increments. Pure fractions (i.e., fractions containing one component as determined by HPLC) of the same component and fractions containing one major and 1–2 minor components were combined, concentrated in a rotary evaporator under reduced pressure at 40 °C, and dried overnight in a vacuum oven at 40 °C.

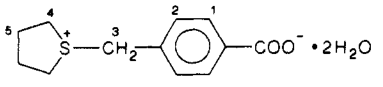
Acetylation of Thiolanium Benzoate Polymer. The polymer (0.10 g) was dissolved in TCE (1 mL), and pyridine (0.040 g) in TCE (0.5 mL) was added with stirring to the polymer solution at ambient temperature. Acetyl chloride (0.040 g) in TCE (0.5 mL) was added with stirring and the reaction mixture stirred for 2 h and then added to a 20-fold excess of diethyl ether. The resulting precipitate was filtered off, washed with water followed by acetone, and then dried overnight in a vacuum oven at 40 °C.

Karl Fischer Titration. Karl Fischer titration for water was performed ampherometrically by using a Labindustries Inc. 1003 Aquametry II Meter-Electrode.

Results and Discussion

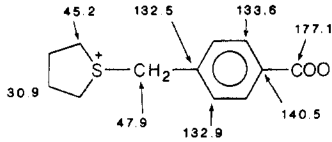
Identification of Thiolanium Benzoate Zwitterion. The zwitterion is a white crystalline solid soluble in methanol, water, and hot DMF and Me_2SO. It is formed as a hydrate with the water of hydration apparently involved in stabilizing the ionic centers as is the case for the tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide inner salt.[3] The methanol-free thiolanium benzoate zwitterion is a dihydrate as determined by three methods. First, ^1H NMR of the zwitterion showed a signal for water of hydration at 4.81 ppm (see below). Second, polymerization of the monomer resulted in a weight loss due to loss of water and tetrahydrothiophene. The total weight loss was corrected for the loss of tetrahydrothiophene (determined by ^1H NMR of the polymer) to yield the water loss. Third, Karl Fisher titration for water was performed ampherometrically. The three methods were in excellent agreement and yielded 2.0 mol water/mol of zwitterion. Karl Fisher titration showed the methanol-containing zwitterion to contain 1.4 mol of water (in addition to 0.4 mol of methanol)/mol of zwitterion.

The structure of the thiolanium benzoate zwitterion was established by IR and NMR spectroscopy. Figure 1 shows the ^1H NMR spectrum of the methanol-free zwitterion with the signal assignments indicated in Ib based on



Ib

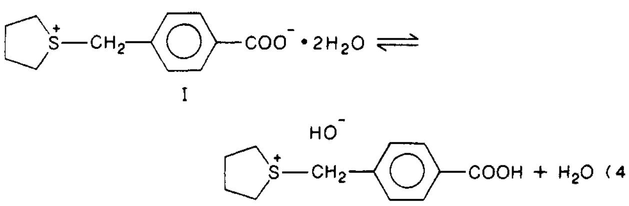
chemical shift values,[3,4] splitting patterns, and signal areas. (When methanol was present in the zwitterion, a singlet was observed at 3.33 ppm for the CH_3O protons.) The proton-decoupled ^{13}C NMR spectrum supported structure I for the thiolanium benzoate zwitterion with the ppm values for various carbons assigned as shown in Ic based



Ic

on the chemical shift values for similar carbons.[3-5] The chemical shifts of the aromatic carbons were calculated on the basis of additive effects of substituents.[5] The substituent parameters for $Me_2S^+CH_2$ and COO^-Na^+ were used in the calculation to simulate those for the thiolanium ring and COO^-, respectively. The observed chemical shift values were in good agreement with the calculated values with the largest difference being 2.7 ppm for the carbon para to COO^-. There is no interaction between the S^+ and COO^- centers due to the presence of the methylene group between the benzene and thiolanium rings. Accordingly, no significant deviations are observed from the parts per million values calculated on the basis of the additivity principle of substituent effects. The situation is quite different for zwitterions in which the thiolanium ring is attached directly to the aromatic ring. Resonance interaction between + and − centers is possible, and large upfield shifts are observed for the aromatic carbon attached to the sulfonium sulfur. For example, the difference between calculated and observed chemical shift values is 28.9 ppm for the tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide inner salt.[3]

The infrared spectrum of the sample in KBr generally supported structure I for the thiolanium benzoate zwitterion. The spectrum showed absorptions at 3400 (H_2O); 3040 (aromatic C–H); 2955, 2918, and 2838 (aliphatic C–H); 1543 (aromatic C–C); 875, 865, 840, 795, 785, and 715 (aromatic C–H); and 1590 and 1360 (COO^-) cm^{-1}. Absorptions at 1440, 1412, 1305, 1295, 1260, 1105, 1012, and 945 cm^{-1} were also compatible with structure I and attributed to aromatic C–C, methylene twisting and wagging vibrations, aromatic C–H in-plane bending vibrations, and SCH_2 and CH_2 ring bending vibrations. A strong absorption at 1641 and a broad absorption at 3230 cm^{-1} (a shoulder on the broad H_2O absorption at 3400 cm^{-1}) did not agree with structure I. The presence of these two absorptions may indicate that I exists in equilibrium with its hydroxide salt IV. The absorptions at 3230 and 1641 cm^{-1} were assigned to the OH and C=O, respectively, of the COOH group of IV. The presence of IV is indicated only for solid samples of the thiolanium benzoate zwitterion since infrared spectroscopy was carried out only on solid samples. The importance of IV in solution samples was not ascertained by infrared spectroscopy since the zwitterion was not soluble in an appropriate solvent. However, NMR analysis of solution samples in D_2O gave no indication of the presence of any form other than I although a fast equilibrium between I and IV cannot be ruled out.



