could be detected. As noted previously for unblended PBT and PEE copolymers, we observed usual and/or unusual spherulitical morphologies, depending on the crystallization conditions.[4,26,27] No indication of separate crystallization was detected and we therefore conclude at this time that cocrystallization is likely in blends of high 4GT content copolymers and PBT.

Conclusions

Measurements of the complex dielectric permittivity show clearly that larger 4GT contents in the poly(ester–ether) segmented block copolymers under consideration favor increase amorphous phase miscibility in blends with PBT. Thermal analysis and morphological evidence suggest that there is extensive cocrystallization in blends of PEE-84 and PBT.

Registry No. PBT, 26062-94-2; PBT (SRU), 24968-12-5; (1,4-butanediol)(polytetramethylene glycol)(terephthalic acid) (block copolymer), 106159-00-6; (1,4-butanediol)(isophthalic acid)(polytetramethylene glycol)(terephthalic acid) (block copolymer), 106159-01-7.

References and Notes

(1) Briber, R. M.; Thomas, E. L. *Polymer* **1985,** *26,* 8.
(2) Gilbert, M.; Hybart, F. J. *Polymer* **1974,** *15,* 408.
(3) Hobbs, S. Y.; Pratt, C. F. *Polymer* **1975,** *16,* 462.
(4) Stein, R. S.; Misra, A. *J. Polym. Sci., Polym. Phys. Ed.* **1980,** *18,* 327.
(5) Zhu, L.-L.; Wegner, G. *Makromol. Chem.* **1981,** *182,* 3625.
(6) Banbara, U.; Droscher, M. *Colloid Polym. Sci.* **1983,** *261,* 26.
(7) Vallance, M. A.; Cooper, S. K. *Macromolecules* **1984,** *17,* 1208.
(8) Briber, R. M.; Thomas, E. L. *Polymer* **1985,** *27,* 66.
(9) Castles Stevenson, J.; Cooper, S. L. *Macromolecules* **1988,** *21,* 1309.
(10) Shih, C. K., unpublished results.
(11) Runt, J.; Harrison, I. R. *Meth. Exp. Phys.* **1980,** *16,* 287.
(12) Illers, K. H. *Colloid Polym. Sci.* **1980,** *258,* 117.
(13) Lilaonetkul, A.; Cooper, S. L. *Macromolecules* **1979,** *12,* 1146.
(14) Boyd, R. H. *Polymer* **1985,** *26,* 323.
(15) Coburn, J. C.; Boyd, R. H. *Macromolecules* **1986,** *19,* 2238.
(16) Havriliak, S.; Negami, S. *J. Polym. Sci., Polym. Symp.* **1966,** *14,* 99.
(17) Watts, D.; Havriliak, S. *Design Data and Analysis*; Marlows, C., Ed. Wiley: New York, 1986; p 129.
(18) Havriliak, S.; Watts, D. *Polymer* **1986,** *27,* 1509.
(19) Wetton, R. E.; Williams, G. *Trans. Faraday Soc.* **1965,** *61,* 2132.
(20) Malik, T. M.; Prud'homme, R. E. *Polym. Eng. Sci.* **1984,** *24,* 144.
(21) Angeli, S. R.; Runt, J. In *Contemporary Topics of Polymer Science* Culbertson, W., Ed.; Vol. 6, in press.
(22) Rellick, G. S.; Runt, J. *J. Polym. Sci., Polym. Phys. Ed.* **1986,** *24,* 313.
(23) Tanaka, H.; Lovinger, A. J. *Macromolecules* **1987,** *20,* 2640.
(24) Castles Stevenson, J.; Cooper, S. L. *J. Polym. Sci., Polym. Phys. Ed.* **1988,** *26,* 953.
(25) Yeh, J.-T.; Runt, J. P. *J. Polym. Sci., Polym. Phys. Ed.*, in press.
(26) Lilaonitkal, A.; Cooper, S. L. *Rubber Chem. Technol.* **1977,** *50,* 1.
(27) Roche, E. J.; Stein, R. S.; Thomas, E. L. *J. Polym. Sci., Polym. Phys. Ed.* **1980,** *18,* 1145.

Mechanistic Investigation of the Photochemistry of Thiosulfate Functional Zwitterions

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ABSTRACT: The synthesis and characterization of a water-soluble zwitterionic polymer that is photochemically reactive is described. The polymer contains reactive thiosulfate groups that upon photolysis undergo sulfur–sulfur bond cleavage and subsequent loss of water sensitivity. Direct photolysis of model compounds clearly indicates the formation of disulfide photoproducts which can also be identified in the polymer films by FTIR analysis. The quantum efficiency for loss of thiosulfate groups, at least in a model compound study, is about 0.2. Preliminary results show that the primary sulfur–sulfur bond cleavage of the thiosulfate chromophore is readily sensitized by a standard triplet sensitizer.

Introduction

Organic thiosulfates were first synthesized by Bunte in 1874[1] by the reaction of alkyl halides with sodium thiosulfate and are often referred to as Bunte salts. Bunte determined that alkyl thiosulfates are quite sensitive to heat and hydrolysis, especially in the acid form:

$$C_2H_5Br + Na_2S_2O_3 \longrightarrow C_2H_5SS(=O)_2O^-Na^+ + NaBr$$

Alkyl thiosulfates are known[2-4] to photodegrade by a homolytic cleavage at the S–S bond caused by exposure to ultraviolet light. The photoproducts have been shown to initiate free-radical polymerizations of methyl methacrylate, styrene, and acrylonitrile.[2,3] Further, alkyl thiosulfate salts bound to a polymer backbone have been photolyzed as supports for graft polymerizations.[4] Unfortunately, there is only limited information about the nature of the photolysis mechanism(s).

