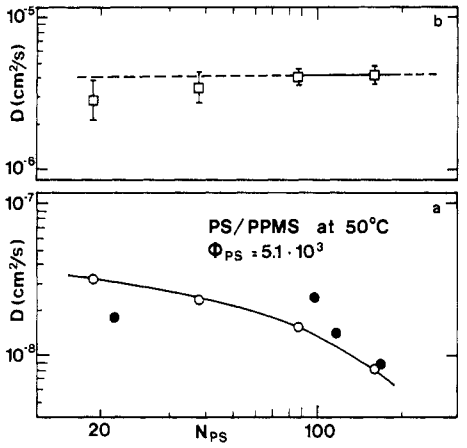

Figure 3. (a) Measured interdiffusion coefficient D in the polymer mixture PS/PPMS with $\Phi_{PS} = 5.1 \times 10^{-3}$ at 50 °C vs the degree of polymerization of PS. The solid symbols are for the interdiffusion data from ref 10. (b) This plot is constructed according to eq 1 and takes into account the thermodynamic interactions in the PS/PPMS blends; the transport coefficient $D°$ based on the data of (a) and the static structure factor listed in Table I. The lines are only to guide the eye.

expected from Kirkwood's diffusion equation;[23] the free-draining term dominates because of the short length of the PS chains and the high viscosity of the polymeric PPO solvent.

The molecular weight dependence in Figure 3a can therefore be accounted for mainly by the variation of $S(0)$ and D_{PS} with M_w(PS). Neglect of $S(0)$ and the type of analysis of $C(q,t)$ performed in ref 10 were probably the reasons for a misinterpretation of the composite interdiffusion coefficient. The latter is also shown (solid symbols) in Figure 3a for comparison. At 50 °C the reported phenomenological molecular weight dependence $D \sim M_w^{-0.34}$, considering only the three highest molecular weight data, contradicts the present discussion of the results for all samples in the framework of existing theories for interdiffusion in compatible blends. Besides, no single scaling law is applicable to the data in Figure 3a. The change of the slope at the highest M_w(PS) sample resembles the increase of $S(0)$ for this sample (Table I). Finally, the thermodynamic slowing down effect expected for unfavorable segment-segment interactions ($\chi_F > 0$) leads to the observed large reduction of the interdiffusion coefficient in Figure 2; i.e., $D \ll D°$.[17-19]

In summary, several aspects emerge from the present photon correlation study of the diffusional dynamics in dilute unentangled PS/PPMS mixtures with $\Phi_{PS} = 5.1 \times 10^{-3}$. A correct analysis of the interdiffusion data should always take into account the thermodynamic interactions between the blend components. For the mixtures with low M_w(PS), the data reduction is complicated by the presence of dynamic light scattering arising from concentration fluctuations in the bulk PPMS sample. As expected for $\chi_F > 0$, the transport coefficient $D°$ (eq 1) is larger than the interdiffusion D near the coexistence curve. There is a strong evidence for a molecular weight independent $D°$ suggesting Rouse behavior for the dynamics of the bare PS chains, in contradiction with the results of a recent study.[10]

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Registry No. PS, 9003-53-6.

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New Synthesis of Poly(phenylene sulfide)s through O_2 Oxidative Polymerization of Diphenyl Disulfide with VO Catalyst

Poly(*p*-phenylene sulfide) (PPS) is commercially produced from *p*-dichlorobenzene and sodium sulfide[1] at a rate of 10^4 tons/yr. Production rates continue to increase year by year. However, this polymerization proceeds at high pressure and temperature and is accompanied by a stoichiometric formation of salt as a byproduct.[2] The salt contamination degrades PPS properties such as electrical performance and moldability.

The ability to facile polymerization via selective oxidation utilizing the abundant and cheap oxidant oxygen often represents a desirable low-cost method for upgrading the value of a raw material. The most successful example is the oxidative polymerization of 2,6-dimethylphenol to yield poly(2,6-dimethyl-1,4-phenylene oxide) with a copper amine catalyst under an oxygen atmosphere at room temperature.[3] But if a similar method is applied to homologous thiophenol, only diphenyl disulfide is yielded due to the coupling of thiophenoxy radicals to each other.[4]

Studies in our laboratory on the preparation of PPS have revealed that thiophenol and diphenyl disulfide can be oxidatively polymerized to PPS via a cationic mechanism by electrical or chemical oxidations.[5,6] This communication describes a novel and convenient synthetic route to poly(phenylene sulfide)s (Scheme I). Diphenyl disulfide is polymerized to PPS with high purity in high yield, in the presence of a catalytic amount of vanadyl

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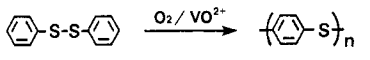
Scheme I



acetylacetonate ($VO(acac)_2$) under an air atmosphere at room temperature.

