theoretical models at the atomic level. Such studies should complement the results obtained from recent staging-kinetics studies (e.g., Raman, optical and X-ray/neutron diffraction).[8,14,25,26,29] A full account of our DHRTEM studies of staging mechanisms will be published in the near future.

Acknowledgment. We are grateful for the use of the National Science Foundation (DMR 8913384)/Arizona State University High Resolution Electron Microscopy and the Center for Solid State Science Materials Preparation Facilities. We also thank the Department of Chemistry for the use of its X-ray Facility and Glass Shop and Dr. G. Ouvrard for preparing the $Hg_{1.25}TiS_2$ samples and helpful discussions.

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(29) Okabe, K.; Tanuma, S. *Synth. Met.* **1988**, *23*, 61-66.

Ultraviolet Radiation-Induced Cross-Linking of Poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene]

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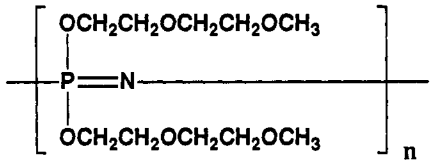
Received June 21, 1991
Revised Manuscript Received August 13, 1991

An increasing interest is evident in the design and development of conductive polymeric electrolytes for the possible fabrication of solid-state batteries.[1] It has been shown previously that poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (1) possesses an ambient temperature ionic conductivity 2-3 orders of magnitude higher than poly(ethylene oxide), when each system is complexed with $LiCF_3SO_3$.[2-6]

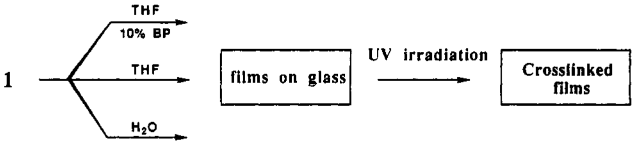


$$\left[\begin{array}{c} OCH_2CH_2OCH_2CH_2OCH_3 \\ | \\ -P{=}N- \\ | \\ OCH_2CH_2OCH_2CH_2OCH_3 \end{array}\right]_n$$

1

However, a problem associated with the practical application of this polymer is its tendency to flow under light pressure. A method that has been employed successfully to increase the dimensional stability is the use of cross-linking. It has been shown that 1 can be cross-linked both chemically and by use of ^{60}Co γ-irradiation.[7-9] Recently, Abraham and co-workers reported another technique that utilizes $LiAlCl_4$ to form a stabilized complex with polymer 1.[10]

Scheme I



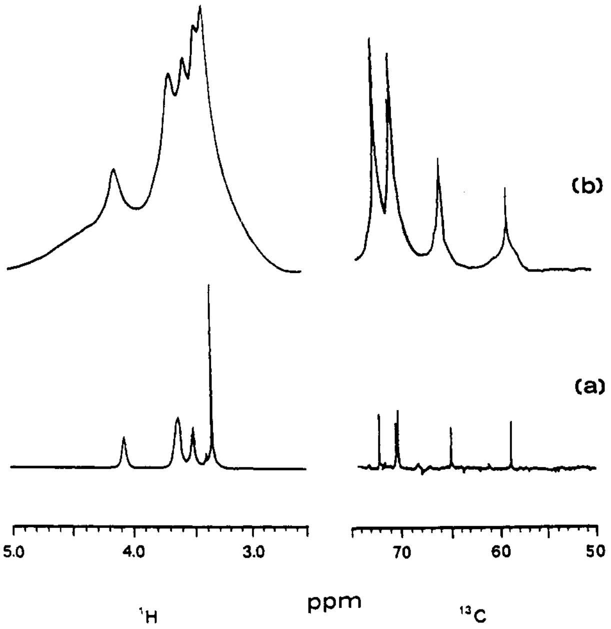


Figure 1. The 360-MHz ^1H and ^{13}C NMR spectra in $CDCl_3$ of (a) polymer 1 and (b) the swollen gel of cross-linked polymer 1.

Chemical cross-linking requires the incorporation of a difunctional reagent, thus introducing impurities into the system. ^{60}Co γ-irradiation is a much cleaner method, but its limited accessibility and related expense make use of this technique less attractive.

We report here that ultraviolet radiation can be used to cross-link polymer 1. This method offers advantages in that it allows efficient cross-linking of 1 via an inexpensive, readily available ultraviolet radiation source and yields a pure product.

The polymer 1 utilized in this study was synthesized via published methods.[2,5,11] In a typical reaction 1 was dissolved in tetrahydrofuran with 10 mol % benzophenone added as the photoinitiator. This mixture was then solution-cast as a film on glass, and the solvent was allowed to evaporate. The polymer-coated glass slides were then placed in quartz reaction tubes, which were purged with argon, sealed, and irradiated for 20 min with a 450-W Hg lamp.[12] The cross-linked films were then purified by

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(1) Shriver, D. F.; Farrington, G. C. *Chem. Eng. News* **1985**, *63*(20), 42.

(2) Blonsky, P. M.; Shriver, D. F.; Austin, P. E.; Allcock, H. R. *J. Am. Chem. Soc.* **1984**, *106*, 6854.