I

IV (4)

Bulk Polymerization. Bulk polymerization of the thiolanium benzoate zwitterion was carried out in sealed tubes and under continuous vacuum. Polymerization

Table I
Effect of Temperature on Bulk Polymerization[a,b]

temp, °C	yield, %	MW by SEC[c] $\bar{M}_n$	MW by SEC[c] $\bar{M}_w/\bar{M}_n$	ratio of repeat units, A/B[d]
Polymerization of CH_3OH-Free Zwitterion				
70	92	17900	1.2	3.2
100	90	23700	3.1	3.0
130	96	17400	2.1	3.2
160	91	9400	2.1	4.0
200	88	5100	1.4	99
Polymerization of CH_3OH-Containing Zwitterion[e]				
100	92	21300	3.0	3.0
160	91	9300	2.1	4.0
Polymerization of CH_3OH-Free Zwitterion under Continuous Vacuum				
100		27200[f]	3.2	3.2
130		41000[f,g]	1.7	

[a] Reaction time: 65 h. [b] All polymerizations were done in sealed tubes unless otherwise noted. [c] All SEC measurements was on purified polymer samples unless otherwise noted. [d] Molar ratio of A to B types of repeat units as determined by ^1H NMR. [e] 0.4 mol of CH_3OH/mol zwitterion. [f] SEC of unpurified reaction mixture. [g] SEC of soluble portion of unpurified reaction mixture.

proceeded with release of water and tetrahydrothiophene which condensed at the top of the reaction tube in sealed tube experiments. The products in all experiments were white solids soluble in hot DMF, DMSO, and TCE except that those obtained by polymerization under continuous vacuum at 130 °C were only partially soluble. The insoluble portion, comprising about half of the total product, swelled in hot DMF. The zwitterion melted during polymerization at temperatures of 130 °C and above; polymerization at 70 and 100 °C proceeded in the solid state. ^1H NMR of the reaction mixtures showed the absence of unreacted zwitterion indicating complete conversion of monomer to products in all polymerizations.

Molecular weights were determined by SEC (based on calibration with polystyrene standards), and the results are shown in Table I. In sealed tube polymerizations with methanol-free zwitterion, the polymer molecular weight increased with reaction temperature, reached a maximum at 100 °C, and then decreased at temperatures above 100 °C. The decrease in polymer molecular weight was gradual until temperatures above 130 °C were reached. The presence of methanol did not have a significant effect on polymer molecular weight and yield. In polymerizations under continuous vacuum the polymer molecular weight was slightly higher at 100 °C and considerably higher at 130 °C compared to those in sealed tube experiments. However, the polymer obtained at 130 °C was only partially soluble in hot DMF, and the reported molecular weight is only for the soluble portion of the polymer. The insoluble portion swelled in hot DMF. The product obtained at 160 °C under continuous vacuum was completely insoluble but swollen by hot DMF. (The insoluble products may be cross-linked.)

Figure 2 shows a typical SEC plot for the thiolanium benzoate polymer. This plot, for polymer synthesized by bulk polymerization at 100 °C, shows a unimodal molecular weight distribution and indicates the absence of significant amounts of oligomers. However, there is a long tail of low molecular weight material. The low molecular weight tails of the SEC plots up to 48.2 min were included in calculating the molecular weights presented in Table I. If the low molecular weight tails are excluded from the calculations, the polymer molecular weights are considerably higher. For example, for the sample whose SEC plot is shown in Figure 2, the number-average molecular weight is 80600 for the portion of the sample eluting between 30 and 37.5 min which corresponds to 80% of the total polymer products.

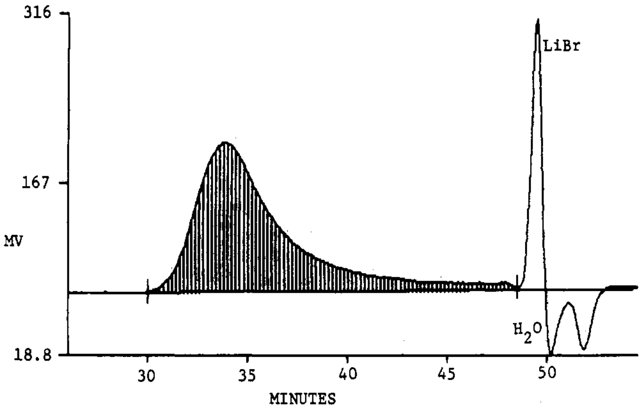


Figure 2. SEC of thiolanium benzoate polymer synthesized by bulk polymerization at 100 °C under continuous vacuum.

