trated. Clearly a large increase in intensity occurs on the first heating as the $T(1)$ transition is tranversed, but there is no change in spherulitic texture (only enhanced brightness occurs). On cooling down the sample from 180 °C to 50 °C, a weak transition is just perceptible about 120 °C, but during the second heating the light intensity decreases noticeably about 140 °C. Upon cooling from 180 °C approximately a slight increase in intensity occurs. After the sample was cooled again, a noticeable transition occurs about 114 °C with a concomitant rise in intensity to a level that remains essentially constant back to 50 °C. The transitional behavior depicted in this figure is consistent with enhanced molecular chains ordering that the finely textured occurs upon cycling the PB(4Cl)PP material through $T(1)$ starting with solution cast material which was of relatively low birefringence. The molecular subtleties of these transition under heating/cooling can only be settled by using other complementary techniques like ^{31}P and ^{13}C solid-state NMR under identical heat treatment conditions.

Conclusion

This preliminary work using thermotropic polyphosphazenes has illustrated the validity of the modified DLI technique for studying (1) kinetics of phase transformation and (2) morphology–temperature–time changes encountered in relatively thin films of solution cast polymers. The technique seems to be suitable for following both fast and slow transformation rates and appears to be a valuable procedure that merits detailed investigations.

Acknowledgment. We thank M. Inoue, J. Kitami, and K. Sasaki of Yamagata University for DSC measurements, material, and film preparations. Support from the Ministry of Education, Science and Culture, Japan, and the International Scientific Research Program, Joint Research, Ser. No. 63044019, is gratefully acknowledged.

References and Notes

(1) Magill, J. H. *Nature (London)* **1960**, *187*, 770.
(2) Hock, C. W.; Arbogast, J. F. *Anal. Chem.* **1961**, *33*, 462.
(3) Magill, J. H. *Polymer* **1961**, *2*, 221.
(4) Phillips, P. J.; Kao, Y. H. *Polymer* **1986**, *27*, 1679.
(5) Mayhen, K. G.; James, W. J.; Bosch, W. *J. Appl. Polym. Sci.* **1965**, *9*, 3605.
(6) Barrall, E. M.; Johnston, J. F.; Porter, R. S. *Appl. Symp.* **1969**, *No. 8*, 191.
(7) Binsbergen, F. L.; deLange, B. G. M. *Polymer* **1968**, *9*, 23.
(8) van Antwerpen, F.; van Krevelan, D. W. *J. Polym. Sci., Poly. Phys. Ed.* **1972**, *10*, 2423.
(9) Binsbergen, F. L. *J. Macromol. Sci., Phys.* **1970**, *B4*, 837.
(10) Ziabicki, A. *Kolloid-Z.* **1967**, *219*, 2.
(11) Clough, S.; Rhodes, M. B.; Stein, R. S. *J. Polym. Sci., Part C* **1967**, *18*, 1.
(12) See also Appendix in ref 7.
(13) A catalog of MK-801 DLI instrument by Kotaki Co., Tokyo; and an instruction manual for Model KP temperature controller by Chino Co., Tokyo, 1988.
(14) Kojima, M.; Magill, J. H. *Makromol. Chem.* **1985**, *186*, 649.
(15) Schneider, N. S.; Desper, C. R.; Singler, R. E.; Alexander, M. M.; Sagalyn, P. L. In *Organometallic Polymers*; Carraher, C. E., Jr., Sheats, J. E., Pittman, C. U., Jr., Eds.; Academic Press: New York, London, 1978; p 271.
(16) Magill, J. H.; Riekel, C. *Makromol, Chem. Rapid Commun.* **1986**, *7*, 287.
(17) Riekel, C.; Magill, J. H., in preparation.
(18) Sun, D. C.; Magill, J. H. *Polymer* **1987**, *28*, 1243.
(19) Ciora, R.; Magill, J. H., submitted for the 18th NATAS Conference, San Diego, CA, Sept 1989.
(20) Avrami, M. *J. Chem. Phys.* **1939**, *7*, 1103; **1941**, *9*, 177.
(21) Flory, P. J.; McIntyre, A. D. *J. Polym. Sci.* **1955**, *18*, 592.
(22) Masuko, T.; Simeone, R. L.; Magill, J. H.; Plazek, D. J. *Macromolecules* **1984**, *17*, 2857.
(23) Young, S. G.; Magill, J. H. *Macromolecules* **1989**, *22*, 2549.
(24) Magill, J. H.; Petermann, J.; Rieck, U. *Colloid Polym. Sci.* **1986**, *262*, 570.
(25) Russell, T. P.; Anderson, D. P.; Stein, R. S.; Desper, C. R.; Beres, J. J.; Schneider, N. S. *Macromolecules* **1984**, *17*, 1795 Schneider, N. S. *Macromolecules* **1984**, *17*, 1795
(26) Note that the temperature scale on all the DLI heating/cooling curves presented is not equally divided everywhere because of the nonlinear heating rates that lie in the range 5–10 °/min.