One interest in developing thiosulfate-functional polymers results from the ability of the Bunte salt group to impart water solubility to an otherwise hydrophobic moiety, coupled with the potential to degrade to disulfide cross-links. Early work showed that copolymers of (*N*-(acrylamido)amino)ethyl thiosulfate with vinyl acetate and methyl acrylate could be cross-linked by the addition of

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sodium sulfide.[5] Later reports demonstrated that alkyl thiosulfate functionalization of preformed polymers by substitution of metal thiosulfate onto poly(epichlorohydrin) resulted in water-soluble polymers.[6,7] It was reported that the degree of substitution, molecular weight, thermolysis time, and temperature could be systematically varied to produce differing degrees of cross-linked polymer, which presumably occurred by disulfide bond formation. In addition, films with added diacrylates could be cross-linked upon heating or exposure to UV radiation. It was recently established that poly(epichlorohydrin) and other poly(oxyalkylene halide) polymers can be converted to Bunte salt polymers by the action of sodium thiosulfate. Such polymers were reported to cross-link at elevated temperatures.[8]

In this paper, we report the synthesis and photolysis of the diglycidyl ether of Bisphenol A modified by end capping with aminoethyl thiosulfate (AETSA). In the synthesis method employed, the primary amine AETSA acts as a difunctional monomer since it possesses two active hydrogen atoms and thus reacts with two epoxy groups. AETSA also acts as a monofunctional end-capping agent, and the combined effect of these two reactions is the formation of a polymer that is designated poly[γ-(amino β-thiosulfate) ether], or PATE. The photolysis of the PATE polymer and appropriate small-molecule models has been investigated in order to elucidate the necessary and sufficient conditions and structural features required for cross-linking.

Experimental Section

Materials. Reagent-grade solvents dimethylformamide (DMF), dimethylacetamide (DMAC), dimethyl sulfoxide (DMSO), and methanol were purchased from Baker, stored over molecular sieves once opened, and used without further purification. Aminoethyl thiosulfate (AETSA), purchased from Kodak, and Taurine, purchased from Alfa, were purified by recrystallization. Each was thrice recrystallized from hot, deionized water. The crystalline precipitate was dried (48 h at 40 °C) in vacuo and subsequently stored in a desiccator. Aminoethyl disulfide (cystamine), aminoethanethiol (AET), and benzophenone (BP) were purchased from Aldrich Chemical Company. Cystamine and aminoethanethiol were used as supplied. Quantacure BTC (BTC), (4-benzolybenzyl)trimethylammonium chloride, was used as supplied by Aceto, Inc., Flushing, NY. Phenyl glycidyl ether (PGE) was purchased from MCB, distilled in vacuo, and stored at −15 °C. Epon 828 was used as supplied by Shell Chemical Company.

The epoxy equivalent weight (EEW) for Epon 828, determined by an appropriate titration, was found to be 187.7.

Elemental Analysis. All samples submitted for elemental analysis were dried at 40 °C in a vacuum oven at less than 1-Torr pressure for 24 h and then sealed in ampules. Analyses were performed by MHW Laboratories of Phoenix, AZ.

Synthesis of PATE. A 3-neck, 500-mL, round-bottom flask fitted with a nitrogen purge, thermometer, addition funnel, and magnetic stir bar was charged with 130 mL of DMF and 30.40 g (0.08941 mol) of Epon 828 EEW = 187.7. A solution of 25.33 g (0.1661 mol) of AETSA, dissolved in 35 mL of water, was adjusted to pH 8.8 with NaOH pellets and then poured into the addition funnel. After purging the solution with nitrogen for 15 min, the aqueous solution was dropped into the flask over a 2-h period. The addition funnel was then replaced with a combination pH electrode and the pH adjusted to 8.3. After a 15-min nitrogen purge, the solution was heated to 60 °C. An aliquot taken from the reaction flask clouded in water as the Epon precipitated. The reaction temperature was maintained at 55–60 °C for 20–40 h, until an aliquot of the mixture was not cloudy in water. The reaction mixture was evaporated in vacuo and diluted with 300 mL of water and twice extracted with ethyl ether. Purification was accomplished by dialyzing the aqueous product solution in 1000 MW cut-off tubing (Spectrapore No. 1, Spectrum Industries, Los Angeles). The product was twice dialyzed for 18 h in 4:1 product:water (pH 7.0). The solutions were filtered and freeze dried. Yields of 70–80% were common. Infrared analysis of the PATE product indicated loss of oxirane rings at 910 cm^{-1} and an increased hydroxyl band at about 3450 cm^{-1} and showed characteristic thiosulfuric acid bands at 639, 1033, and 1170–1230 cm^{-1}, but the latter two overlapped symmetrical and asymmetrical stretching absorbances of the phenyl ether backbone. The behavior of aqueous PATE solutions complicated further characterization. Aqueous solutions of greater than 15% solids were gel-like at room temperature but became free flowing upon heating to above 50 °C. However, solutions more concentrated than about 20% were impossible to form. Therefore, ^{13}C NMR analysis was performed at 80–90 °C to break up the gel structure, but the polymer could not be concentrated sufficiently for high resolution. However, characteristic chemical shifts of oxirane carbons at 52.2 and 46.3 ppm are lost, and the presence of thiosulfate methylene at 35.4 ppm indicates that the AETSA addition has occurred. The polymer is designated as PATE.

Synthesis of AETSAPPE. The synthesis of [2-[(2-hydroxy-3-phenoxypropyl)amino]ethyl] thiosulfate (AETSAPPE) was carried out by the addition of AETSA to phenyl glycidyl ether (PGE) using the following procedure.

A 3-neck, 500-mL, round-bottom flask fitted with a nitrogen purge, thermometer, addition funnel, and magnetic stir bar was charged with 250 mL of DMF, 25 mL of water, 53.58 g (0.3408 mol) of AETSA, and 1.4226 g (0.0356 mol) of NaOH. The reaction mixture was then heated to 40 °C with stirring. When dissolution was complete, the heating mantle was replaced with an ice bath and purged for 15 min at 10 °C. A solution of 5.0029 g (0.0334 mol) of PGE in 50 mL of DMF was introduced from an additional funnel over a 30-min period. After completion, the addition funnel was replaced with a combination pH electrode, and the heating mantle was replaced. The reaction temperature was maintained at 38–48 °C for 48 h until an aliquot of the mixture was not cloudy in water. The solvents were evaporated in vacuo until AETSA crystallized on the flask sides. The product was redissolved in minimum water and dilute base. A 3-fold volume excess of acetone was added, and AETSA crystallized and precipitated. The liquid phase was evaporated in vacuo and redissolved. AETSA was again precipitated by addition of acetone. The liquid phase was evaporated and the residue placed under high vacuum for 48 h. The dry residue was dissolved in a minimum of hot water and then cooled to 5 °C for 24 h, whereupon approximately 1 g of AETSAPPE was deposited on the sides of the beaker.

