$T_{iso} - T$ difference. However, in the case of these polysiloxanes, which have both nematic and smectic A phases, no discontinuity is observed, within the sensitivity of the experiments, at the nematic–smectic A transition temperature.

Conclusion

This ^{13}C NMR study of side-chain liquid-crystal polysiloxanes has led to a detailed description of molecular order and local motions in the different parts of the molecule: spacer, mesogenic core, and terminal group of the side chain. It has shown the different influence of the spacer and terminal group on the order parameter associated with the mesogenic core. Moreover, apparent variations of the order parameter along the side chain can be interpreted quantitatively in terms of several motional processes occurring simultaneously in the oriented mesophase. Among them are the trans–gauche conformational changes in the spacer, the internal rotation of the phenyl rings about their symmetry axis, the motion of the COO plane associated with the β_2 transition of polysiloxanes, and the overall rotation of the whole side group about its molecular axis.

References and Notes

(1) Mauzac, M.; Hardouin, F.; Richard, M.; Achard, M. F.; Sigaud, G.; Gasparoux, H. *Eur. Polym. J.* **1986**, *22*, 137.
(2) Keller, P.; Carvalho, B.; Cotton, J. P.; Lambert, M.; Moussa, F.; Pepy, G. *J. Phys. Lett.* **1985**, *46*, L-1065.
(3) Moussa, F.; Cotton, J. P.; Hardouin, F.; Keller, P.; Lambert, M.; Pepy, G.; Mauzac, M.; Richard, H. *J. Phys.* (*Les Ulis, Fr.*) **1987**, *48*, 1079.
(4) Njeumo, R. Thèse de Docteur-Ingénieur, Lille, France, 1986.
(5) Attard, G. S. *Mol. Phys.* **1986**, *58*, 1087.
(6) Araki, K.; Attard, G. S. *Liq. Cryst.* **1986**, *1*, 301.
(7) Attard, G. S.; Williams, G. *Liq. Cryst.* **1986**, *1*, 253.
(8) Attard, G. S.; Moura-Ramos, J. J.; Williams, G. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1099.
(9) Zentel, R.; Strobl, G. R.; Ringsdorf, H. *Macromolecules* **1985**, *18*, 960.
(10) Parneix, J. P.; Njeumo, R.; Legrand, C.; Le Barny, P.; Dubois, J. C. *Liq. Cryst.* **1987**, *2*, 167.
(11) Haase, W.; Pranoto, H.; Bormuth, F. J. *Ber. Bunsen-Ges. Phys. Chem.* **1985**, *89*, 1229.
(12) Boeffel, C.; Hisgen, B.; Pschorn, U.; Ringsdorf, H.; Spiess, H. W. *Isr. J. Chem.* **1983**, *23*, 388.
(13) Spiess, H. W. *Pure Appl. Chem.* **1985**, *57*, 1617.
(14) Pschorn, U.; Spiess, H. W.; Hisgen, B.; Ringsdorf, H. *Makromol. Chem.* **1986**, *187*, 2711.
(15) Pines, A.; Chang, J. J. *Phys. Rev. A* **1974**, *10*, 946.
(16) Pines, A.; Chang, J. J. *J. Am. Chem. Soc.* **1974**, *96*, 590.
(17) Rutar, V.; Blinc, R.; Vilfan, M.; Zann, A.; Dubois, J. C. *J. Phys.* (*Les Ulis, Fr.*) **1982**, *43*, 761.
(18) Stejskal, E. D.; Schaefer, J. *J. Magn. Reson.* **1975**, *18*, 560.
(19) Tegenfeldt, J.; Haeberlen, U. *J. Magn. Reson.* **1979**, *36*, 453.
(20) Schaefer, J.; Stejskal, E. D.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384.
(21) Wehrli, F.; Wirthlin, T. *Interpretation of Carbon-13 NMR Spectra*; Heyden: London, 1976.
(22) Mueller, K.; Meier, P.; Kothe, G. *Prog. NMR Spectrosc.* **1985**, *17*, 211.
(23) Adams, J. M.; Morsi, S. E. *Acta Crystallogr.* **1976**, *B32*, 1345.
(24) Edmonds, A. R. *Angular Momentum in Quantum Mechanics*, 3rd ed.; Hofstadter, R., Ed.; Princeton University Press: Princeton, NJ, 1974, p 7.
(25) Maricq, M. M.; Waugh, J. S. *J. Chem. Phys.* **1979**, *70*, 3300.
(26) Wemmer, D. E.; Pines, A.; Whitehurst, D. D. *Philos. Trans. R. Soc. London* **1981**, *A-300*, 15.
(27) Tegenfeldt, J.; Feucht, H.; Ruschitzka, G.; Haeberlen, U. *J. Magn. Reson.* **1980**, *39*, 509.
(28) Harbison, G. S.; Vogt, V. D. Spiess, H. W. *J. Chem. Phys.* **1987**, *86*, 1206.
(29) Lifshitz, E.; Goldfarb, D.; Vega, S.; Luz, Z.; Zimmermann, H. *J. Am. Chem. Soc.* **1987**, *109*, 7280.
(30) Vanderhart, D. L. *J. Chem. Phys.* **1976**, *64*, 830.
(31) Sergot, P.; Laupretre, F.; Louis, C.; Virlet, J. *Polymer* **1981**, *22*, 1150.
(32) Hsi, S.; Zimmermann, H.; Luz, Z. *J. Chem. Phys.* **1978**, *69*, 4126.
(33) Samulski, E. T.; Toriumi, H. *J. Chem. Phys.* **1983**, *79*, 5194.