Notes

Synthesis and Electrochemical Characterization of Siloxane Polymers Containing Hydroquinone and 1,4-Naphthohydroquinone

T. INAGAKI, H. S. LEE, P. D. HALE, and T. A. SKOTHEIM*

Materials Science Division, Department of Applied Science, Brookhaven National Laboratory, Upton, New York 11973

Y. OKAMOTO*

Department of Chemistry, Polytechnic University, 333 Jay Street, Brooklyn, New York 11201.
Received February 28, 1989;
Revised Manuscript Received May 4, 1989

Introduction

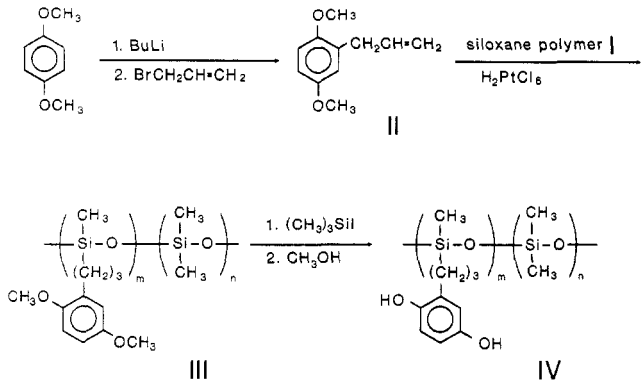
Recent work in our laboratory has demonstrated the utility of several siloxane-based redox polymers in mediating electron transfer between an oxidoreductase enzyme and a conventional electrode surface.[1] The unique flexibility of the polysiloxane backbone allows a sufficiently close contact to occur between the redox couples of the polymeric system and the enzyme's redox centers so that efficient charge transfer can be achieved. For example, siloxane polymers containing ferrocene or 1,1'-dimethylferrocene[2] have been shown to facilitate electron transfer from reduced glucose oxidase to an electrode.[1] These redox polymers provide an important advantage in the design of enzyme-based sensors: because the redox species are covalently bound to the polymer backbone, they are not free to diffuse away from the electrode surface into the bulk solution. Thus, unlike systems based on freely diffusing electron-transfer mediators, such as ferrocene and its derivatives[3-5] or tetracyanoquinodimethane (TCNQ),[6-10] sensors incorporating these polymeric redox systems may be of potential clinical value in implantable measuring devices. With this in mind, we have extended our studies of siloxane-based redox polymers to include systems that contain quinone moieties as the electroactive species. Quinones have previously been employed as freely diffusing electron-transfer mediators in enzyme-based bioanalytical sensors.[11-15] In this paper, we describe the synthesis and electrochemical characterization of siloxane polymers that contain hydroquinone and 1,4-naphthohydroquinone and discuss the potential use of these materials in sensor applications.