Diphenyl disulfide (1×10^{-2} mol) is allowed to react with a catalytic amount of vanadyl acetylacetonate (1×10^{-4} mol) in the presence of a strong acid such a trifluoromethanesulfonic acid (1×10^{-3} mol) and trifluoroacetic anhydride (2×10^{-2} mol) in tetrachloroethane (100 mL) under an air atmosphere at room temperature. White powder separated out over time. After the filtration of the precipitate from the reaction mixture, the soluble part of the polymer was precipitated by methanol. The polymer was isolated in >95% total yield (tetrachloroethane-insoluble part is ca. 85% of the total) as a white and high-purity powder having empirical formula $C_6H_4S_1$.[7] A PPS structure composed of 1,4-phenylene unit was confirmed by spectroscopy.[8]

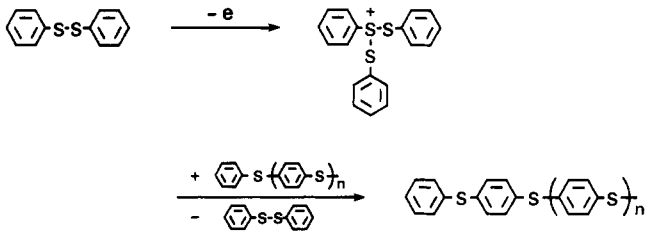
When thiophenol was used as a starting material, the same reaction condition also gave PPS. Thiophenol is considered to be first oxidized to diphenyl disulfide and then polymerized. This VO-catalyzed polymerization not only enables efficient PPS formation at room temperature but also is applicable to the synthesis of alkyl-substituted PPSs. For example, bis(3-methylphenyl) disulfide and bis(3,5-dimethylphenyl) disulfide yield poly(3-methyl-1,4-phenylene sulfide) and poly(3,5-dimethyl-1,4-phenylene sulfide), respectively. Their structures were confirmed by IR, solid ^{13}C NMR, and elemental analysis.[9] These polymers were soluble in benzene and their molecular weights were 4200–5500 (vapor pressure osmometry).

Oxygen is essential for the polymerization of diphenyl disulfide. In the presence of $VO(acac)_2$, the polymerization is accompanied with a quantitative oxygen uptake. More oxygen uptake was observed whenever additional diphenyl disulfide was added to the reaction mixture. Vanadyltetraphenylporphyrin was also effective as the catalyst for this polymerization.[10]

The typical blue color of $VO(acac)_2$ solution (λ_{max} = 604, 678 nm ascribed to d–d transition of V(IV)) was immediately faded out upon the addition of a strong acid under oxygen atmosphere. ESR signal was not detected in the VO(IV) mixture in the presence of the acid. These results suggest that $VO(acac)_2$ disproportionates to the III and V^{11} species in the acidic environment of this experiment. It is considered that the V valence species reacts with diphenyl disulfide to form the active species of the polymerization. This was supported by the result that equimolar V_2O_5 (V valence) reacted with diphenyl disulfide to yield PPS (ca. 90% yield) even under an oxygen-free atmosphere. The III valence species was reoxidized to $VO(acac)_2^{IV}$ with molecular oxygen, just as the $V(acac)_3$ is easily oxidized to $VO(acac)_2$ with oxygen. The redox potential of $VO(acac)_2$ and $V(acac)_3$ shows at 0.9 and 1.2 V (vs Ag/AgCl), respectively. That is, the VO catalyst acts as an excellent electron mediator to bridge a 1.0-V potential gap between the oxidation potential of diphenyl disulfide (ca. 1.5 V vs Ag/AgCl) and the reduction potential of oxygen (ca. 0.5 V vs Ag/AgCl).

The oxidized species of diphenyl disulfide by the VO(V) was studied by using nonpolymerizable dimethyl disulfide as a model compound. Methylbis(methylthio)sulfonium cation salt was isolated and confirmed by ^1H NMR spectra and elemental analysis.[12] It is considered that phenylbis(phenylthio)sulfonium cation is the active species of the polymerization and that it electrophilically reacts with the p position of the benzene ring[13] to yield PPS (Scheme II).

Scheme II



In conclusion, this VO-catalyzed oxidative polymerization of diphenyl disulfides utilizing molecular oxygen as the oxidant conveniently provides pure PPSs under mild conditions.