Diaphragmatic Chemical Polymerization of Pyrrole in the Nafion Film

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ABSTRACT: A diaphragmatic procedure, in which a supporting film (Nafion) was put between pyrrole monomer and oxidant solution chambers, gave conducting polypyrrole–Nafion composite films through chemical polymerization of pyrrole. Two types of composite films were obtained with respect to the polarity of the adopted oxidants. One was the asymmetrical conducting composite film in the case of an anionic $S_2O_8^{2-}$ oxidant. The anionic oxidant scarcely penetrated into the Nafion owing to the Donnan exclusion effect of the fixed negative charge in the Nafion. Pyrrole permeating the Nafion was polymerized only in the oxidant side of the Nafion. The oxidant side of the resulting composite film was conducting, while its monomer side was insulating. The other showed considerable conductivity at both the oxidant side and the monomer side, when a cationic Fe^{3+} oxidant was used.

Introduction

Polypyrrole (PPy)[1-6] and its analogues, of great interest as a new type of polymer material, have been studied widely in the field of pure and applied material science. PPy has applications in such equipment as electronic devices,[7,8] electrochromic displays,[9-11] polymer batteries,[12-15] polymer-modified electrodes,[16] functional

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membranes,[17-20] etc. From a practical point of view, good mechanical properties of the PPy film are required for these applications. Recently, many hybridized procedures have been developed to endow the native properties of PPy with high functionality.[21-40] Several groups have reported that PPy–conventional polymer composites had good mechanical properties and high conductivities. These composites were prepared by electrochemical polymerization of pyrrole on an electrode covered with conventional insulating polymers[25-27] or by electrochemical polymerization of pyrrole in the presence of anionic polymers.[28,30,32]

On the other hand, it has not been easy to obtain homogeneous and free-standing PPy films during the chemical polymerization of pyrrole, although the polymerization is effective for preparing large amounts of conducting polymers.[41-46] We utilized the diaphragmatic procedure, in which the supporting film was put between monomer and oxidant solution chambers, for the chemical hybridization of PPy. The present methods have two advantages: (1) the polymerization rate can be limited by the permeation of a monomer and an oxidant through the supporting film, and (2) the mechanically strong free-standing PPy composite film is easily obtained. In this paper, a cation-exchange membrane, Nafion, was adopted as a supporting film, and the preparations of two types of PPy–Nafion composite with an anionic $S_2O_8^{2-}$ oxidant and a cationic Fe^{3+} oxidant are discussed. The present diaphragmatic chemical polymerization of pyrrole in the cation-exchange membrane is considered to be one of the effective methods for preparing a charge-controllable membrane.[32,37,38]

Experimental Section

Materials. Pyrrole (Aldrich Chemical) was distilled and stored under N_2 atmosphere. Potassium peroxodisulfate (Wako Chemical) and ferric chloride hexahydrate (Wako Chemical) were used without further purification. Prior to use of the Nafion film (Du Pont, Nafion-117, H^+ type) the following ion-exchange treatment was carried out in order to eliminate the effect of H^+ concentration on the polymerization of pyrrole. When $S_2O_8^{2-}$ was used as an oxidant the Nafion film was soaked in a 3 mol dm^{-3} KCl aqueous solution until there is no further decrease of pH in the solution. When Fe^{3+} was used as an oxidant the film was soaked in a 3 mol dm^{-3} $FeCl_3$ aqueous solution until no further change was observed in the visible absorption spectra of the film containing Fe^{3+}. Although this pretreatment is not essential for the present diaphragmatic chemical polymerization, it is required for quantitative film evaluation.

Preparation of the PPy–Nafion Composite. The Nafion film (thickness, 1.8×10^{-4} m; effective area, 1 cm^2) was put between pyrrole and oxidant ($K_2S_2O_8$ or $FeCl_3$) aqueous solution chambers. The polymerization was quenched by removal of pyrrole and oxidant solutions and by washing of both chambers with distilled water. The resulting Nafion film was washed with distilled water and then dried in vacuo.