Infrared analysis of the product indicated loss of oxirane rings at 910 cm^{-1} and an increased hydroxyl band at about 3450 cm^{-1} and showed characteristic thiosulfuric acid bands at 639, 1033, and 1170–1230 cm^{-1}. Likewise, comparison of the ^{13}C NMR of PGE to the product spectrum was conclusive of the addition of AETSA to the oxirane ring. Additionally, the solubility was as expected, the product being soluble in neutral or basic water but insoluble in dilute acid. However, the acid insolubility was reversible upon addition of dilute base. Elemental analysis also confirmed formation of AETSAPPE. Expected: C, 42.98; H, 5.54; N, 4.56, S, 20.88. Actual: C, 44.71; H, 5.41; N, 3.77; S, 19.45.

Synthesis of PASE. Addition of Taurine (sodium aminoethanesulfate) to Epon 828 resulted in formation of a polyether identical with the PATE polymer, except that the thiosulfate group is replaced with a sulfonic acid. Thus, the product polymer is designated as PASE.

A 3-neck, 500-mL, round-bottom flask fitted with a nitrogen purge, thermometer, addition funnel, and magnetic stir bar was charged with 100 mL of DMF, 200 mL of water, and 14.6675 g (0.1172 mol) of Taurine. The pH was adjusted to 9 and the temperature to 40 °C to form a homogeneous solution. A solution of 10.4319 g (0.1104 mol) of Epon 828 in 250 mL of DMF was introduced for 15 min. The Epon solution was dropped into the flask over a 2-h period. The addition funnel was then replaced with a combination pH electrode, and the pH was adjusted to 8.5. After 36 h of reaction at 50 °C, the reaction mixture was evaporated in vacuo, diluted with a minimum of water, and dialyzed twice for 12 h in 4 L of neutral water. The product was freeze dried and stored in a desiccator.

The product was soluble in neutral or slightly basic water with warming but precipitated upon addition of dilute acid. Addition of base resulted in a clear solution again upon heating. The limited

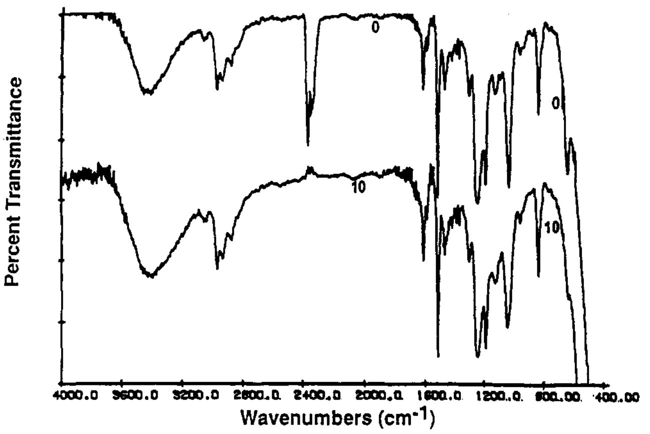


Figure 1. FTIR of PATE film (a) before and (b) after 10-min photolysis with an unfiltered, 450-W, medium-pressure mercury lamp.

solubility of this product resulted in ^{13}C NMR of poor resolution. Infrared analysis of the products indicated loss of oxirane rings at 910 cm^{-1} and an increased hydroxyl band at about 3450 cm^{-1} and showed characteristic sulfonic acid bands at 1040 and 1170–1230 cm^{-1}.

PATE films (5–20 μm thick) were obtained by casting on glass 10–20% solids aqueous solutions containing 0.02% surfactant. The resultant films, heated in a drying oven at 100 °C for 4 min, were quite water soluble.

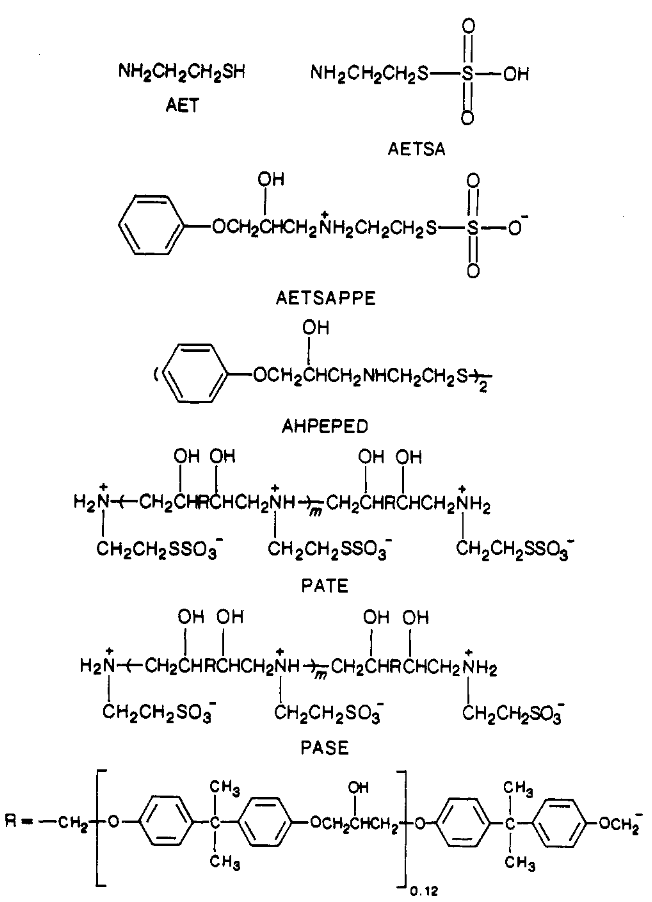
For IR studies, films of 5–10 μm were applied to NaCl disks by injecting known, small volumes of dilute solutions of PATE in DMSO. The solutions were spread to cover a 1-cm-diameter area on the NaCl disk and subsequently dried 10 min at 105 °C followed by photolysis.