Table II
Effect of Temperature and Concentration on Solution Polymerization[a]

temp, °C	yield, %	MW SEC[b] $\bar{M}_n$	MW SEC[b] $\bar{M}_w/\bar{M}_n$	MW VPO $\bar{M}_n$	ratio of repeat units, A/B
Polymerization of CH_3OH-Containing Zwitterion[c]					
100	68	7400	2.3		4.3
130	69	5400	1.7	3370	4.1
160	38	4100	1.2		4.7
130[d]	81	7300	1.9	5800	3.7
Polymerization of CH_3OH-Free Zwitterion					
100	68	7400	2.7		4.5
160	63	3000	1.3		6.9

[a] Polymerization in sealed tubes for 65 h. [b] SEC of purified polymers. [c] 0.4 mol of CH_3OH/mol zwitterion. [d] Monomer concentration was 60% (w/v) for this experiment; 30% concentration was used in all other polymerizations.

Solution Polymerization. Solution polymerization was carried out in the 100–160 °C temperature range, and the results are shown in Table II. The polymer products were white solids soluble in hot DMF, DMSO, and TCE. The polymer molecular weight decreased with increasing reaction temperature and increased with increasing monomer concentration. The molecular weights and yields were much lower than those obtained in bulk polymerization. The molecular weights of two samples were determined by vapor pressure osmometry (VPO), and the results are shown in Table II. The number-average molecular weights by SEC were higher than those determined by VPO. The difference is attributed to the use of polystyrene standards for calibration of SEC. (The thiolanium benzoate polymer is more polar, is more solvated by DMF, and elutes faster in SEC compared to polystyrene.) Methanol affected the polymer yield at 160 °C but had negligible effect for polymerizations at lower temperatures. When a 2-fold molar excess of methanol was added to the thiolanium benzoate zwitterion, the polymer yield dropped to 6% for polymerization at 160 °C.

Characterization of Polymer. The thiolanium benzoate polymers were characterized by IR, elemental analysis, and ^1H and ^{13}C NMR. Figure 3 shows the ^1H NMR spectrum of the polymer prepared in bulk at 100 °C under continuous vacuum. The spectrum was consistent with structure II for the copolymer in which oxycarbonyl-1,4-phenylenemethylene and oxycarbonyl-1,4-phenylenemethylenethiotetramethylene repeats units

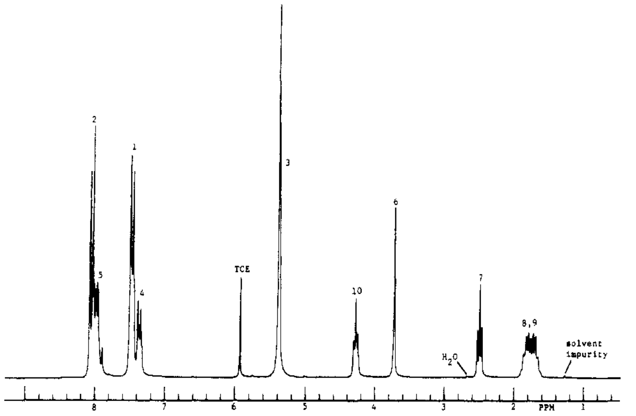


Figure 3. 200.1-MHz ^{1}H NMR spectrum of thiolanium benzoate polymer synthesized by bulk polymerization at 100 °C under continuous vacuum.

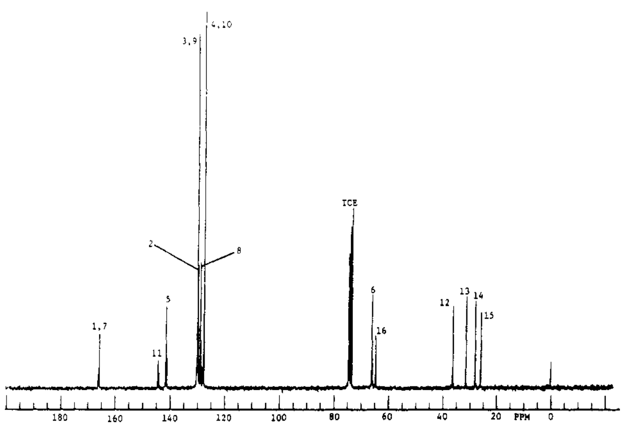
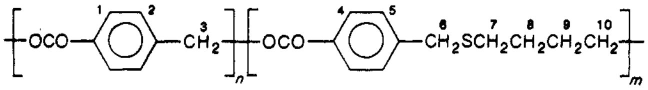


Figure 4. 50.3-MHz ^{13}C NMR spectrum of thiolanium benzoate polymer synthesized by bulk polymerization at 160 °C.

(subsequently referred to as A and B repeat units, respectively) are randomly placed along the polymer chain. The various ^{1}H NMR signals are assigned as shown in IIb.



