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Sulfur Trioxide Doped Poly(phenylene sulfide)

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ABSTRACT: Sulfur trioxide doping of poly(phenylene sulfide) produces a material with an electrical conductivity as high as 10^{-4} S/cm at room temperature. Samples of poly(phenylene sulfide) films were exposed to SO_3 at various pressures between 26 and 260 torr at room temperature. Although the samples were hygroscopic after doping, they did not decompose on exposure to air. In addition to raising the conductivity of the polymer, SO_3 also changed the structure of the polymer itself, possibly by sulfonation or cross-linking or both. Elemental analyses were consistent with the dopant species being SO_3^{2-}. X-ray diffraction of films before and after doping showed that doping induced substantial disorder in the polymer, possibly the result of incorporation of dopant between chains or of cross-linking.

Introduction

Since the discovery of high conductivity in polyacetylene,[1] much work has been done to understand the reasons for its high conductivity and to investigate the electrical properties of other polymers, such as polypyrrole,[2] poly(phenylene sulfide),[3] poly(phenylene),[4] pyrolyzed poly(acrylonitrile),[5] poly[(phthalocyaninato)siloxanes,[6] etc. A limitation of many of the systems, including polyacetylene, has been their poor stability toward ambient conditions. In particular, some are readily oxidized by oxygen in the air, and some of the common dopants are decomposed by moisture.

Our efforts have been directed at preparing materials with greater stability than those commonly available. One of the polymers we have worked with extensively is poly(phenylene sulfide) (PPS). Its attractive properties include its excellent thermal stability, relatively simple processing characteristics, and the fact that it is commercially available. PPS melts at 300 °C without decomposition and can be made into films and fibers from the melt. The polymer is quite crystalline after annealing, and its changes on annealing have been thoroughly characterized.[7] Doping of the polymer with AsF_5 has been investigated extensively by groups at Allied, IBM, and GTE.[3,8] The doped polymer has a conductivity of 1 S/cm at room temperature, but the conductivity can be as high as 25 S/cm if doping is carried out in AsF_3 solution.[9] During doping the polymer is believed to undergo some cross-link formation that changes the relative orientations of the polymer chains, increasing the planarity of the system.[3a] As with any AsF_5-doped system, however, this doped polymer is extremely moisture-sensitive. Many other common dopants, which are more stable to ambient conditions, are not sufficiently strong oxidizing agents to oxidize PPS and raise the con-

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Table I
Characteristics of SO_3-Doped PPS

SO_3 press., torr	time exposed to SO_3, min	time open to vacuum, min	max conduct.		steady-state conduct.	
			S/cm	time	S/cm	time, days
26	1220	155	1.7×10^{-5}	40 min	1.4×10^{-5}	2
40	40	*a*	2.4×10^{-4}	3.2 days	1.8×10^{-4}	4.1
60	45	*a*	1.4×10^{-4}	155 min	2.4×10^{-5}	6.8
112	265	*b*	2.0×10^{-4}	35 min	6.3×10^{-5}	8.8
260	60	90	1.6×10^{-4}	85 min	1×10^{-4}	6

[a] Kept under dynamic vacuum to end of experiment. [b] Nitrogen added and not evacuated.

ductivity. One of the dopants we have investigated in searching for a stable dopant with a high electron affinity is sulfur trioxide, SO_3. Although SO_3 is hygroscopic, it is not decomposed by moisture. This report will describe the results of this work.

Experimental Section

Sample Preparation. Films of PPS were prepared from PPS powder supplied by Phillips Petroleum (Ryton [illegible] by electrostatically spraying the powder on a plate heated [illegible]0 °C. Immediately after the powder had fused, the plate [illegible] quenched in ice water to prevent crystallization. Sulfur trioxide (Aldrich, 98%) was sublimed from the ampule in which it was supplied into an evacuated bulb fitted with a Teflon needle valve [illegible] simplified handling. Samples of PPS were exposed to various pressures of SO_3 between 40 and 260 torr as measured on a manometer. All doping experiments were conducted at room temperature.

Electrical Measurements. PPS films were attached to a four-in-line probe apparatus that made it possible to monitor conductivity during doping. A constant current of approximately 10^{-6} A was provided by a Hewlett-Packard 711A power supply. Current and potential were measured by Keithley 610A electrometers. Output from the electrometers was read directly into an ISAAC 91A A/D converter attached to an Apple II+ computer. This arrangement allowed for continuous monitoring of conductivity over an extended time or temperature range.

Elemental Analysis. Elemental analyses were determined with a Perkin-Elmer 240C elemental analyzer. Samples were exposed to the same pressures of SO_3 used in electrical measurements and then sealed in aluminum capsules under N_2. A sample of PPS film was also measured under the same conditions to verify the procedure.