Instrumentation. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 5DX using standard techniques. Spectra were measured from various sample supports, including KBR pellets, free polymer films, and films cast on NaCl windows. Spectra for quantitative analysis were recorded in the absorbance mode. The height of the 639-cm^{-1} absorbance was measured after the spectrum was expanded or contracted such that the 829-cm^{-1} absorbance was a constant height. In some spectra, an artifact due to instrumental response appeared near 2300 cm^{-1} (see Figure 1 for example).

Proton-decoupled ^{13}C NMR spectra were obtained by using a JEOL FX90Q spectrometer. Polymer solutions for analysis were 5–15 wt %. All chemical shifts are referenced externally to trimethylsilane. Ultraviolet spectroscopy was performed with a Perkin-Elmer Model 330 spectrophotometer, using double-beam, background-canceling techniques. HPLC analysis was performed by using an LDC Minipump, a Rheodyne 7125 sample injector, and a Perkin-Elmer LC-75 variable-wavelength UV detector operating at 245 nm. The detector used air as a reference with offset background canceling. The mobile phases were mixtures of acetonitrile and water, most commonly 85 parts water and 15 parts acetonitrile by volume. The columns were a Waters μ-Bondapak CN alone or in series with a Waters C-18 column (3.9 mm i.d. × 30 cm). The flow rate varied between 0.9 and 1.0 mL/min to generate a pressure of less than 2000 psi at the pump exit.

Preparative Photolysis. The preparative photolysis of an aqueous solution (pH 8.5) of AETSAPPE (2.5 M) was conducted in a 1-in.-diameter quartz test tube in a Rayonet reactor (Southern New England Radiation Co.) fitted with 254-nm lamps. Within 2 h the solution gelled and the reaction was terminated. Upon acidification, the solution cleared, and the product could be reprecipitated by addition of base. This confirms loss of the thiosulfate functionality. The product was dissolved in dilute HCl, precipitated with acetone, and filtered. This process was repeated 3 times, and the final precipitate was washed with water. The product (20–30 mg) was dried in vacuo for 24 h and stored in a dessicator until use. Comparison of the ^{13}C NMR spectrum of the product with the starting AETSAPPE ^{13}C NMR spectrum clearly shows that the thiosulfate methylene peak shifted upfield, from 39 to 35 ppm. Further, elemental analysis of the product confirmed that the product was the desired disulfide product [2-[(2-hydroxy-3-phenoxypropyl)amino]ethyl] disulfide (AHPEPED). Expected: C, 58.39; H, 7.08; N, 6.20; S, 14.18. Actual: C, 58.26; H, 7.22; N, 6.06; S, 14.28.

Scheme I



Quantitative Photolysis. Photolysis experiments were performed by exposing samples to a 450-W, medium-pressure mercury lamp. A shutter was placed between the samples and the lamp so that the exposure time could be accurately controlled. Unless otherwise stated, the samples were placed 4 in. from the lens. Filters (254, 280, and 366 nm), when used, were placed immediately in front of the shutter. Sample holders were available for 1-in. × 1-in. quartz plates, NaCl windows, and quartz UV cuvettes, and samples of each type were utilized.

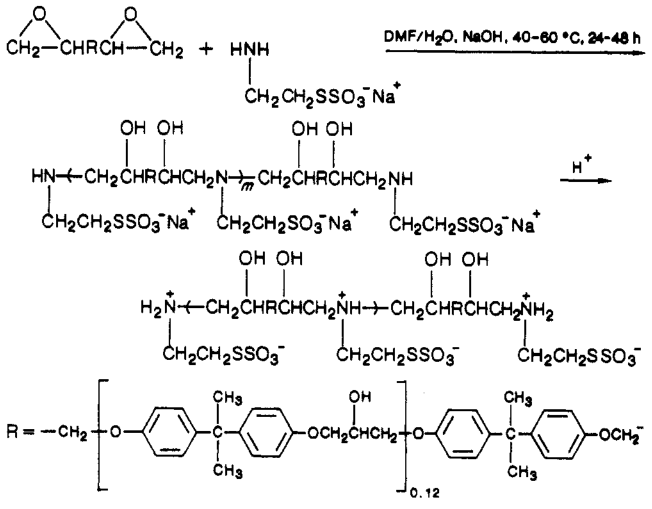
UV intensity measurements were made with an International Light 700A Research radiometer. The measuring head was tightly covered with aluminum foil for zeroing and then exposed to the lamp output exactly as the actual samples (i.e., same distance, angle, elevation, etc.). The results of these experiments were used to evaluate the quantum yield or efficiency of the photochemical process. Specifically, photolysis of AETSAPPE to yield AHPEPED was followed quantitatively by HPLC (Waters) using a 50:50 water:acetonitrile mobile phase and a C-18/cyano column combination in series. AETSAPPE eluted at a retention volume of 5.9 mL and AHPEPED at an elution time of 3.2 mL. Three unknown products of relatively low amounts also eluted with retention volumes of 3.0, 5.3, and 7.9 mL. For the sensitized photolysis, a 85:15 water:acetonitrile mobile phase was used to separate AHPEPED and BTC from AETSAPPE.

Results and Discussion

The structures of the model compounds and polymers used in this study are shown in Scheme I for ready reference throughout this section.

Synthesis of PATE. A general scheme for the synthesis of PATE is shown in Scheme II. A particularly challenging aspect of characterizing PATE is the interpretation of the elemental analysis to ascertain its degree

Scheme II



of polymerization (DP) and therefore molecular weight. This problem is due to the multiplicity of product species that may form. However, sulfur and nitrogen analyses can be used to evaluate the ratio of disulfide cross-links to free thiosulfate functionality for PATE polymers and to evaluate the DP of PATE. Given the molecular weights of the starting epoxy and AETSA, a DP of 16.3, corresponding to a polymer with molecular weight of approximately 9000, is calculated.