Measurements and Analyses. Ultrathin sections of the composite films were prepared for inspection with an optical microscope (Olympus BH) by cutting the films with an ultramicrotome (Sorvall MT-6000). Conductivity of the film was measured according to a standard van der Pauw method. Cyclic voltammetry was carried out in a 0.1 mol dm^{-3} KCl aqueous solution with the composite film as a working electrode, which was prepared by attaching the composite film to the Pt plate with carbon paste. The four edges of the composite film were sealed with epoxy resin. The ion-exchange capacity of the composite film, prepared by using $FeCl_3$ as oxidant, was estimated by the following titration method. The composite film was immersed in a 3 mol cm^{-3} HCl aqueous solution so that the countercation of the sulfonate moiety was replaced by H^+. Then the resulting composite film was washed with distilled water. When the composite film was immersed in a 3 mol dm^{-3} KCl aqueous solution, the amount of released H^+ was titrated with an aqueous NaOH solution.

Results and Discussion

Composite Film Prepared by an Anionic $S_2O_8^{2-}$ Oxidant. The diaphragmatic chemical polymerization of pyrrole (0.2 mol dm^{-3}) with an anionic $S_2O_8^{2-}$ oxidant (0.1 mol dm^{-3}) produced black composite films, shown in Figure 1. A black PPy layer was observed only in the oxidant side of the Nafion. In the transparent part of the cross section (Figure 1c) transversal scratches were found on cutting the film with a microtome. Apparently the PPy layer did not grow from the top surface of the Nafion toward the oxidant solution but, instead, grew inward from the top surface of the Nafion, since the thickness of the resulting Nafion film did not change during polymerization. The thickness of the PPy layer, estimated by the photographs, increased with polymerization time up to ca. 10^{-5} m for 10 h and then ceased growing, as shown in Figure 2. Figure 3 shows the conductivity change of the oxidant side of the composite film with polymerization time. The monomer side had very low conductivity ($\sigma_{app} < 10^{-5}$ S cm^{-1}). Here, σ_{app} and σ_{real} are apparent and real conductivities determined from the thickness of the Nafion (1.8×10^{-4} m) and from the thickness of the conducting layer (d) in Figure 2, respectively. σ_{real} increased rapidly with polymerization time at <30 min and then decreased a little. The resulting PPy layer had as high a conductivity as the PPy prepared by electrochemical polymerization of pyrrole in H_2O. Since it has been found that PPy has a tendency to degenerate under high anodic polarization conditions, it is likely that the present decrease of σ_{real} after polymerization for 30 min resulted from further oxidation.

Interestingly, the conducting composite was produced only in the oxidant side of the Nafion. We concluded that the difference between the permeation rates of pyrrole and $S_2O_8^{2-}$ through the Nafion resulted in a composite film with asymmetric conductivity, i.e., very different conductivities between surfaces of the composite film. Figure 4 shows the relationship between the initial concentration of pyrrole and σ_{app} on the oxidant side of the composite film after polymerization for 24 h. The concentration of $K_2S_2O_8$ was kept constant (0.1 mol dm^{-3}). Figure 5 shows the relationship between the initial concentration of $K_2S_2O_8$ and σ_{app} of the oxidant side of the composite film. The concentration of pyrrole was kept constant (0.2 mol dm^{-3}). While σ_{app} was hardly affected by pyrrole concentration, it increased with oxidant concentration at <0.1 mol dm^{-3}, and decreased abruptly at >0.2 mol dm^{-3}. An optical photograph of an ultrathin section of the composite film prepared by using a $K_2S_2O_8$ aqueous solution at high concentration (1.0 mol dm^{-3}) is shown in Figure 6. The PPy layer did not seem to grow from the top surface of the film but rather from a location several micrometers below the surface. Independently, we have found that the rate of pyrrole polymerization is affected by the oxidant concentration in homogeneous solution. Accordingly, the concentration of $S_2O_8^{2-}$ in the Nafion film is considered to be an important factor in polymerization of pyrrole. The redox reaction of the present oxidant is described as follows

$$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-} \qquad (1)$$

An oxidant ($S_2O_8^{2-}$) and a product (SO_4^{2-}) are anionic species. It has been reported that the concentration of the anion in a cation-exchange membrane was very low with respect to that in the outer solution owing to the Donnan exclusion effect.[47-49] Equation 2 shows the Don-