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(7) Purity of the formed polymer was analyzed by inductively coupled plasma emission spectroscopy. The V content was below 1 ppm. The spectroscopy also revealed no salts such as sodium chloride with which a commercially available PPS is often contaminated.
(8) Poly(*p*-phenylene sulfide). Anal. Calcd for C_6H_4S: C, 66.67; H, 3.70; S, 29.63. Found: C, 66.53; H, 3.86; S, 29.52. IR (KBr, cm^{-1}): 3000, 3050 (ν_{C-H}); 1380, 1460, 1560 ($\nu_{C=C}$); 820 (δ_{C-H}); 480, 550, 700, 740, 1050, 1080, 1090. The spectrum agrees with that of commercially available PPS. The absorption attributed to 1,4-phenylene at 820 cm^{-1} indicates a linear or 1,4-conjugated phenylene sulfide structure. No typical absorption at ca. 850 cm^{-1} based on isolated ring hydrogen excludes a branching and cross-linking structure. These spectroscopic data do not exclude the possibility that the 1,2- and 1,3-phenylene unit are slightly contained in the 1,4-phenylene sulfide structure. The spectrum in region between 1000 and 1150 cm^{-1} also denies that the formed polymer contains a sulfoxide and sulfone structure. This formed PPS was soluble in hot *N*-methylpyrrolidone. This indicates that molecular weight of the formed polymer remains ca. 10^3 due to the insolubility of PPS in any common solvent at room temperature.
(9) Poly(3-methyl-1,4-phenylene sulfide). Anal. Calcd for C_7H_6S: C, 68.85; H, 4.92; S, 26.23. Found: C, 68.63; H, 5.01; S, 26.17. IR (KBr, cm^{-1}): 2875, 2950 (ν_{C-H}); 1480, 1540, 1575 ($\nu_{C=C}$); 820, 860 (δ_{C-H}); 700, 1050, 110, 1200, 1260, 1380. ^1H NMR ($CDCl_3$, 90 Mz): δ 6.8–7.3 (m, 3 H, aromatic), 2.3 (s, 3 H, methyl). ^{13}C NMR ($CDCl_3$, 90 Mz): δ 127.3, 130.1, 131.2, 134.0, 136.5, 141.1 (aromatic C), 20.5 (methyl C). Poly(3,5-dimethyl-1,4-phenylene sulfide). Anal. Calcd for C_8H_8S: C, 70.54; H, 5.92; S, 23.54. Found: C, 69.92; H, 6.02; S 23.31. IR (KBr, cm^{-1}): 2850, 2925, 2950, 2980, 3040 (ν_{C-H}); 1460, 1575 ($\nu_{C=C}$); 860, 875 (δ_{C-H}); 710, 1000, 1030, 1050, 1130, 1260, 1380, 1400. ^1H NMR ($CDCl_3$, 90 MHz): δ 6.70 (s, 2 H, aromatic), 2.31 (s, 6 H, methyl). ^{13}C NMR ($CDCl_3$, 90 Mz): δ 125.1, 127.2, 140.1, 144.3 (aromatic C), 21.9 (methyl C). These IR spectra agree with ones prepared by the Phillips' method.
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Mz): 3.0, 3.6 (9 H, methyl). UV (CH_2Cl_2, nm): λ_{max} 272.

(13) MNDO calculation indicates that the high-frontier π-electrodensity in the p position of diphenyl sulfide is higher than those in the m position and the o position. This indicates that the 1,4-structure is preferentially formed by the electrophilical attack of the sulfonium cation to the p position of the benzene ring.

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A Novel Self-Organized, Nonbilayer-Type Assembly in a Composite Film Made of Cholesterol, Dimethyldioctadecylammonium, and Poly(styrenesulfonate)

Cholesterol is a common component of mammalian cellular membranes, and among lipids it has an outstanding chemical structure characterized by a relatively small hydrophilic group (3β-OH) and a bulky fused ring that is a stereochemically rigid flat group. For these reasons, the effects of cholesterol on phospholipid in model membrane systems have been widely studied with a variety of techniques.[1-3] The nature of the cholesterol–lipid mixture is not completely understood; however, one functional role of cholesterol has been suggested to be to control the fluidity of the lipid hydrocarbon chain and stabilize the membranes. Cholesterol is also known to affect the morphology of a lipid assembly[4] as well as the physical properties of lipid bilayers.

We studied the effect of cholesterol on the polyion complex films prepared from cationic lipid surfactants and anionic polymers, which are unique materials having physically stable bilayer structure,[5] in order to modify the physical property, e.g., the rigidity of the films. Then we found that, by adding a small amount of cholesterol, the structure of the polyion complex was changed from bilayer to nonbilayer at a limited concentration range accompanying a change in mechanical property. In this paper, we report the novel morphology found in the composite films as studied X-ray diffraction.