Photolysis of PATE Films. Photolysis of the PATE films using a 450-W, medium-pressure mercury lamp for times ranging from 5 to 10 min resulted in hard, solvent-resistant films that were totally insoluble in water as well as common organic solvents such as methanol, acetone, THF, benzene, etc. Upon soaking in warm water for 10 min, the films could be removed totally intact. Suspension in water for periods of greater than 9 months resulted in no visible signs of swelling.

FTIR analysis of the photolyzed PATE film confirmed loss of thiosulfate by reduction of the 639-cm^{-1} absorption (Figure 1). No other changes were noted in the FTIR spectrum. This suggests that the thiosulfate moiety decomposes and cross-links via disulfide formation upon exposure to UV light.

While the UV spectrum of PATE exhibits an absorbance maximum at 268 nm, a maximum is found near 245 nm for AETSA. The 268-nm peak is, in fact, consistent with the maximum of a phenyl ether. Therefore, filters that isolate the 254-nm line and the 280-nm line of the medium-pressure mercury lamp were employed for rate studies. Figure 2a shows the loss of the 639-cm^{-1} thiosulfate absorbance band, which is not obscured by some other group associated with the polymer backbones upon photolysis through a 254-nm-line filter. Clearly, the rate of loss of thiosulfate moiety (Figure 2b) is greatest in the initial stages of photolysis, reaching an ultimate conversion of 53%. The decrease in the reaction rate is consistent with the formation of a chromophore, such as a disulfide, which competes with the thiosulfate for UV radiation. Similar results are noted upon photolysis with a 280-nm-line filter which resulted in 76% loss of thiosulfate over an 80-min period.

In an attempt to sensitize the thiosulfate bond cleavage, benzophenone (BP; 10% by weight) was incorporated into the polymer film. Upon photolysis at 366 nm, the 639-cm^{-1} thiosulfate band was reduced by about 10% after 60 min. However, photolysis of the polymer film without benzophenone at 366 nm for 110 min resulted in no loss of the thiosulfate IR absorption band at 639 cm^{-1}. Thus, we conclude that it is possible to sensitize the S–S bond cleavage in the thiosulfate group using a standard triplet sensitizer such as benzophenone.

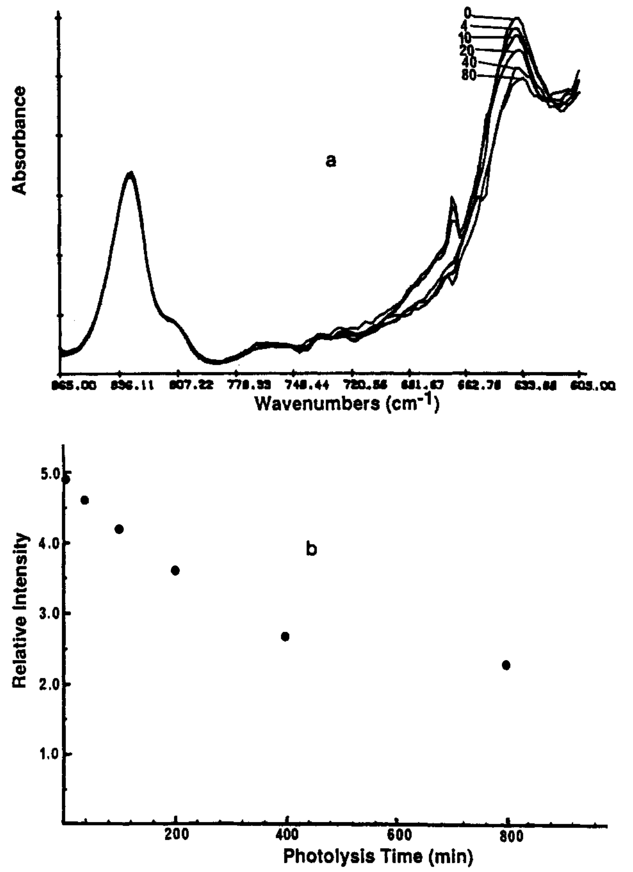


Figure 2. (a) FTIR of PATE film photolyzed for time periods of 0, 4, 10, 20, 40, and 80 min with an isolated 254-nm line of a 450-W, medium-pressure mercury lamp. (b) Plot of relative IR band intensity at 639 cm^{-1} as a function of photolysis time (filtered 254-nm mercury line).

The above experiments confirm that the thiosulfate group is photochemically active. However, in our experiments, the loss of thiosulfate is linear with time only during the early stages of photolysis. This is consistent with photolysis of the thiosulfate and subsequent formation of the disulfide. Since the extinction coefficients of the disulfides are higher than thiosulfates and absorb over the same wavelength range as thiosulfate groups, disulfides are expected to compete for incoming radiation, thereby reducing the rate of the cross-linking reaction.

Given the distinct possibility that PATE resins cross-link by degradation of the S–S bond in the thiosulfate with concomitant disulfide formation, a study was undertaken using PASE (see structure), which is identical with PATE, except for its lack of an S–S bond. Therefore, PASE cannot photochemically degrade by the proposed S–S bond cleavage.

Films of PASE were drawn from aqueous solution onto glass and oven dried, resulting in films of 10–20 μm. The films were photolyzed under the full arc of the medium-pressure mercury lamp at a distance of 4 in. After 120 min of exposure, the films remained water soluble, indicating that no cross-linking had occurred. Photolyzed films on NaCl plates showed no changes in the IR spectrum even after 120 min, thereby providing corroborative indirect evidence for the proposed mechanism for photolysis of PATE by a primary S–S bond cleavage.