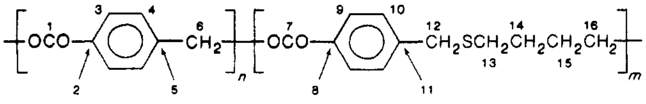
IIb

The ratios of A to B repeat units for various polymer samples were determined by ^{1}H NMR spectroscopy using the ratio of signal areas for the two different types of benzylic protons (signals 3 and 6), and the results are shown in Table I. Polymers obtained by bulk polymerization in the 70–130 °C temperature range contained three A repeat units for each B repeat unit. The ratio A/B increased to 4 at 160 °C, and the product was a homopolymer of A at 200 °C. Rapid removal of water and tetrahydrothiophene from the zwitterion during polymerization had no effect on the copolymer composition as the A/B ratio was identical for sealed tube and continuous vacuum experiments. (The presence of tetrahydrothiophene among the reaction products was verified by ^{1}H NMR analysis of the unpurified reaction mixture from a sealed tube bulk polymerization. The spectrum showed two triplets at 1.92 and 2.80 ppm, assigned to CH_2 and SCH_2 protons, respectively, of tetrahydrothiophene, in addition to the polymer signals. These two signals were absent in the spectrum of the purified polymer since tetrahydrothiophene dissolves in the ether layer during purification.)

The A/B ratio was determined by kinetic factors not thermodynamic factors. This was ascertained by heating at 200 °C a polymer sample originally synthesized at 100 °C. No change in the A/B ratio was observed upon heating at the higher temperature.

The elemental analysis (Found: C, 68.86; H, 5.38; S, 4.92) for the polymer synthesized at 100 °C was in good agreement with that calculated for a copolymer with an A/B ratio of three (Theory: C, 69.21; H, 5.17; S, 5.13).

^{13}C NMR spectroscopy supported structure II for the thiolanium benzoate polymer. Figure 4 shows the ^{13}C NMR spectrum of the polymers and the signals are assigned as shown in IIc. The methylene carbon region of the spectrum was simple, and the signal assignments were made on the basis of chemical shift values for similar carbons. The spectrum of the aromatic region was somewhat complicated. The chemical shift values for the various aromatic carbons were calculated on the basis of additive effects of substituents on the aromatic ring.[5] The substituent parameters for $COOCH_3$ and CH_2OCOCH_3 were used to simulate those on the aromatic ring of repeat unit A; the parameters for $COOCH_3$ and CH_2SCH_3 to simulate those on the aromatic ring of repeat unit B. The calculated chemical shift values were in excellent agreement with the observed values with the largest difference being only 1.0 ppm. The carbonyl carbons and several of the aromatic carbons showed multiple signals attributable to AB diads in the copolymer structure. Significantly higher intensities of these signals indicated the copolymer to be mostly random and not a block copolymer. A block copolymer would have very low concentrations of AB junctions and consequently low intensity carbon signals for the corresponding carbons. The A/B ratio of the copolymer synthesized at 100 °C was calculated from the signal areas (obtained from an inverse gated decoupling experiments) for signals 6 and 12 which represented repeat units A and B, respectively. The A/B ratio obtained, 3.0, was in excellent agreement those calculated from ^{1}H NMR and elemental analysis.



IIc

NMR (^{1}H and ^{13}C) spectra of polymers obtained in solution polymerization under various conditions were similar to those of polymers obtained in bulk polymerization. The spectral data were consistent with structure II. The A/B ratio was about 4, slightly higher than found in bulk polymerization, for all polymers except the polymer obtained at 160 °C with methanol-free thiolanium benzoate zwitterion which had a ratio of 6.9.

The infrared spectrum of the thiolanium benzoate polymer showed major absorption peaks at 3140 (aromatic C—H), 2940 (aliphatic C—H), 1575 and 1505 (aromatic C—C), 1265 and 1100 (C—O), 842 and 750 (aromatic C—H), and 1717 cm^{-1} (ester C=O). Additional absorptions at 1450, 1412, 1372, 1310, 1175, and 1015 cm^{-1} are consistent with CO, CH_2, aromatic CH, SCH_2, and other moieties of structure II.

Polymer End Groups. The polymer end groups were identified by ^{1}H NMR as hydroxyl (HO), carboxyl (COO-H), and ester methyl ($COOCH_3$) for thiolanium benzoate polymers synthesized under various reaction conditions in solution polymerization. The polymers prepared from methanol-free monomer contained only hydroxyl and carboxyl end groups whereas those synthesized from methanol-containing monomer contained all three types of end groups.