Experimental Section

A. Polymer Synthesis. The synthetic route for the siloxane polymer containing hydroquinone is described in Scheme I. The

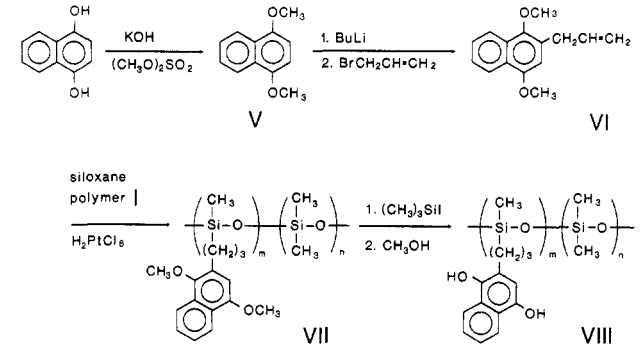
0024-9297/89/2222-4641$01.50/0

Scheme I
Preparation of Polymer IV[a]



[a] $m:n$ = 1:2.

Scheme II
Preparation of Polymer VIII[a]



[a] $m:n$ = 1:2.

methylhydro/dimethyl (1:2) siloxane copolymer I (MW 2000–2100) was obtained from Petrarch Systems, and all other chemicals were purchased from Aldrich Chemical. 1-Allyl-2,5-dimethoxybenzene (II) was synthesized by the reaction of lithiated 1,4-dimethoxybenzene with allyl bromide under nitrogen atmosphere in ether at the reflux temperature (~3 h). The product was isolated by distillation; bp 63–65 °C (0.1 mmHg). ^{1}H NMR ($CDCl_3$): δ 3.35 (d, 2 H), 3.7 (s, 6 H), 5.0 (d, 2 H), 5.7–6.3 (m, 1 H), 6.65 (s, 3 H) ppm. Compound II (2.33 g) was hydrosilylated by using the siloxane copolymer I (0.72 g) in dry THF solution (15 mL) in the presence of catalyst prepared from chloroplatinic acid and 1,2-dimethoxyethane.[16] The reaction was continued at reflux temperature until the Si–H IR absorption band (2161 cm^{-1})[17] disappeared to show that all of the starting polymer was converted to polymer III. Ether was added to the reaction mixture; it was then washed with water and dried. After removal of solvent, the residual allyl compound was removed under 0.05 mmHg pressure. The colorless polymer III (1.2 g) was obtained. ^{1}H NMR ($CDCl_3$): δ 0.18 (s, 15 H), 0.4–0.75 (m, 2 H), 1.3–1.8 (m, 2 H) 2.4–2.8 (m, 2 H), 3.75 (s, 6 H), 6–7 (s, 3 H) ppm. The copolymer III (1.2 g) was dissolved in 5 mL of dry methylene chloride. To the solution was added 1.5 mL of trimethylsilyl iodide under nitrogen atmosphere. After the reaction mixture was allowed to stand at room temperature for 60 h, methanol (3 mL) and then ether (20 mL) were added into the solution. The solution was then washed successively with aqueous sodium sulfite, aqueous sodium bicarbonate, and water. Removal of the solvent yielded the methyl-γ-(2,5-dihydroxyphenyl)propyl/dimethyl (1:2) siloxane copolymer IV (1.0 g) as a clear light brown liquid. IR (neat): no Si–H absorption; 3350.9 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$): δ 0.2 (s, 15 H, CH_3), 0.7 (b, 2 H, CH_2), 1.7 (b, 2 H, CH_2), 2.6 (b, 2 H, CH_2), 6.6 (s, 3 H, Ar) ppm.