According to the procedure reported previously,[5] the polyion complexes, I and II, which have stoichiometric composition of surfactants and ionic polymers, were prepared from dimethyldioctadecylammonium bromide and sodium poly(styrenesulfonate) and from dimethyldihexadecylammonium bromide and sodium poly[2-(acrylamido)-2-methyl-1-propanesulfonate] (kindly supplied by Nittoh Co., Ltd., Tokyo), respectively. About 5% chloroform solutions of the mixture of cholesterol (Nakarai Chemicals Co., Ltd., Tokyo) and the polyion complexes were cast on flat glass plates siliconized with octadecyltrichlorosilane. When the solvent was evaporated and vacuum dried, transparent films with thickness of about 200 μm were obtained. The films were annealed in water at 60 °C for the formation of the novel morphology.

Calorimetric data as shown in Figure 1 were obtained using a Du Pont 9900 differential scanning calorimeter at a heating rate of 10 K/min. Samples were hermetically sealed in aluminum sample pans with the same weight of water as pieces of the films. Addition of 20 wt % cholesterol into the polyion complexes caused a broadening of the phase transition from the gel to liquid-crystalline state and a loss in the transition enthalpy accompanied by a decrease in the transition temperature. The DSC results

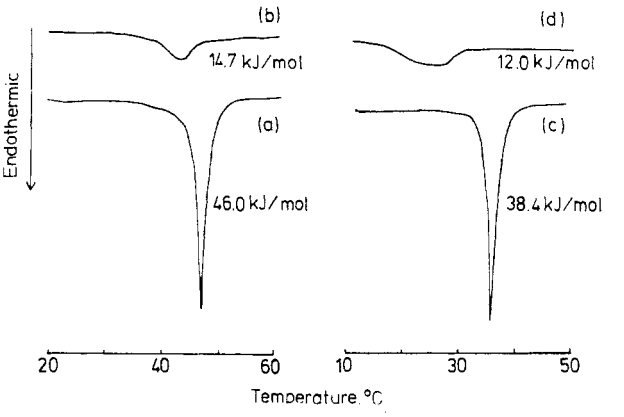

Figure 1. Differential scanning calorimetry of the composite films containing cholesterol. Heating rate: 10 K/min. (a) Dimethyldioctadecylammonium–poly(styrenesulfonate) film (I); (b) I containing 20 wt % cholesterol; (c) dimethyldihexadecylammonium–poly[2-(acrylamido)-2-methyl-1-propanesulfonate] film (II); (d) II containing 20 wt % cholesterol.

suggest that cholesterol has a significant effect on the property of the polyion complexes, which was comparable to that on the phospholipid bilayer systems.[1]

The X-ray photographs of the composite films were obtained by using Ni-filtered Cu Kα radiation (1.542 Å) for short spacings and V-filtered Cr Kα radiation (2.291 Å) for long spacings. The distance between the sample and X-ray film was 80 and 110 mm, respectively. The wide-angle X-ray diffraction of the film (I) containing cholesterol showed a broad ring having the interplannar distance of 4.6 Å (see Figure 3). This distance was longer than that of the "pure" polyion complex film (4.1 Å). The pure polyion complex film had also a meridional diffraction at 34 Å (the longest spacing) during X-ray irradiation parallel to the film surface. However, in the case of the polyion complex containing cholesterol, the equatorial diffraction appeared at 53 Å (the longest spacing) and 18 Å during X-ray irradiation parallel to the film surface. This suggests that the film containing cholesterol had a quite different higher order structure. The same features were observed in the case of II, except for the difference in long spacings (48 and 17 Å).

A stretched film was prepared in order to clarify the structure of the composite film. After immersing the film in water at 60 °C, the film was slowly stretched to about 250%. In Figure 4, the arrangement of the stretched sample and X-ray photographic films is shown. Orientation of the film caused a drastic change in the X-ray diffraction pattern but had virtually no effect on the long spacing. The direction of the diffraction pattern during X-ray irradiation along the X and Z axes was perpendicular to the stretch direction, as shown in parts a and b of Figure 4. On the contrary, the diffraction pattern during X-ray irradiation along the Y axis had no directionality (part c).

We propose a simple model of the supramolecular structure of the composite films as shown in Figure 3e. Considering the X-ray photographs in Figure 3 showing that the long spacing pattern had directionality in (a) but not in (c), a basic microstructure may be a rodlike assembly composed of ionic polymer, surfactant, and cholesterol. When the film was stretched mechanically the rods were directed in the same manner as the polymer main chain without changing long spacings. This fact supports the existence of microrods in the film. The original cast film has a macroscopic supramolecular assembly made up of the rodlike microassembly oriented in the direction perpendicular to the film surface.

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