(3) Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *Polym. Mater. Sci. Eng.* **1985**, *53*, 118.

(4) Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. *Solid State Ionics* **1986**, *18/19*, 258.

(5) Allcock, H. R.; Austin, P. E.; Neenan, T. X.; Sisko, J. T.; Blonsky, P. M.; Shriver, D. F. *Macromolecules* **1986**, *19*, 1508.

(6) Bennett, J. L.; Dembek, A. A.; Allcock, H. R.; Heyen, B. J.; Shriver, D. F. *Chem. Mater.* **1989**, *1*, 14.

(7) Tonge, J. S.; Shriver, D. F. *J. Electrochem. Soc.* **1987**, *134*, 269.

(8) Allcock, H. R.; Kwon, S.; Riding, G. H.; Fitzpatrick, R. J.; Bennett, J. L. *Biomaterials* **1988**, *9*, 509.

(9) Allcock, H. R.; Fitzpatrick, R. J.; Gebura, M.; Kwon, S. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1987**, *28* (1), 321.

(10) Abraham, K. M.; Alamgir, M. *Chem. Mater.* **1991**, *3*, 339.

(11) Polymer 1 was characterized by ^1H NMR ($CDCl_3$): OCH_2CH_2 4.1 ppm; CH_2OCH_2 3.65 ppm; CH_2OCH_3 3.57 ppm; CH_3 3.38 ppm. ^{13}C NMR: OCH_2CH_2 72.0, 70.3 ppm; OCH_2CH_2 70.4, 65.0 ppm; OCH_3 58.8 ppm. ^{31}P NMR: $\delta = -8.4$ (s). GPC: $M_w = 4 \times 10^6$, $M_n = 2 \times 10^6$. DSC: $T_g = -84.4$ °C. Anal. Calcd: C, 42.40; H, 7.83; N, 4.94; Cl, 0.00. Found: C, 42.99; H, 7.77; N, 4.43; Cl, 0.02.

(12) A Canrad-Hanovia medium-pressure, quartz, mercury vapor lamp equipped with a water-cooled quartz immersion well was utilized. The typical emitted ultraviolet radiation for this system is between 220 and 400 nm. The samples were irradiated in quartz reaction tubes which were placed in a rotating carousel at an approximate distance of 7 cm from the unfiltered source.

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extraction of the swollen gels in tetrahydrofuran (see Scheme I).

Irradiation of 1 induces side-group coupling reactions to form a stable, cross-linked polymer matrix. The presence of cross-links was apparent from the swelling behavior and failure of the polymer to dissolve in tetrahydrofuran or water. The effect of the cross-linking was further evidenced in the ^{1}H and ^{13}C NMR spectra (see Figure 1). The broadening of the peaks, compared to those in the non-cross-linked polymer 1, was indicative of a decrease in side-group mobility.[13] A probable mechanism for cross-linking involves photolytic cleavage of C–H bonds followed by carbon radical recombination.[14]

It was also found that ultraviolet cross-linking of 1 was possible even in the absence of a photoinitiator and that this reaction was not dependent on the type of solvent (see Scheme I). The degree of cross-linking was found qualitatively to be greater for a given exposure time when benzophenone was utilized.[15] However, a cross-linking process that does not involve the addition of a photoinitiator has obvious advantages if the system is to be used for conductivity experiments. Previous studies have demonstrated that cross-linking of polymer 1 provides increased dimensional stability without reducing the ionic conductivity.[6,7]

Due to the similarity of the substituents in polymer 1 to the backbone structure of poly(ethylene oxide), films of the latter polymer were also investigated. Films of poly(ethylene oxide) were also shown to undergo cross-linking both in the presence and absence of benzophenone.[16]

Acknowledgment. We thank the Office of Naval Research for financial support, Dr. A. A. Dembek for helpful discussions, and W. H. Chapman and J. Sczepanski for the use of UV photolysis facilities.

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(13) Further evidence for the decrease in side-group mobility was given by the increase in the measured glass transition temperature for the cross-linked polymer 1: $T_g = -77.4$ °C.

(14) Oster, G.; Oster, G. K.; Moroson, H. *J. Polym. Sci., Polym. Symp.* **1959**, *34*, 671. Oster, G.; Shibata, O. *J. Polym. Sci.* **1957**, *26*, 233. Oster, G. *J. Polym. Sci.* **1956**, *22*, 185.

(15) Samples of polymer 1 with and without benzophenone present were irradiated with the ultraviolet source for 20 min. However, the films cross-linked without a photoinitiator present swelled more in THF or water than the gels formed in the presence of benzophenone. This indicates a lower rate of cross-linking in the absence of a photoinitiator.

(16) Films of poly(ethylene oxide) were cast onto glass slides (a) in the absence of benzophenone from H_2O and (b) with 10 mol % photoinitiator, from solutions in $CHCl_3$ or THF. Following solvent evaporation the polymer-coated glass slides were placed in quartz reaction tubes, which were purged with argon, sealed, and irradiated for 20 min with a 450-W Hg lamp. The cross-linked films were then immersed in H_2O to form solvent swollen gels.