The 1,4-naphthohydroquinone moiety was introduced into the polysiloxane backbone as shown in Scheme II. 1,4-Dimethoxynaphthalene (V) was prepared by a modification of the method of Wakae et al.[18] To a mixture of 1,4-naphthohydroquinone and dimethyl sulfate was slowly added a solution of potassium hydroxide in water under nitrogen at room temperature over the course of 1 h. The reaction mixture was then heated at 80 °C for 3 h. After cooling, the precipitate was collected and washed with water and ethanol. Recrystallization from ethanol gave a white plate crystal, mp 85–86 °C. V was used for the synthesis of VI using the same procedure described for I. The product of this reaction was a liquid, bp 110–112 °C (0.1 mm). ^{1}H NMR ($CDCl_3$): δ 3.9 (s, 6 H), 4.15 (d, 2 H), 5.1 (t, 2 H), 5.8–6.4 (m, 1 H), 6.75 (s, 1 H), 7.4–7.8 (m, 2 H), 8.1–8.5 (m, 2 H) ppm. The hydrosilylation was carried out as described in the preparation of III. After removal of volatile materials at 100 °C under 0.1 mmHg, the product was identified by IR and ^{1}H NMR measurements. IR (neat): no Si–H absorption; 3060 cm^{-1} (=CH). ^{1}H NMR ($CDCl_3$): δ 0.15 (s, 15 H, CH_3), 0.8 (s, 2 H, CH_2), 1.7 (s, 2 H, CH_2), 3.3 (s, 2 H, CH_2), 3.95–4.0 (s, 6 H, OCH_2), 6.75 (s, 1 H, Ar), 7.5 (m, 2 H, Ar), 8.25 (m, 2 H, Ar) ppm. The demethylated product, the methyl-γ-(2,9-dihydroxynaphthyl)-propyl/dimethyl (1:2) siloxane copolymer (VIII), was obtained by the reaction of VII with trimethylsilyl iodide as described in the preparation of IV. IR (neat): no Si–H absorption; 3350.9 cm^{-1} (OH). ^{1}H NMR ($CDCl_3$): no OCH_3 signal.

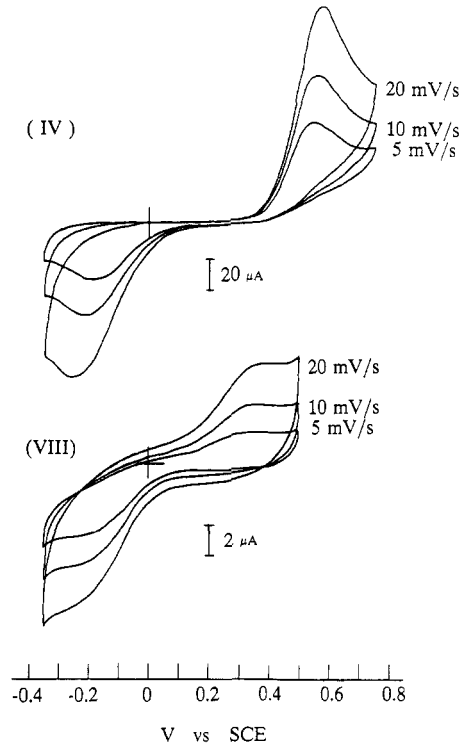


Figure 1. Cyclic voltammograms of polymers IV and VIII in 0.1 M $TEABF_4/CH_3CN–H_2O$ (1:1) by volume: IV, 1.35 mg/mL; VIII, 0.08 mg/mL.

B. Electrochemical Characterization. In order to determine the electrochemical properties of these new polymers, acetonitrile was twice purified by distillation over CaH_2 and was stored under argon. The supporting electrolyte, tetraethylammonium tetrafluoroborate ($TEABF_4$), was twice recrystallized from methanol–hexane and was dried thoroughly under vacuum. The cyclic voltammetry experiments were performed by using a Bioanalytical Systems Model CV-27 potentiostat. The electrochemical cell was conventional with a Pt wire working electrode and a Pt-on-glass auxiliary electrode. A saturated calomel electrode (SCE) was chosen as the reference, to which all stated potentials are referred. All measurements were made at room temperature (23 ± 2 °C) in a mixed solvent system consisting of acetonitrile and water in a 1:1 ratio by volume and 0.1 M $TEABF_4$ as the supporting electrolyte. The pH value of this solution system was about 6.5. The solutions were deaerated by argon bubbling prior to the experiments, and the electrochemical cell was kept under argon atmosphere throughout the measurements.