The end group signals in the ^{1}H NMR spectrum (Figure 5) of a polymer prepared from methanol-free zwitterion

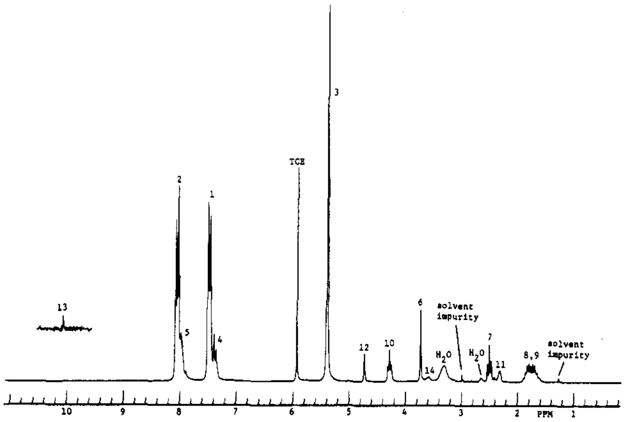


Figure 5. 200.1-MHz ^1H NMR spectrum of thiolanium benzoate polymer synthesized by solution polymerization at 160 °C.

are assigned as shown in V and VI where $\sim\sim$ represents the A and B repeat units. The COOH proton signal was very

$$\overset{11}{H}O\overset{12}{C}H_2Ph\sim\sim COO\overset{13}{H} \qquad \overset{11}{H}O\overset{14}{C}H_2(CH_2)_3SCH_2Ph\sim\sim COO\overset{13}{H}$$

V VI

weak, presumably due to slow exchange with water present in the sample (water appears as a broad signal at 3.30 ppm in Figure 5). The hydroxyl proton is seen as a relatively strong signal indicating it does not exchange rapidly with water (perhaps due to its being in the hydrophobic portion of the polymer). If exchange were slow enough, we would expect splitting between signals 11 and 12 and between signals 11 and 14. Signals 11 and 14 appear at high magnification of the NMR spectrum to have shoulders—which may comprise unresolved splitting. Signal 12 is clearly not split and the reason is not evident. (There is a second but smaller water signal at 2.65 ppm which is assigned to undissolved water. We have previously observed the phenomenon of two water signals due to dissolved and undissolved water. One can observe this in some NMR samples which show only one water signal by deliberately adding water. A second water signal appears at some point and grows continuously in size as one reaches the situation where heterogeneity is visible to the eye. Further water addition results in further increase in the size of the second water signal. Both water signals exchange with D_2O.)

The assignments of the hydroxyl, carboxyl, and two water signals were aided by an experiment in which D_2O was added to the NMR sample. This resulted in the disappearance of all four signals—signal 11 (hydroxyl), signal 13 (carboxyl), and the two water signals at 2.65 and 3.30 ppm. Additional verification of hydroxyl and carboxyl end groups was obtained from ^1H NMR spectroscopy of the acetylated thiolanium benzoate polymers. Signals 11–14 disappeared and were replaced by signals due to various CH_3 and CH_2 protons for the acetylated end groups with the observed parts per million values shown in VII and VIII. The signal area for the anhydride methyl signal

$$\underset{\textstyle CH_3}{\overset{2.08}{\downarrow}}COO\underset{\textstyle CH_2}{\overset{5.13}{\downarrow}}Ph\sim\sim COOCO\underset{\textstyle CH_3}{\overset{2.33}{\downarrow}}$$

VII

$$\underset{\textstyle CH_3}{\overset{1.97}{\downarrow}}COO\underset{\textstyle CH_2}{\overset{3.97}{\downarrow}}CH_2CH_2CH_2SCH_2Ph\sim\sim COOCO\underset{\textstyle CH_3}{\overset{2.33}{\downarrow}}$$

VIII

(acetylated polymer) was much larger than that for the COOH signal (unacetylated polymer)—corroborating that there was exchange between COOH and water.

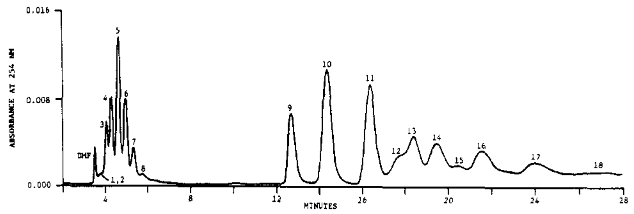


Figure 6. HPLC of ether-soluble oligomer fraction on a μ-Porasil column. Mobile phase: CH_2Cl_2–CH_3CN (100:5).

Since the polymer sample had an A/B ratio of 6.9, the concentration of end groups of type VII would be 6.9-fold greater than that of VIII.

The signal areas for the various end group signals were in excellent agreement with structures V and VI in a ratio of 6.9.

The ^1H NMR spectrum of the polymer synthesized at 160 °C in DMF solution from methanol-containing zwitterion showed signals at 4.73 (s, $HOCH_2Ph$), 3.88 (s, $COOCH_3$), 3.60 (m, $HOCH_2CH_2$), and 2.31 (s, OH) ppm due to end groups as shown in IX and X. The ^1H NMR

$$HOCH_2Ph\sim\sim COOCH_3 \qquad HOCH_2CH_2CH_2CH_2SCH_2Ph\sim\sim COOCH_3$$

IX X

spectrum did not show a COOH proton signal presumably due to low concentration of COOH and exchange with water present in the sample. Evidence for the presence of carboxyl end groups was obtained from the presence of an anhydride methyl signal at 2.33 ppm in the ^1H NMR spectrum of an acetylated polymer sample. Furthermore, the ^1H NMR spectrum of the same acetylated sample recorded after standing 2 months showed the disappearance of the anhydride methyl signal and the appearance of signals for COOH (10.06 ppm) and methyl of acetic acid (2.04 ppm). This change was attributed to hydrolysis of the anhydride group to acetic acid and carboxyl end group.