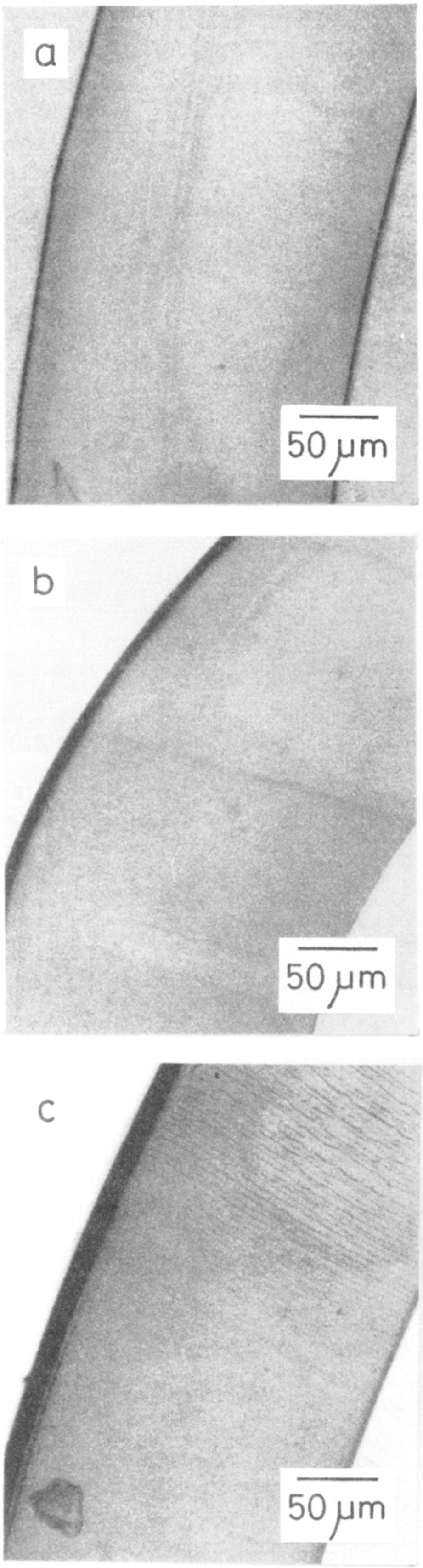

Figure 1. Optical photographs of cross sections of PPy–Nafion composite films prepared from 0.2 mol dm^{-3} pyrrole and 0.1 mol dm^{-3} $K_2S_2O_8$. Polymerization time was (a) 30 min, (b) 7 h, and (c) 23 h. The left side and the right side of the Nafion in the photograph were in contact with $K_2S_2O_8$ and pyrrole aqueous solutions, respectively.

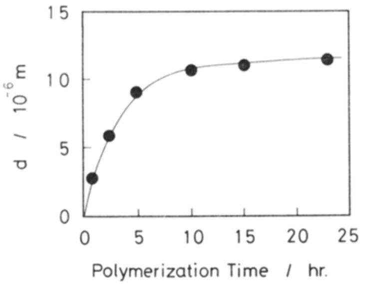

Figure 2. Growth in thickness of the PPy layer (d) estimated from the photographs.

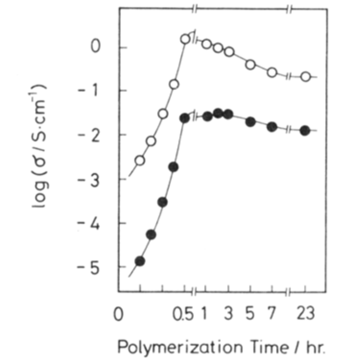

Figure 3. Apparent conductivity (σ_{app}; ●) and real conductivity (σ_{real}; ○) of the oxidant side of the PPy–Nafion composite films after various polymerization times. [pyrrole] = 0.2 mol dm^{-3}, [$K_2S_2O_8$] = 0.1 mol dm^{-3}.

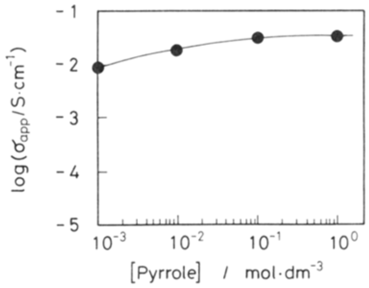

Figure 4. Relationship between the initial concentration of pyrrole and σ_{app} on the oxidant side of the PPy–Nafion composite films polymerized for 24 h. [$K_2S_2O_8$] = 0.1 mol dm^{-3}.

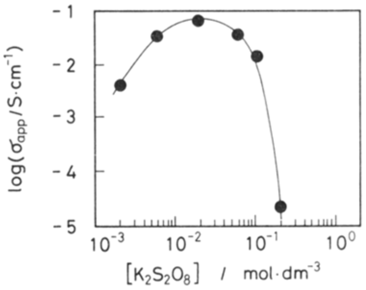

Figure 5. Relationship between initial concentration of $K_2S_2O_8$ and σ_{app} on the oxidant side of the PPy–Nafion composite films polymerized for 24 h. [pyrrole] = 0.2 mol dm^{-3}.

nan equilibrium for divalent anionic species between the outer solution and the cation-exchange membrane

$$c_-(c_- + \phi x/2)^2 = Kc^3 \qquad (2)$$

where c_-, ϕx, K, and c are the concentration of anion in the cation-exchange membrane, the effective fixed negative charge density, the equilibrium partition coefficient, and the concentration of ion in the outer solution, respectively. Here, the fixed negative charge presumably corresponds to the sulfonate moiety of the Nafion.