Results and Discussion

Typical voltammetric response curves for polymers IV and VIII in the mixed solvent are shown in Figure 1 for

potential scan rates of 5, 10, and 20 mV/s. These voltammograms confirm that the electroactivity of the quinone moieties is maintained after covalent attachment to the siloxane polymer backbone. The results for polymer IV consist of widely separated anodic and cathodic peaks, indicating a high degree of electrochemical irreversibility. For a scan rate of 10 mV/s, the anodic peak potential (E_{pa}) is +0.555 V (vs SCE) and the cathodic peak potential (E_{pc}) is −0.215 V, giving a peak separation (ΔE) of 770 mV; these values are dependent on the scan rate, as shown in Figure 1. The redox behavior of the benzoquinone/hydroquinone system is quite sensitive to the electrode and solution conditions,[19-22] so for comparison we also performed cyclic voltammetry experiments for unbound methylhydroquinone in the 1:1 acetonitrile–water solution. The results are very similar to those found for the polymeric system, with E_{pa} = +0.548 V and E_{pc} = −0.065 V, indicating only slightly more reversible behavior for the unbound species. The voltammetric results for polymer VIII shown in Figure 1 (E_{pa} = +0.350 V and E_{pc} = −0.250 V for a scan rate of 10 mV/s) are also very similar to those measured for the unbound 1,4-naphthohydroquinone species (E_{pa} = +0.330 V; E_{pc} = −0.205 V) under the same conditions.

These results demonstrate that these newly synthesized siloxane copolymers containing hydroquinone and 1,4-naphthohydroquinone maintain the electroactivity of the unbound quinone moieties. In order to test the utility of these siloxane polymers for enzyme-based amperometric sensors, an electrode was constructed by thoroughly mixing 100 mg of graphite powder with 1.0 mg of the polymers, 10.0 mg of glucose oxidase, and 20 μL of paraffin oil, and the resulting mixture was blended into a paste. The paste was packed into a glass tubing (6-mm inner diameter). The preliminary result indicated that these polymers efficiently mediate the charge transfer from reduced flavoenzyme to a conventional electrode surface.

Acknowledgment. We thank H. I. Karan for many useful discussions. T. I. would like to thank UBE Industries for a fellowship. This research has been sponsored by the U.S. Department of Energy, Division of Materials Science, under Contract DE-AC02-76CH00016.

Registry No. II, 19754-22-4; V, 10075-62-4; VI, 123597-09-1; $BrCH_2CH{=}CH_2$, 106-95-6; $(CH_3O)_2SO_2$, 77-78-1; 1,4-dimethoxybenzene, 150-78-7; 1,4-dihydroxynaphthalene, 571-60-8; glucose oxidase, 9001-37-0.