The end group signals of polymers obtained in bulk polymerization were very weak due to the considerably higher molecular weight compared to those from solution polymerization. The presence or absence of methanol did not change the nature of the end groups. All polymers contained hydroxyl and carboxyl groups as noted by weak signals at 2.30 and 10.05 ppm, respectively; no methyl ester end groups were present.

Characterization of Ether-Soluble Products. Solution Polymerization. The ether-soluble products obtained in solution polymerization of methanol-containing thiolanium benzoate zwitterion constituted about 32% of the total products for polymerizations at 100 and 130 °C and 62% at 160 °C. The ether-soluble products obtained at 160 °C were characterized by HPLC and ^1H NMR. The analytical HPLC (Figure 6) showed the presence of at least 18 different compounds. The mixture was fractionated by preparative HPLC. Compounds **9** and **10** were obtained in pure form as shown by analytical HPLC. The remaining compounds were obtained in purities ranging from 60 to 80%.

Compound **9** was identified as methyl 4-(hydroxymethyl)benzoate (XI) on the basis of ^1H NMR spectroscopy. The ^1H NMR spectrum showed signals at 8.03 (d,

$$HOCH_2PhCOOCH_3$$

XI

$$HOCH_2PhCOOCH_2PhCOOCH_3$$

XII

2 H, aromatic), 7.44 (d, 2 H, aromatic), 4.78 (s, 2 H, CH_2), 3.92 (s, 3 H, OCH_3), and 1.86 ppm (s, 1 H, OH). Compound **10** was identified as XII on the basis of ^1H NMR signals at 8.07 (m, 4 H, aromatic), 7.48 (m, 4 H, aromatic),

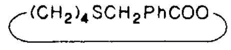
5.41 (s, 2 H, OCH_2), 4.78 (s, 2 H, $HOCH_2$), 3.92 (s, 3 H, OCH_3), and 1.92 ppm (s, 1 H, OH). Compound **11** was obtained in 80% purity with compounds **10** and **12** as the impurities in it. The ^1H NMR spectrum was consistent with structure XIII for compound **11**. The ^1H NMR

$$HOCH_2PhCOOCH_2PhCOOCH_2PhCOOCH_3$$

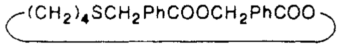
XIII

spectra of other fractions indicated that compounds **12** through **18** were low molecular weight linear thiolanium benzoate polymers (i.e., oligomers of VII and VIII). That is, the ^1H NMR spectra of these fractions showed signals for the A and B repeat units and for the hydroxyl and methyl ester end groups. Signal areas for the repeat units relative to those for end groups indicated that molecular size increased progressively for compounds **12** through **18**. The average ratio of A to B repeat units was 2 on the basis of the ^1H NMR signal areas for methylene protons in OCH_2 of A and SCH_2 in B.

Although the compounds (**1**–**8**) in the group with significantly shorter retention times were not isolated in pure form, several fractions were obtained with compounds **3**, **4**, **5**, **6**, and **7**, respectively, as the major components. The ^1H NMR spectrum of the fraction with compound **3** as the major component showed major signals at 7.83 (d, aromatic), 7.42 (d, aromatic), 4.26 (t, OCH_2), 3.79 (s, SCH_2Ph), 2.45 (t, SCH_2CH_2), and 1.73 ppm (m, CH_2CH_2). The spectrum did not show signals due to $HOCH_2$ or CH_3COO (or any other) end groups. End groups, if present, in these low molecular weight products would be easily detected under the conditions of our ^1H NMR experiments. The spectral data plus the short retention time compared to those for the linear oligomers (compounds **9**–**18**) indicated compound **3** had the cyclic structure XIV. The ^1H NMR spectrum of a fraction containing compounds **3** and **4** as the major components (40/60) showed signals at 7.94 (m, aromatic), 7.38 (m, aromatic), 5.42 (s, OCH_2Ph), 4.26 (m, $COOCH_2CH_2$), 3.79 and 3.69 (s, SCH_2Ph of compounds **3** and **4**), 2.40 (m, CH_2CH_2S), and 1.72 ppm (CH_2CH_2). The spectrum was consistent with a mixture of XIV and XV. Mass spectroscopy was performed on the two fractions—the one containing mostly compound **3** and the other containing a mixture of compounds **3** and **4**. The mass spectra corroborated the NMR data. Compounds **3** and **4** have the structures XIV and XV, respectively. The ^1H NMR spectra of other HPLC fractions containing compounds **5** through **8** indicated those compounds to have cyclic structures similar to XV with progressively increasing ring size and an average A/B ratio of 2. The total amount of cyclic compounds in the ether-soluble fraction was determined as 26% (16% of the total products) from the HPLC peak areas.