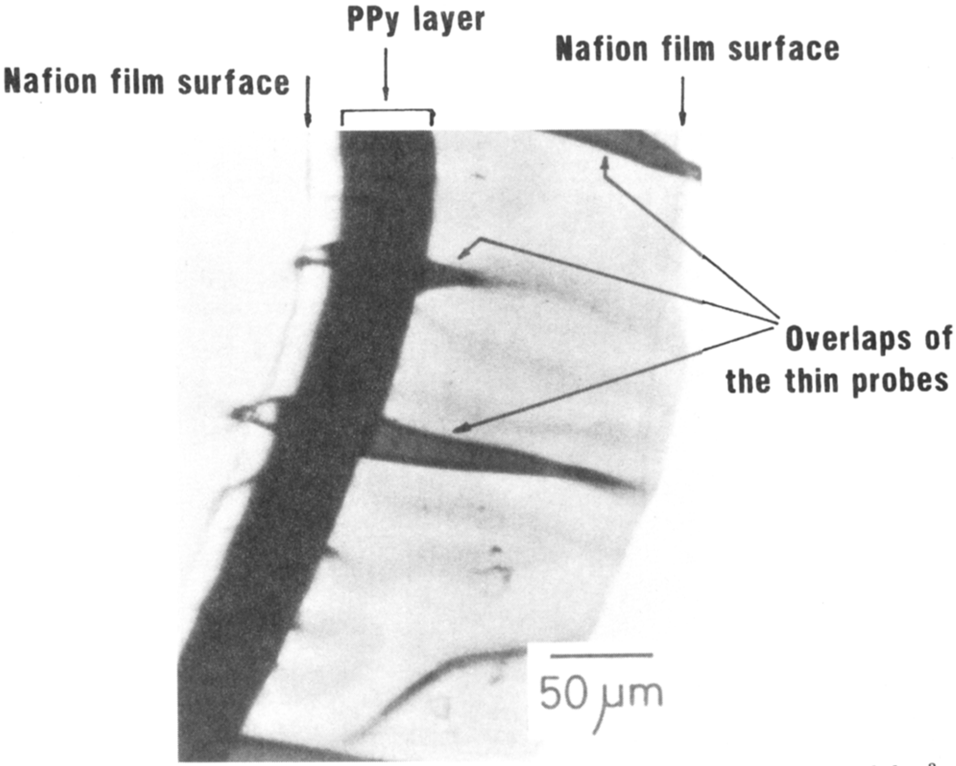

Figure 6. Optical photograph of a cross section of PPy–Nafion composite film prepared from 0.2 mol dm^{-3} pyrrole and 1.0 mol dm^{-3} $K_2S_2O_8$ polymerized for 23 h. The left side and the right side of the Nafion in the photograph were in contact with $K_2S_2O_8$ and pyrrole aqueous solutions, respectively.

It is well-known that the permeation rate of the species through the membrane is controlled mainly by two factors, the partition of the concerned species between membrane and solution phases and the diffusion rate in the membrane. It can be expressed by the following simple equation:

$$P = KD \tag{3}$$

where P, K, and D are the permeation rate, the partition coefficient, and the diffusion rate, respectively. In the present experiments, the partition of the $S_2O_8^{2-}$ between the Nafion and the oxidative solution phases is considered to be more important than it's diffusion rate in the Nafion, since there is sufficient pyrrole in the Nafion film for the polymerization, as stated below. According to eq 2, when the ion concentration in the outer solution is low with respect to the effective fixed negative charge density of the Nafion, c_- is very low; i.e., the anion scarcely penetrates. In contrast, when the ion concentration in the outer solution is high, the concentration of the penetrated anion is high. Because the neutral species is not affected by the Donnan exclusion, pyrrole must penetrate fast in the Nafion. At a concentration of <0.1 mol dm^{-3}, the $S_2O_8^{2-}$ could hardly penetrate into the Nafion, and consequently pyrrole was polymerized in the neighborhood of the surface of the Nafion. At a concentration of >0.2 mol dm^{-3}, the Donnan exclusion effect weakened and $S_2O_8^{2-}$ could diffuse toward the other side of the Nafion, causing pyrrole to polymerize inside the Nafion. The low σ_{app} observed at a concentration of >0.2 mol dm^{-3} resulted from poor electric contact between the inner growing PPy layer and the measurement electrodes, where an insulating Nafion layer existed between them. It was concluded that the difference between permeation rates of $S_2O_8^{2-}$ and pyrrole, due to the high charge density of the Nafion, resulted in a composite film with asymmetric conductivity.

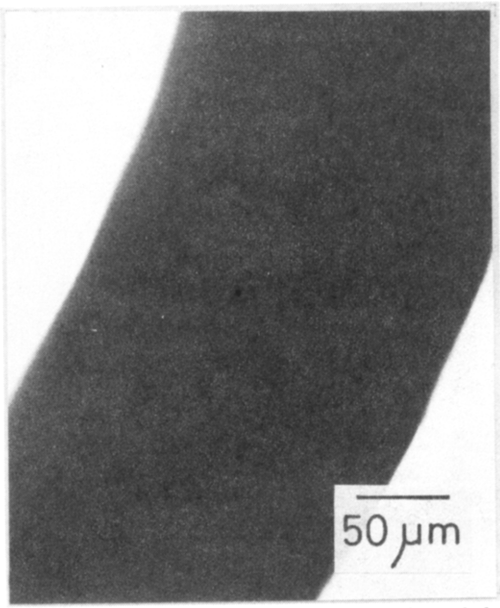

Figure 7. Optical photograph of a cross section of the PPy–Nafion composite film prepared from 0.1 mol dm^{-3} pyrrole and 0.1 mol dm^{-3} $FeCl_3$ polymerized for 1 h. The left side and the right side of the Nafion in the photograph were in contact with $FeCl_3$ and pyrrole aqueous solutions, respectively.