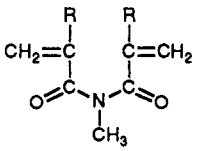
References and Notes

(1) Hale, P. D.; Inagaki, T.; Karan, H. I.; Okamoto, Y.; Skotheim, T. A. *J. Am. Chem. Soc.* **1989**, *111*, 3482–3484.
(2) Inagaki, T.; Lee, H. S.; Skotheim, T. A.; Okamoto, Y. *J. Chem. Soc., Chem. Commun.* **1989**, 1181–1183.
(3) Cass, A. E. G.; Davis, G.; Francis, G. D.; Hill, H. A. O.; Aston, W. J.; Higgins, I. J.; Plotkin, E. V.; Scott, L. D. L.; Turner, A. P. F. *Anal. Chem.* **1984**, *56*, 667–671.
(4) Lange, M. A.; Chambers, J. Q. *Anal. Chim. Acta* **1985**, *175*, 89–97.
(5) Iwakura, C.; Kajiya, Y.; Yoneyama, H. *J. Chem. Soc., Chem. Commun.* **1988**, 1019–1020.
(6) Kulys, J. J.; Čėnas, N. K. *Biochim. Biophys. Acta* **1983**, *744*, 57–63.
(7) Albery, W. J.; Bartlett, P. N.; Craston, D. H. *J. Electroanal. Chem.* **1985**, *194*, 223–235.
(8) McKenna, K.; Brajter-Toth, A. *Anal. Chem.* **1987**, *59*, 954–958.
(9) Hale, P. D.; Wightman, R. M. *Mol. Cryst. Liq. Cryst.* **1988**, *160*, 269–279.
(10) Hale, P. D.; Skotheim, T. A. *Synth. Met.* **1989**, *28*, 853–858.
(11) Alberti, B. N.; Klibanov, A. M. *Enzyme Microb. Technol.* **1982**, *4*, 47.
(12) Ikeda, T.; Katasho, I.; Kamei, M.; Senda, M. *Agric. Biol. Chem.* **1984**, *48*, 1969 and references therein.
(13) Ikeda, T.; Hamada, H.; Miki, K.; Senda, M. *Agric. Biol. Chem.* **1985**, *49*, 541.
(14) Ikeda, T.; Hamada, H.; Senda, M. *Agric. Biol. Chem.* **1986**, *50*, 883–890.
(15) Bourdillon, C.; Laval, J. M.; Thomas, D. *J. Electrochem. Soc.* **1986**, *133*, 706.
(16) Kennedy, J. P.; Chang, V. S. C.; Guyot, A. *Carbocationic Synthesis and Characterization of Polyolefins with Si-H and Si-Cl Head Groups*. In *Advances in Polymer Science 43—Polymerization and Polymer Properties*; Springer-Verlag: Berlin, 1982; p 1.
(17) Anderson, R.; Arkles, B.; Larson, G. L. *Silicon Compounds Review and Register*; Petrarch Systems: Bristol, PA, 1987; p 69.
(18) Wakae, M.; Kouishi, K. *Ind. Res. Inst., Osaka Prefect.* **1955**, *712*, 59.
(19) Chambers, J. Q. In *The Chemistry of the Quinoid Compounds, Part 2*; Patai, S., Ed.; Wiley: New York, 1974; p 737 and references therein.
(20) Jaworski, J. S.; Lesniewska, E.; Kalinowski, M. K. *J. Electroanal. Chem.* **1979**, *105*, 329.
(21) Bailey, S. I.; Ritchie, I. M.; Hewgill, F. R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 645.
(22) Bailey, S. I.; Ritchie, I. M. *Electrochimica Acta* **1985**, *30*, 3.

Communications to the Editor

Cyclopolymerization. 16. Anionic Cyclopolymerization of *N*-Methyldiacrylamide: 5-Membered Ring Formation through Head-to-Head and Tail-to-Tail Additions

Radical cyclopolymerizations of N-substituted dimethacrylamides (RDMA)[1-5] and diacrylamides (RDA)[6-8] have been reported. Both groups of monomers have extremely high cyclization tendencies and yield polymers with a 5-membered ring as the main repeating cyclic unit. Despite the structural similarity of the polymers formed, the reactivities of the double bonds involved in RDMA and RDA are essentially different. This can be seen from the polymerizabilities of N,N-disubstituted methacrylamides and acrylamides, which are considered to correspond to the monofunctional counterparts of RDMA and RDA, respectively. The former cannot be polymerized,[3,4,9] while the latter have a high polymerization tendency.[10] Thus, fundamental aspects for the formation of a highly cyclized polymer in radical polymerization are considered to be different for RDMA[4] and RDA.[8] Although considerable accumulated data are thus available for the radical polymerization of RDMA and RDA, especially for the former, anionic polymerization of these monomers has not been reported except for preliminary results on *N*-methyldimethacrylamide (MDMA),[2] which showed that 6-membered rings are formed as the main repeating unit in



MDA, R = H
MDMA, R = CH_3

0024-9297/89/2222-4643$01.50/0