A Conductive, Anisotropic Polymer Film Formed by Electroprecipitation of π-Stacks of an Imide Anion Radical and a Polycation

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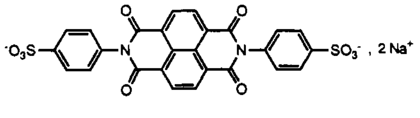
Received May 7, 1991
Revised Manuscript Received July 1, 1991

It has recently been shown that the anion radical of disulfonate salt 1 aggregates into π-stacks in aqueous salt solutions.[1] Described here are studies that demonstrate that this solution-phase aggregation can be enhanced by small amounts of cationic polymers, e.g., 2^+, and that it is possible to electroprecipitate thin films composed of $1^-/2^+$. Spectroscopic studies show that these air-stable films are somewhat anisotropic with stacks of 1^- anion radicals running preferentially along the plane of the thin film. Because of this structure the electrical conductivity is much higher along the film than across the thin dimension. These films have the further unusual property that the conductivity increases by 10^3 as the relative humidity changes from 0 to 90%. Close analogues of this material are conductive films composed of $TCNQ^-$ and cationic polymers.[2] These $TCNQ^-$ films are, however, isotropic and decomposed by moisture. Nonpolymeric, but anisotropic, films of 1 have been prepared by using the Langmuir–Blodgett method,[3] as have conducting LB films containing $TCNQ^-$.[4]



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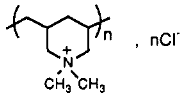

2^+

To study the aggregation in solution, aqueous solutions of 1^- (1–5 mM) were formed by reduction of 1 with sodium dithionite. As previously demonstrated,[1] these solutions are composed primarily of π-dimers, which have an absorption maximum at 1140 nm. Addition of an amount of polymer 2^+ sufficient to balance the charge on the trianion 1^- led to a spectrum with a near-infrared absorption maximum at 1700 nm. This band is characteristic of π-stacks.[1,5] Thus, the cationic polymer provided a template to organize the dimers into stacks in solution. We know of no previous example of this phenomenon.

Although it was possible to precipitate the salt $1^-,2^+$ as a black solid[1,6] a more interesting result was obtained by electroprecipitation.[7] Thus an aqueous solution of 1 (1 mM), with 2^+Cl^- (0.1 M) present as the supporting electrolyte, was reduced at a platinum electrode. The potential was held at −0.2 V vs SCE. Over a period of many minutes the current held steady at 0.01 mA cm^{-2}, and a shiny film grew on the surface. When thin, the film was brown; when thicker, it was black. After drying in vacuum, films 10–50 μm thick could be peeled off of the electrode. They were stable in air for more than 1 month. XPS analysis confirmed the elemental composition to be consistent with the structure $1^-,2^+$, with substantial chloride but only traces of sodium.

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[‡] IBM Almaden Laboratories.

(1) Penneau, J. F.; Stallman, B. J.; Kasai, P. H.; Miller, L. L. *Angew. Chem.*, in press.

(2) Stankovic, R. I.; Lenz, R. W.; Karasz, F. E. *Eur. Polym. J.* **1990**, *26*, 675. Skorobogaty, A.; Smith, T. D. *Coord. Chem. Rev.* **1984**, *53*, 55. Mostovoy, R. M.; Sukharev, V. Ya.; Berendyayev, V. I.; Kotov, B. V.; Myasnikov I. A. *J. Phys. Chem. Solids* **1989**, *6*, 541. Lupinski, J. H.; Kopple, K. D.; Hertz, J. J. *J. Polym. Sci: Part C* **1967**, *16*, 1561. Oshima, R.; Kumanotani, J. *J. Polym. Sci., Part C* **1987**, *25*, 2343.

(3) Cammarata, V.; Kolaskie, C. J.; Miller, L. L.; Stallman, B. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1290.

(4) Richard, J.; Vandevyver, M.; Lesieur, P.; Ruaudel-Teixier, A.; Barraud, A.; Bozio, R.; Pecile, C. *J. Chem. Phys.* **1987**, *86*, 2428. Ikegami, K.; Kuroda, S.-I.; Saito, M.; Saito, K.; Sugi, M. *Thin Solid Films* **1988**, *160*, 139. Vandevyer, M.; Richard, J.; Barraud, A.; Ruaudel-Teixier, A.; Lequan, M.; Lequan, R. M. *J. Chem. Phys.* **1987**, *87*, 6754.

(5) Torrance, J. B.; Scott, B. A.; Welber, B.; Kaufman, F. B.; Seiden, P. E. *Phys. Rev. B* **1979**, *19*, 730. Jacobsen, C. S.; Johanssen, I.; Bechgaard, K. *Phys. Rev. Lett.* **1984**, *53*, 194.

(6) Conducting imide anion radical salts: ref 1 and Heywang, G.; Born, L.; Fitzky, H. G.; Hassel, T.; Hocker, J.; Muller, H. K.; Pittel, B.; Roth, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 483.

(7) Ward, M. D. *Electroanal. Chem.* **1981**, *16*, 181.