Composite Film Prepared by a Cationic Fe^{3+} Oxidant. The diaphragmatic chemical polymerization of pyrrole (0.1 mol dm^{-3}) with a cationic Fe^{3+} oxidant (0.1 mol dm^{-3}) also produced black composite films. It was observed that pyrrole was polymerized from the surface of the monomer side toward that of the oxidant side at the outset. However, after 1 h, there was no specific structure in the section of the film shown in Figure 7. Figure 8 shows the change in σ_{app} of the composite with the polymerization time. The conductivity shown in the figure was mea-

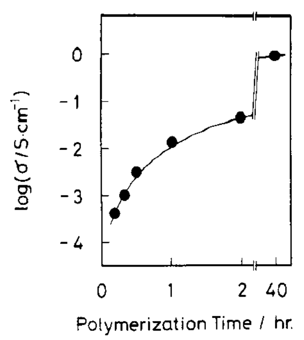

Figure 8. σ_{app} of the monomer side of the PPy-Nafion composite films representing various polymerization times. [pyrrole] = 0.1 mol dm^{-3}, [$FeCl_3$] = 0.1 mol dm^{-3}.

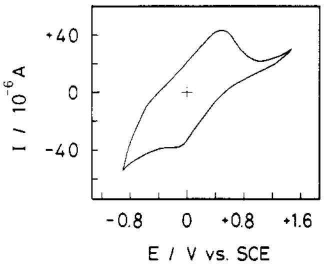

Figure 9. Cyclic voltammogram of the PPy-Nafion composite film prepared from 0.2 mol dm^{-3} pyrrole and 0.1 mol dm^{-3} $K_2S_2O_8$ polymerized for 23 h.

sured for the monomer side of the film. The oxidant side showed the same order of conductivity.

Independently, we have examined the diaphragmatic chemical polymerization of pyrrole with Fe^{3+} using K^+-exchanging Nafion, which was prepared by ion-exchange treatment with KCl aqueous solution. However, no quantitative data on conductivity were obtained at the initial stage. We assumed that its reaction involved a fast and unreproducible ion-exchange reaction ($K^+ \rightarrow Fe^{3+}$). Accordingly, pretreated Nafion films having Fe^{3+} as a countercation of the sulfonate moiety were used in the present study.

The redox reaction of the present oxidant is described as follows:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \qquad (4)$$

An oxidant (Fe^{3+}) and a product (Fe^{2+}) are cationic species. Equation 5 shows the Donnan equilibrium for trivalent cationic species between the outer solution and the cation-exchange membrane:

$$c_+(c_+ - \phi x/3)^3 = Kc^4 \qquad (5)$$

where c_+, ϕx, K, and c are the concentration of cation in the cation-exchange membrane, the effective fixed negative charge density, the equilibrium partition coefficient, and the concentration of ion in the outer solution, respectively. According to eq 5, a high concentration of cation in the cation-exchange membrane is maintained regardless of the ion concentration in the outer solution. It was considered that the fast permeation rates of both pyrrole and Fe^{3+} resulted in the composite film with an isotropic conductivity.

Electrochemical Behavior of a Composite Film. Figure 9 shows a cyclic voltammogram of a composite film prepared from the $K_2S_2O_8$ oxidant. Broad oxidation and reduction peaks were observed at +600 mV and -100 mV versus SCE, respectively. We have reported that the electrochemical properties of the PPy prepared by electrochemical polymerization in H_2O were affected by the type of incorporated anion.[37] In comparison with ordinary PPy, the composite film showed broad and anodically shifted redox peaks, which were assigned to a so-called doping–undoping process. The resulting PPy in the Nafion is considered to be an electroactive material similar to PPy prepared by electrochemical polymerization.

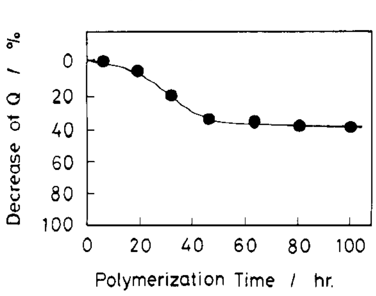

Figure 10. Change in cation-exchange capacity of the PPy-Nafion composite films through diaphragmatic chemical polymerization. Q is the ratio of the cation-exchange capacity of the PPy-Nafion composite film to that of the original Nafion. [pyrrole] = 0.1 mol dm^{-3}, [$FeCl_3$] = 0.1 mol dm^{-3}.