Photolysis of Model Compounds. The UV spectra of freshly prepared aqueous solutions of AETSA (Figure 3a), aminoethyl disulfide (cystamine) (Figure 3b), and amino-

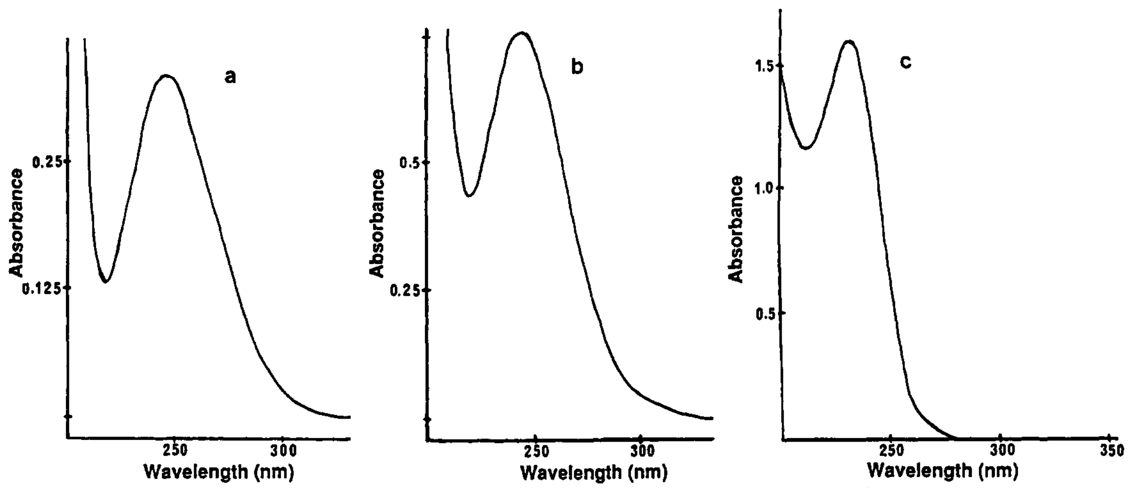


Figure 3. UV spectra of freshly prepared aqueous solutions of (a) AETSA (6.13×10^{-3} M), (b) aminoethyl disulfide (cystamine, 2.26×10^{-3} M), and (c) AET (4.5×10^{-4} M).

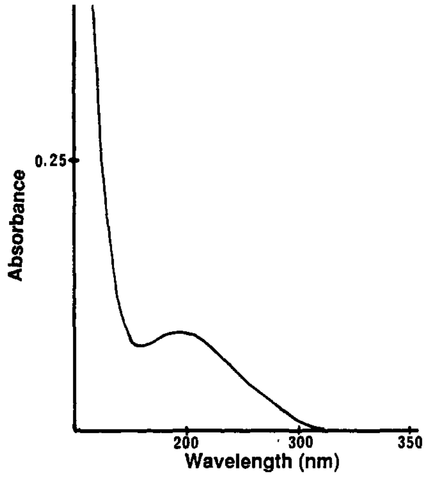


Figure 4. UV spectrum of an aqueous solution of AET (original concentration 4.5×10^{-4} M) after 24-h aging in the dark.

Table I
UV Spectral Characteristics of AETSA, AET, and Cystamine

sample	concn, mol L^{-1}	absorbance max, nm	extinction coeff at max
AETSA	6.13×10^{-3}	245	54.8
cystamine	2.26×10^{-3}	245	336.9
AET (fresh)	4.50×10^{-4}	232	3564.4
AET (aged)	2.25×10^{-4}	245	377.8

ethanethiol (AET) (Figure 3c) were recorded. AETSA and cystamine have similar absorbance maxima with cystamine exhibiting a significantly higher extinction coefficient (Table I). Of particular interest is the evaluation of AET. Interestingly, 24 h after solution preparation (Figure 4), the absorption maximum shifts to about 245 nm, indicating conversion of AET to aminoethyl disulfide (cystamine). Further, the extinction coefficient of the new product is 377, agreeing with the calculated extinction coefficient of cystamine (377) providing strong evidence for conversion of aminoethanethiol to the disulfide. In view of these results, it is highly unlikely that photolysis of a thiosulfate to a stable thiol will occur.

In an initial evaluation of the photolysis of AETSA, a 0.007 M solution of AETSA in water was exposed to UV light from the 254-nm lamps in the Rayonet reactor. The results in Figure 5 clearly show loss of thiosulfate, but the product formed absorbs so near the thiosulfate, and apparently more strongly, that quantification of the photoefficiency of the reaction is impossible.

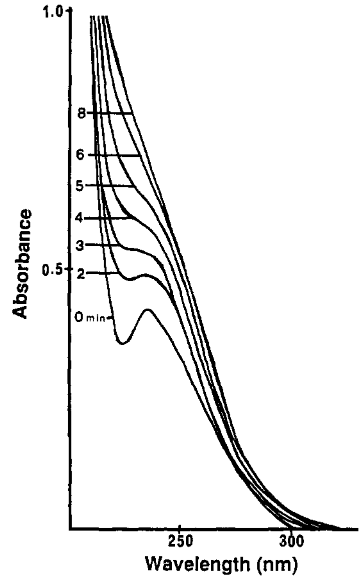


Figure 5. UV spectra of 0.007 M aqueous solution of AETSA photolyzed for 0, 2, 3, 4, 5, 6, and 8 min in a Rayonet reactor equipped with 254-nm, low-pressure mercury lamps.

In summary, the data in Figures 3–5 imply that the photolysis of AETSA results in loss of thiosulfate and formation of a product that absorbs UV radiation of similar wavelength to AETSA and has a higher extinction coefficient, as the disulfide product would be expected to have. Positive confirmation of this tenet is provided by an appropriate model study.

AETSAPPE was chosen as a model for PATE photolysis. AETSAPPE possesses identical functionality to PATE, but being only monofunctional, AETSAPPE is incapable of forming insoluble polymer upon photolysis. Preparative photolysis of a 0.25 M aqueous solution of AETSAPPE at 254 nm (see Experimental Section for details) results in isolation of the major product, AHPEPED. Photolysis of AETSAPPE in a quartz cuvette at 254 nm (450-W, medium-pressure mercury lamp and 254-nm mercury line filter) resulted in a gradual loss (Figure 6a) in AETSAPPE (HPLC analysis) with concomitant formation of AHPEPED (Figure 6b). [Note that there is a small amount of the disulfide present initially before photolysis.] Similar results were obtained for photolysis at 280 nm. In addition to formation of AH-