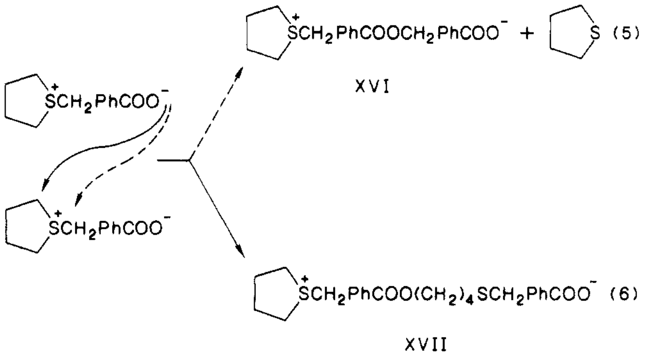
XIV

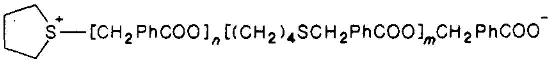


XV

Bulk Polymerization. The amount of ether-soluble products (4–12%) in bulk polymerization was much lower than obtained in solution polymerization. The polymerization temperature and the presence or absence of methanol did not affect the amount of ether-soluble products. The ^1H NMR spectra of the ether-soluble products formed at 100 and 160 °C were very similar to that of the polymer spectrum (Figure 3). Further, the spectrum showed signals due to COOH and OH end groups indicating the ether-soluble products were mostly linear oligomers. (The identity of the end groups were unaffected by the presence or absence of methanol.) Cyclic oligomers did not comprise a significant portion of the ether-soluble products.

Polymerization Mechanism. Bulk polymerization is initiated by loss of water of hydration (and methanol, when present) followed by nucleophilic attack of the carboxylate anionic center of one zwitterion on the benzylic carbon (eq 5) or α-carbon of the tetrahydrothiophenium ring (eq 6) of a second zwitterion. The nucleophilic attack on the benzylic carbon occurs with release of tetrahydrothiophene to yield dimer XVI while attack at the α-carbon of the tetrahydrothiophenium ring results in ring scission to yield dimer XVII. Propagation proceeds by reactions of dimers XVI and XVII with themselves, each other, and I to produce linear tetramers and trimers. The trimer and tetramer can react with themselves, each other, XVI, XVII, and I. Growth continues in a step-reaction manner with the formation of different-sized molecules of type XVIII with random (not block) placement of A and B repeat units.

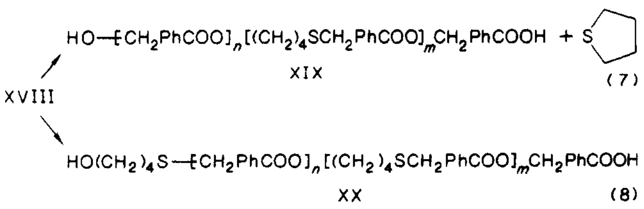




XVIII

A and B repeat units are formed by attack of the carboxylate anion on the benzylic carbon and α-carbon of tetrahydrothiophenium ring, respectively. Attack at the benzylic carbon is the favored reaction in bulk and solution polymerization as determined by analysis of the copolymer compositions by NMR and elemental analysis. This result is analogous to that observed by Burrows and Cornell for the solid-state thermal decomposition of various benzyldimethylsulfonium salts.[6] The benzyl-to-methyl displacement ratio varied from 6 for m-$NO_2PhCH_2S(CH_3)_2Br$ to 130 for p-$CH_3OPhCH_2S(CH_3)_2I$.

The carboxyl and hydroxyl end groups of polymer and linear oligomer are formed by reaction of the propagating species XVIII with water (and OH^- formed via reaction 4) to substitute hydroxide at the benzylic carbon (predominate reaction) or α-carbon of the tetrahydrothiophenium ring (eq 7 and 8, respectively.) The oligomer fraction was very small (4–12%) in bulk polymerization and consisted mostly of linear oligomer. Very little cyclic oligomer (formed by cyclization of XVIII via intramolecular attack of carboxylate at benzylic carbon and α-carbon of tetrahydrothiophenium ring) was formed. The large polymer fraction and its high molecular weight is accounted for by the insolubility of XVIII in water which precludes early termination of XVIII. Higher reaction



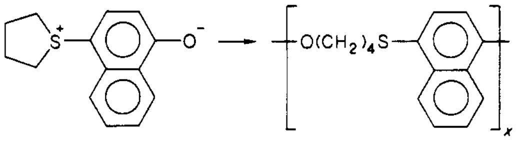
temperatures (160–200 °C) result in lower molecular weights as there is some miscibility between XVIII and water. The lack of any effect of methanol (relative to water) on bulk polymerization is similiarly attributed to an incompatibility of XVIII and methanol. The higher polymer molecular weight obtained in bulk polymerization under continuous vacuum is due to the quicker removal of water (and methanol as well as tetrahydrothiophene) from the reaction system which decreases further the extent of termination by reactions 7 and 8. Fast water removal may also affect the reaction by facilitating a molecular weight increase via esterification between hydroxyl and carboxyl end groups of different polymer molecules.