Cation-Exchange Capacity of a Composite Film. Figure 10 shows the change of cation-exchange capacity of the composite film during diaphragmatic preparation with Fe^{3+} oxidant. Here, Q is the ratio of the cation-exchange capacity of the composite film to that of the original Nafion film (0.88 × 10^{-3} equiv g^{-1}). The cation-exchange capacity of the resulting composite film was estimated by the above-stated titration method. We speculated that the partial sulfonate moiety of the Nafion was doped to the PPy in the composite film and that PPy and Nafion made up a polyion complex. It has been reported that the PPy–polyanion complex was not difficult to replace with other ions.[31,32,37] In the present titration method the sulfonate moiety of the Nafion doped to the PPy could not be detected as the undoped (i.e., H^+ type) sulfonate moiety. Therefore, it was assumed that the decrease of Q, shown in Figure 10, resulted from the formation of a PPy–Nafion polyion complex. It has also been reported that the chemical polymerization of pyrrole in the porous filter produced conducting PPy–porous filter composites.[24,46] Compared with them, the present PPy–Nafion composite film was characterized by molecular level hybridization between the partially oxidized PPy chain and the sulfonate moiety of the Nafion. In other words, the Nafion plays a role as a polymer dopant as well as a supporting material. It is expected that the present PPy–Nafion composite acts as a "charge-controllable membrane", whose properties can be controlled by the applied potential.[32,37,38]

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References and Notes

(1) Diaz, A. F.; Kanazawa, K. K.; Gardini, G. P. *J. Chem. Soc., Chem. commun.* **1979**, 635.
(2) Kanazawa, K. K.; Diaz, A. F.; Geiss, R. H.; Gill, W. D.; Kwak, J. F.; Logan, J. A.; Rabolt, J. F.; Street, G. B. *J. Chem. Soc., Chem. Commun.* **1979**, 854.
(3) Diaz, A. F.; Castillo, J. I. *J. Chem. Soc., Chem. Commun.* **1980**, 397.
(4) Diaz, A. F.; Castillo, J. I.; Logan, J. A.; Lee, W.-Y. *J. Electroanal. Chem.* **1981**, *129*, 115.
(5) Diaz, A. F.; Martinez, A.; Kanazawa, K. K.; Salmon, M. *J. Electroanal. Chem.* **1981**, *130*, 181.
(6) Diaz, A. F.; Castillo, J. I.; Kanazawa, K. K.; Logan, J. A.; Salmon, M.; Fajardo, O. *J. Electroanal. Chem.* **1981**, *133*, 233.
(7) White, H. S.; Kittlesen, G. P.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 5375.