Infrared Spectroscopy. Infrared spectra were collected on a Nicolet 7199 Fourier transform IR spectrometer. Exposure of the samples to air prior to collecting the spectra was minimized to the brief period for removal from the sample container to the spectrometer compartment (<30 s).

X-ray Diffraction. X-ray diffraction patterns of the polymers were collected on pressed powders and films by using Ni-filtered Cu Kα radiation in a Philips DMS-31 ICD diffractometer. In general, pressed-powder disks were used because shorter sampling time was required to collect an acceptable diffraction pattern, and the patterns were the same between films and powders treated similarly.

Results and Discussion

Poly(phenylene sulfide) (PPS) has the attractive properties of being especially stable and commercially available. The only compounds hitherto known to be effective dopants, however, have been the pnicogen fluorides AsF_5, SbF_5, and $NOSbF_6$. All of these compounds are extremely moisture-sensitive. A significant part of our effort has been spent to identify and characterize other, more stable dopants for PPS. In particular, we have found that SO_3 is an effective dopant and more stable to ambient conditions than AsF_5. Our goal to this point has been to develop an understanding of the chemical reaction occurring during doping and the effect of doping on the electrical properties of the polymer.

For doping with AsF_5, the reaction is thought to be[10]

$$3AsF_5 + 2e^- \rightarrow AsF_3 + 2AsF_6^-$$

with the electrons being removed from the polymer chains. In order to understand the doping reaction with SO_3, we have sought to identify the products of that reaction. By analogy with AsF_5, there are several reactions that are plausible in the case of SO_3 because of the numerous stable sulfur–oxygen anions. Among them are

$$SO_3 + 2e^- \rightarrow SO_3^{2-}$$

$$SO_3 + 2e^- \rightarrow SO_4^{2-} + SO_2$$

$$2SO_3 + 2e^- \rightarrow S_2O_5^{2-} + {}^1/_2O_2$$

$$2SO_3 + 2e^- \rightarrow S_2O_6^{2-}$$

In order to identify the S–O species in the film, we applied vibrational spectroscopy and elemental analysis. Infrared spectroscopy provided information about the lightly doped samples. The electrical conductivity of the films and its changes under various conditions were also measured. X-ray diffraction patterns of the films revealed structural changes that occur on doping. Raman spectroscopy, which could have provided further information about the species in the film, did not prove effective, as the samples decomposed under laser irradiation. Mass spectroscopy, which could have provided information about the volatile products, was not effective as it was impossible to get a reliable spectrum of any of the likely gaseous products of the doping reaction.

While this work was in progress, workers at Tokyo University of Agriculture and Technology reported results of ESR and electrical conductivity studies on SO_3-doped PPS,[11] and workers at Allied Corp. also reported on ESR spectra.[12] Both groups found a *g* value of 2.008 for SO_3-doped PPS, consistent with the unpaired electron localized in part on sulfur and in part on the aromatic moieties of the chains. Moreover, the number of spins tracked the conductivity as a function of dopant level.

Electrical Conductivity. While attached to electrodes, film samples of PPS were exposed to SO_3 (26–260 torr) at room temperature, as given in Table I. The conditions of exposure were varied as shown in the table to see the effect on the final product. Each sample was exposed to SO_3 for the time shown and then the samples were either held under dynamic vacuum, backfilled with nitrogen, or evacuated for a period of time and then backfilled with nitrogen, as shown in the table. We anticipated that the duration of gas exposure or evacuation might affect the final conductivity of the sample. As shown by the conductivities observed, however, these variations in the procedure had no visible effect on the final conductivity, which was generally between 10^{-5} and 10^{-4} S/cm. The conductivity was monitored over an extended period, and the results are shown in Figure 1. The conductivity increased rapidly to a maximum within 40–60 min of the initial exposure and then dropped somewhat to an equilibrium value that was stable for an extended time in the absence of air. The samples were not evacuated until the

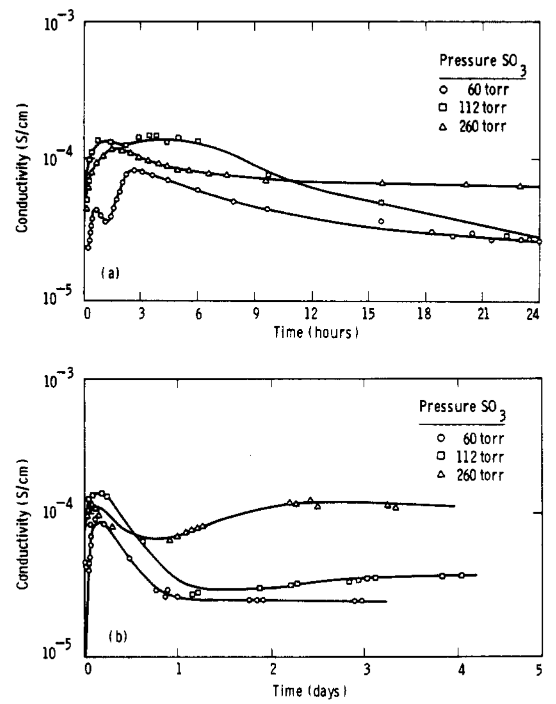

Figure 1. Room-temperature conductivity of SO_3-doped PPS: (a) during first 24 h; (b) during first 5 days.