The presence of water and methanol in sealed tube experiments was shown to inhibit and, in fact, decrease polymer molecular weight. In separate experiments, methanol or water was added to purified polymer and the reaction tube sealed and heated at 130 °C for 2 days. The polymer molecular weights decreased about 10 and 35%, respectively, when methanol and water were present.

There was a significant difference between bulk and solution polymerization. Solution polymerization gave decreased polymer yields (increased oligomer yields), and the polymer molecular weight was considerably decreased (Table II). The water of hydration of the thiolanium benzoate zwitterion is not removed from the reaction system as it is in bulk polymerization (either being condensed at the top of the polymerization tube in sealed tube experiments or quickly removed in continuous vacuum experiments). Water is soluble in DMF and is present throughout the polymerization process. This results in increased termination by substitution to decrease both the polymer yield and polymer molecular weight. The presence of methanol in the thiolanium benzoate zwitterion affected the identity of the end groups for the polymer and linear oligomer at all reaction temperatures. Hydroxyl end groups were unchanged by the presence of methanol, but a portion of the carboxyl end groups were esterified to form methyl ester end groups. The presence of methanol greatly decreased the polymer fraction for polymerization at 160 °C. This is attributed to transesterification of linear polymer by methanol. Verification for the transesterification mechanism came from an experiment in which methanol was added to a DMF solution of the linear polymer. Heating that solution at 160 °C resulted in solubilization of 32% of the polymer in diethyl ether. Since transesterification usually requires high temperatures, no significant effect of methanol on polymer yield and molecular weight was observed for polymerization at 100 and 130 °C.

For bulk polymerizations under continuous vacuum, approximately one-half of the polymer at 130 °C was insoluble while the polymer synthesized at 160 °C was completely insoluble. Whether or not these insoluble polymers are cross-linked is unclear. At a minimum, the insoluble products must be of considerably higher molecular weight than the soluble products. If the products are cross-linked, the mechanism responsible for cross-linking is not understood. Further work in this area is contemplated.

It is interesting to compare the difference in bulk polymerization between the thiolanium benzoate zwitterion and tetrahydro-1-(4-hydroxy-1-naphthyl)thiophenium hydroxide inner salt (XXI). The latter is referred to as naphthyl zwitterion. Polymerization of the naphthyl zwitterion was previously reported[3] to yield three-fourths linear polymer, poly(oxytetramethylenethio-1,4-naphthalene) (XXII), and one-fourth oligomer (consisting of 91% cyclics). Initiation and propagation proceeds by ring-opening nucleophilic attack by the arene oxide anionic center of one zwitterion on the α-carbon of the tetrahydrothiophenium ring of another zwitterion. Termination occurs by cyclization, β-elimination, and substitution. For polymerization of the thiolanium benzoate zwitterion, the attacking species is a carboxylate anion and termination involves cyclization and substitution. The absence of elimination for the thiolanium benzoate zwitterion is attributed to two factors. First, the carboxylate anion is too poor a base compared to phenoxide anion (the respective pK_a values for the corresponding acids are 4.19 and 9.89[7]) to affect proton abstracton. Second, the thiolanium benzoate polymer is rich in A repeat units which are not capable of undergoing elimination.



XXI XXII

The absence of any significant amount of cyclization in the thiolanium benzoate system is attributed to the low flexibility of the polymer chains due to the high content of the rigid A repeat units. Since there is only one significant mode of termination, the polymer yield and molecular weight are generally higher than obtained in polymerization of the naphthyl zwitterion. Furthermore, the terminated thiolanium benzoate polymer contains hydroxyl and carboxyl end groups which can undergo esterification to increase polymer molecular weight.

Acknowledgment. We gratefully acknowledge financial support of this work under grants from the Dow Chemical Company, National Science Foundation (Polymers Program, DMR) and PSC-CUNY of City University of New York.

Registry No. Ia, 118375-93-2; Ia (homopolymer), 118375-94-3; 4-(chloromethyl)benzoic acid, 1642-81-5; tetrahydrothiophene, 110-01-0.

References and Notes

(1) (a) Saegusa, T. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 826. (b) Saegusa, T.; Kobayashi, S. *Pure Appl. Chem.* **1978**, *50*, 281.
(2) (a) Odian, G.; Gunatillake, P. A. *Macromolecules* **1984**, *17*, 1297. (b) Gunatillake, P. A.; Odian, G. *Macromolecules* **1985**, *18*, 605.
(3) Gunatillake, P.; Odian, G.; Schmidt, D. L. *Macromolecules* **1986**, *19*, 1779.
(4) Silverstein, R. M.; Bassler, G. G.; Morril, T. C. *Spectroscopic Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981.
(5) Ewing, D. F. *Org. Magn. Reson.* **1979**, *12*, 499.
(6) Burrows, W. D.; Cornell, J. H. *J. Org. Chem.* **1967**, *32*, 3840.
(7) Lowry, H. T.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981; p 333.