Macromolecules **1990**, *23*, 1976–1979

(8) Kittlesen, G. P.; White, H. S.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 7389.
(9) Garnier, F.; Tourillon, G.; Gazard, M.; Dubois, J. C. *J. Electroanal. Chem.* **1983**, *148*, 299.
(10) Bjorklund, R.; Andersson, S.; Allenmark, S.; Lundstrom, I. *Mol. Cryst. Liq. Cryst.* **1985**, *121*, 263.
(11) Kuwabata, S.; Yoneyama, H.; Tamura, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2247.
(12) Kaneto, K.; Yoshino, K. *Kino Zairyo (Jpn.)* **1984**, *4*, 8.
(13) Mohammadi, A.; Inganas, O.; Lundstrom, I. *J. Electrochem. Soc.* **1986**, *133*, 947.
(14) Mermilliod, N.; Tanguy, J.; Petiot, F. *J. Electrochem. Soc.* **1986**, *133*, 1073.
(15) Osaka, T.; Naoi, K.; Sasaki, H.; Ogano, S. *J. Electrochem. Soc.* **1987**, *134*, 285.
(16) Diaz, A. F. *Chem. Scr.* **1981**, *17*, 145.
(17) Burgmayer, P.; Murray, R. W. *J. Am. Chem. Soc.* **1982**, *104*, 6139.
(18) Burgmayer, P.; Murray, R. W. *J. Phys. Chem.* **1984**, *88*, 2515.
(19) Zinger, B.; Miller, L. L. *J. Am. Chem. Soc.* **1984**, *106*, 6861.
(20) Shinohara, H.; Aizawa, M.; Shirakawa, H. *Chem. Lett.* **1985**, 179.
(21) Bull, R. A.; Fan, F.-R. F.; Bard, A. J. *J. Electrochem. Soc.* **1983**, *130*, 1636.
(22) Noufi, R. *J. Electrochem. Soc.* **1983**, *130*, 2126.
(23) Okabayashi, K.; Ikeda, O.; Tamura, H. *J. Chem. Soc., Chem. Commun.* **1983**, 684.
(24) Bjorklund, R. B.; Lundstroem, I. *J. Electron. Mater.* **1984**, *13*, 211.
(25) Niwa, O.; Tamamura, T. *J. Chem. Soc., Chem. Commun.* **1984**, 817.
(26) Lindsey, S. E.; Street, G. B. *Synth. Met.* **1984**, *10*, 67.
(27) De Paoli, M.; Waltman, R. J.; Diaz, A. F.; Bargon, J. *J. Chem. Soc., Chem. Commun.* **1984**, 1015.
(28) Bates, N.; Cross, M.; Lines, R.; Walton, D. *J. Chem. Soc., Chem. Commun.* **1985**, 871.
(29) Ojio, T.; Miyata, S. *Polym. J.* **1986**, *18*, 95.
(30) Fan, F.-R. F.; Bard, A. J. *J. Electrochem. Soc.* **1986**, *133*, 301.
(31) Yoneyama, H.; Hirai, T.; Kuwabata, S.; Ikeda, O. *Chem. Lett.* **1986**, 1243.
(32) Iyoda, T.; Ohtani, A.; Shimidzu, T.; Honda, K. *Chem. Lett.* **1986**, 687.
(33) Iyoda, T.; Ohtani, A.; Shimidzu, T.; Honda, K. *Synth. Met.* **1987**, *18*, 725.
(34) Shimidzu, T.; Ohtani, A.; Iyoda, T.; Honda, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1414.
(35) Shimidzu, T.; Ohtani, A.; Iyoda, T.; Honda, K. *J. Chem. Soc., Chem. Commun.* **1986**, 1415.
(36) Shimidzu, T.; Ohtani, A.; Iyoda, T.; Honda, K. *J. Chem. Soc., Chem. Commun.* **1987**, 327.
(37) Shimidzu, T.; Ohtani, A.; Iyoda, T.; Honda, K. *J. Electroanal. Chem.* **1987**, *224*, 123.
(38) Shimidzu, T.; Ohtani, A.; Honda, K. *J. Electroanal. Chem.* **1988**, *251*, 323.
(39) Shimidzu, T.; Ohtani, A.; Honda, K. *Bull. Chem. Soc. Jpn.*, in press.
(40) Shimidzu, T.; Ohtani, A.; Aiba, M.; Honda, K. *J. Chem. Soc., Faraday Trans.* **1988**, *84*, 3941.
(41) Salmon, M.; Kanazawa, K. K.; Diaz, A. F.; Krounbi, M. *J. Polym. Sci., Polym. Lett. Ed.* **1982**, *20*, 187.
(42) Yoshino, K.; Hayashi, S.; Sugimoto, R. *Jpn. J. Appl. Phys., Part 2* **1984**, *23*, L899.
(43) Bocchi, V.; Gardini, G. P. *J. Chem. Soc., Chem. Commun.* **1986**, 148.
(44) Myers, R. E. *J. Electron. Mater.* **1986**, *15*, 61.
(45) Chao, T. H.; March, J. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 743.
(46) Bocchi, V.; Gardini, G. P.; Papi, S. *J. Mater. Sci. Lett.* **1987**, *6*, 1283.
(47) Teorell *Proc. Soc. Exptl. Biol. Med.* **1935**, *33*, 282.
(48) Mayer, K. H.; Sievers, J. F. *Helv. Chem. Acta* **1936**, *19*, 649.
(49) Toyoshima, Y.; Kobatake, Y.; Fujita, H. *Trans. Faraday Soc.* **1967**, *63*, 2814.
(50) Tasaka, M.; Aoki, N.; Kondo, Y.; Nagasawa, M. *J. Phys. Chem.* **1975**, *19*, 1307.
(51) Kinoshita, T.; Yamashita, T.; Iwata, T.; Takizawa, A.; Tsujita, Y. *J. Macromol. Sci. Phys.* **1983**, *22* (1), 1.

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Molecular Model for the Mechanical Properties of Elastomers. 3. Networks Cross-Linked in a State of Strain

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ABSTRACT: A molecular model developed previously has been extended to a study of the elastic properties of elastomers cross-linked in a state of strain. The model allows a detailed analysis of both the network connectivity upon cross-linking and the mechanical properties upon tensile deformation. The nonaffine displacements of the network junctions during deformation is also fully taken into account. The results show that the permanent set and modulus values in the state of ease increase with an increase in the strain at which the cross-links are introduced. However, in contrast to the predictions of previous theories, these moduli and permanent set values level off at high cross-linking strains.

1. Introduction

In the first paper of this series,[1] we have introduced a new molecular model for the study of the factors controlling the deformation behavior of elastomeric networks. The main emphasis of the work was on the role of entanglements latent in the polymer prior to cross-linking. Our approach has been quite successful in predicting the dependence of mechanical properties on molecular weight of the starting polymer, cross-link functionality, and degree of advancement of the reaction. For simplicity, the study was restricted to the case of poly(dimethylsiloxane) networks formed through chemical end-linking of difunctional polymer chains with plurifunctional monomers.

That previous work is extended here to polymer networks cross-linked in a state of strain. Cross-link formation in stretched networks is of great technological importance since it is closely related to the the phenomenon of ageing in rubber materials. Another motivation for the present work is to be found in recent experimental

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