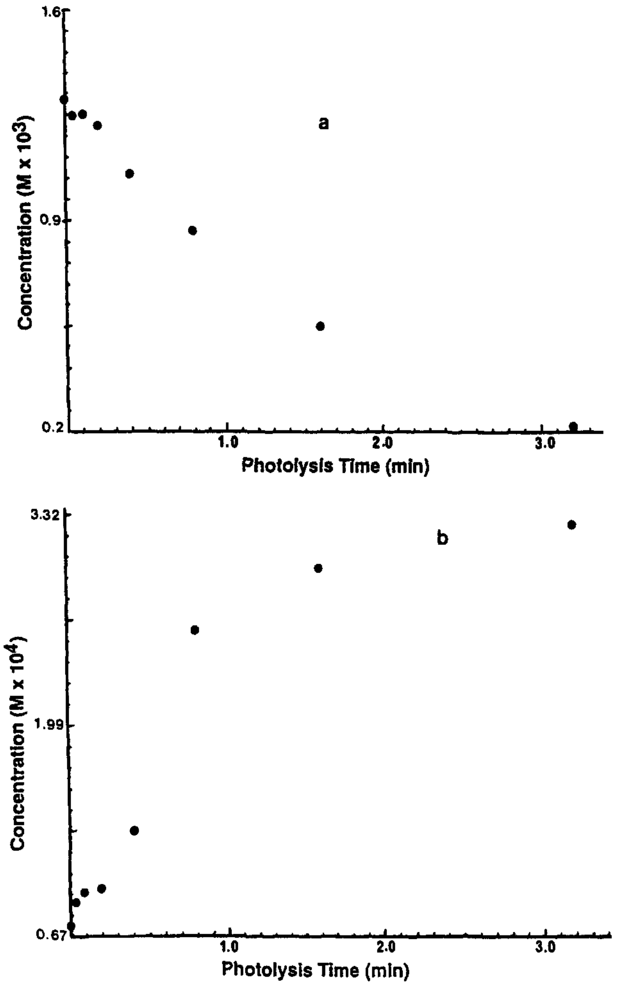


Figure 6. (a) Plot of concentration of AETSAPPE versus photolysis time with the 254-nm isolated line of a 450-W, medium-pressure mercury lamp. (b) Plot of concentration of AHPEPED versus photolysis time of an aqueous AETSAPPE solution with the 254-nm isolated line of a 450-W, medium-pressure mercury lamp.

Table II
Quantum Yields for Loss of AETSAPPE (ϕ_{LOSS}) and Formation of AHPEPED ($\phi_{AHPEPED}$)

λ_{ex}, nm	ϕ_{LOSS}	$\phi_{AHPEPED}$	sensitizer
254	0.23	0.30	none
280	0.22	0.15	none
360	0.00	0.00	none
360	0.23	*a*	yes (OD = 0.84 at 366 nm)

[a] See text for explanation.

PEPED, three other minor products appear, which additional work has shown are probably due to AHPEPED photolysis products.

Sensitization of AETSAPPE in an aqueous solution was accomplished with a water-soluble benzophenone derivative, (4-benzoylbenzyl)trimethylammonium chloride (BTC). Rather than using the minimum BTC required for observation of loss of thiosulfate, as was the case for PATE films with BP, the BTC was dissolved in such a quantity as to show an absorbance of 0.838 at 366 nm. As was the case for PATE films, photolysis of AETSAPPE at 366 nm (BTC) results in significant loss of thiosulfate at 366 nm (Figure 7).

Table II shows the results of quantum yield calculations for direct photolysis of AETSAPPE at 254 and 280 nm and sensitized BTC photolysis at 366 nm using the data from Figures 6 and 7. Although the product quantum yield calculations at 254 and 280 nm are subject to error (obviously $\phi_{AHPEPED}$ cannot be greater than ϕ_{LOSS}), it is readily apparent that AHPEPED is the major product resulting from AETSAPPE photolysis being formed in extremely high yield. In addition, it is quite noteworthy that sensitized photolysis at 366 nm results in a quantum yield for loss of AETSAPPE essentially the same as for direct photolysis, leading to the speculation that direct photolysis proceeds in large part through a triplet state, as must the sensitized reaction. Unfortunately, analysis of the AHPEPED product for the sensitized photolysis was not possible since we were not able to effect separation from the sensitizer BTC.

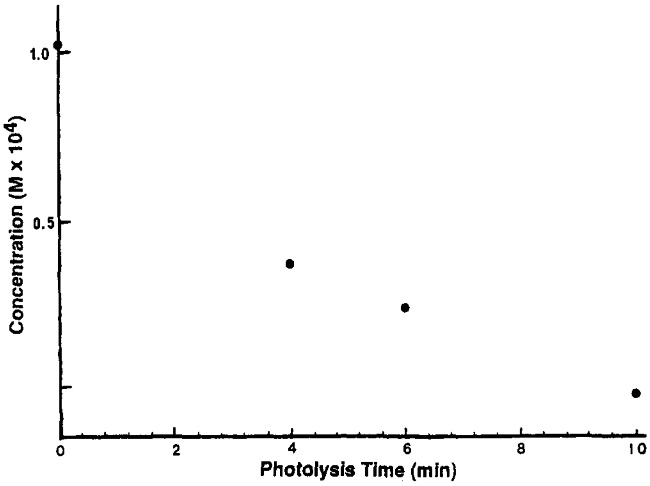


Figure 7. Plot of concentration of AETSAPPE versus photolysis time with the 366-nm isolated line of a 450-W, medium-pressure mercury lamp of an aqueous solution of AETSAPPE with BTC ($A = 0.838$ at 366 nm).

Conclusions

This paper describes the synthesis and subsequent photolysis of a polymeric oligomer (MW ~ 9000) based upon a difunctional epoxy and aminoethyl thiosulfate. The zwitterionic polymer can be readily cast from aqueous solution to give excellent films which are photochemically reactive. By use of model compounds, the photolysis is shown to result in formation of disulfide linkages with accompanying loss of ionic character and water sensitivity. From sensitization studies using a water-soluble benzophenone-type compound, it is postulated that the primary photochemical reaction proceeds by a sulfur–sulfur bond cleavage from the triplet excited state.

The photopolymer described in this initial paper has potential application as a water-soluble photoresist. In addition, it shows promise as a viscosity-modifying agent for aqueous based coatings, the subject of which will be discussed in a future publication. Finally, it is envisioned that modification of other types of oligomeric prepolymers (i.e., polyurethanes, polyesters, etc.) is possible allowing for the creation of a whole series of photopolymers. This paper constitutes a detailed study of an entirely new class of photochemically reactive oligomers with potential use in a wide variety of thin-film applications ranging from water-soluble photocurable coatings to water-based photoresists.

Registry No. (AETSA)(Epon 828) (copolymer), 120712-64-3; AETSAPPE, 120712-62-1; AHPEPED, 120712-63-2; BTC, 78697-25-3; (Epon 828)(taurine) (copolymer), 105035-18-5; benzophenone, 119-61-9.

Macromolecules **1989,** *22,* 3919–3928

References and Notes

(1) Bunte, H. *Ber.* **1874**, *7*, 646.
(2) Tsunooka, M., et al. *Kogyo Kagaku Zasshi* **1970**, *73*, 805.
(3) Tsunooka, M., et al. *Kogyo Kagaku Zasshi* **1968**, 1574.
(4) Tsunooka, M.; Ando, N.; Tanaka, M. *J. Appl. Polym. Sci.* **1974**, *18*, 1197.
(5) Beerman, C. German Patent 1 143 330, 1963.
(6) Vandenberg, E. US Patent 3,706,706, 1972.
(7) Okawara, M.; Ochiai, Y. *ACS Symp. Ser.* **1980**, *121*, 41.
(8) Stewart, M.; Dawson, J. UK Patent 2 050 438 A, 1979.

Probe for the Conformational Transition of Carrageenans. Effect of Mn^{2+}-Induced ^1H NMR Relaxation of Tetramethylammonium Ions in Aqueous Tetramethylammonium Carrageenate Solutions

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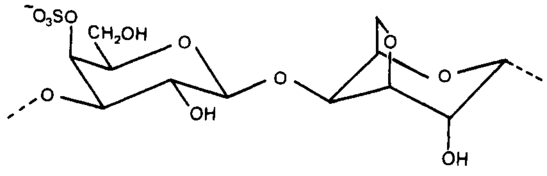
ABSTRACT: Longitudinal NMR relaxation rates of tetramethylammonium (TMA) protons in D_2O solutions containing $MnCl_2$, tetramethylammonium carrageenates, and added TMA salts have been measured. The enhancements of the Mn^{2+}-induced relaxation caused by the different carrageenans were analyzed by using the Poisson–Boltzmann equation for cylindrical geometry to obtain the distribution of mobile ions with respect to the polymer. A pronounced increase in the relaxation rates accompanying the coil–helix transition in ι- and κ-carrageenan offers a sensitive probe for detecting and analyzing conformational transitions of carrageenans. The calculated magnitudes of the relaxation enhancements and their dependence on the chain conformations were found to be in agreement with single-stranded random coils at low ionic strength and with side-by-side single helices or intertwined double helices in the ordered conformation of ι- and κ-carrageenans. For κ-carrageenan, a specific site binding of iodide anions to ordered molecules, as indicated by ^{127}I NMR, may increase the polymer charge sufficiently to make single helices account for the data as well. The tertiary structure of the ordered conformations seemed to remain unchanged after salt addition in 2–3 times excess of the critical concentration for the conformational transition to occur.

Introduction

Carrageenans are D-galactans containing hemisulfate groups. They occur in certain red algae and consist of linearly alternating α(1→3)- and β(1→4)-linked residues. The 4-linked residues are in the 3,6-anhydro form in the idealized ι- and κ-carrageenan structures, as shown in 1 and 2, respectively,[1] whereas λ-carrageenan, being of another chemical family,[1,2] has the idealized structure 3.



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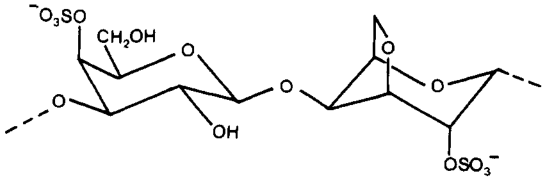

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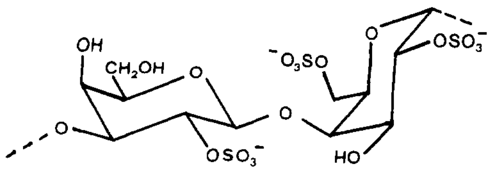

3

All the carrageenans mentioned are believed to have a single-stranded random coil conformation at low polymer concentrations in salt-free solutions at high temperatures.[3]

The first observation of a cooperative salt-induced thermoreversible conformational transition of ι- and κ-carrageenans in aqueous solutions, as reflected in optical rotation measurements, was reported by Rees and coworkers in 1969.[4,5]

After continuous interest and investigations during recent years, there is still some controversy regarding the stoichiometry of the ordered conformation of ι- and κ-carrageenan. The coil–helix transition has been interpreted in two different ways: either as a dimerization process[5,6] or as a monomolecular process.[7,8]

Regarding ι-carrageenan, light-scattering, differential scanning calorimetry, and osmometric studies suggested that a doubling of the molecular weight occurs to segments on cooling by transition from disordered to ordered conformation.[6,9–11] On the basis of X-ray fiber diagrams,[12] the ordered conformation in solution was therefore proposed to be an intertwined double helix.

The aggregation tendency seen for both ι- and κ-carrageenans in the presence of salt causes problems in molecular weight determinations.[6,13] Smidsrød et al.[8,14] found that the aggregation and gelation could be suppressed by adding iodide salts. Iodide also stabilized the ordered conformation in κ-carrageenan, as reflected in optical rotation measurements.[8]

In the presence of iodide, the conformational change in κ-carrageenan occurred without any observable change in molecular weight.[15] The ^{127}I NMR line broadening accompanying the disorder–order transition of tetramethylammonium κ-carrageenate upon addition of tetramethylammonium iodide[14] was therefore interpreted as resulting from specific site binding of iodide to single chains in the ordered conformation. Similar NMR ob-

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