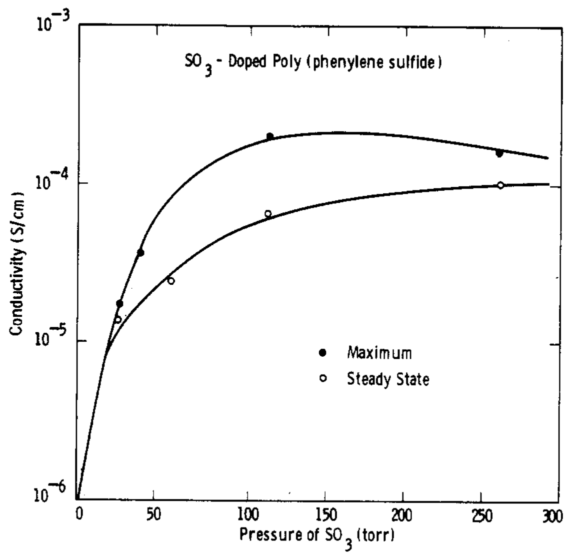

Figure 2. Pressure dependence of room-temperature conductivity of SO_3-doped PPS.

conductivity had started to fall. Even when the samples were exposed to SO_3 for much longer, the conductivity after 40 min was the highest observed. Figure 1a shows the initial response, and Figure 1b shows the response over a longer period. The conductivity has been followed for periods as long as 12 days, as shown in the table. These data are summarized in Figure 2, which shows the pressure dependence of the conductivity. The behavior of conductivity with gas pressure shown in Figure 2 is typical for doping of conductive polymers and has been reported for $(CH)_x$,[13] AsF_5-doped PPS,[3] and I_2-doped $[M(Pc)O]_n$.[6]

The temperature dependence of the conductivity has also been investigated. In the case of AsF_5-doped PPS, pressed-powder samples of the doped material show a thermal activation linear with $1/T^{1/2}$.[3a] Such behavior is consistent with tunneling of charge carriers between conducting regions[14] or with one-dimensional hopping.[15] Although the data could be fit to other powers of $1/T$, a $1/T^{1/2}$ dependence (Figure 3) gave the best fit over the temperature range available to us. The slopes were comparable for samples at different gas pressures, suggesting that the activation energies are comparable at different doping levels.

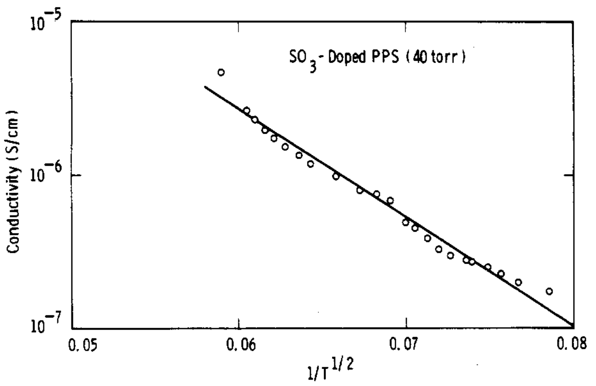

Figure 3. Temperature dependence of conductivity of SO_3-doped PPS (40 torr).

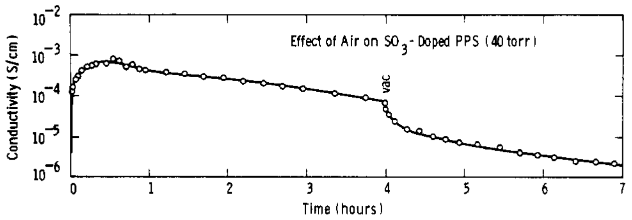

Figure 4. Effect of air on SO_3-doped PPS (40 torr).

The results of electrical measurements on SO_3-doped PPS resemble the results of work with PPS doped with a gas mixture of AsF_3 and AsF_5.[9] The doping rate using the gas mixture and using SO_3 is enhanced significantly over the rate with AsF_5 alone. There is SEM evidence that the doping is much more homogeneous through the thickness of the film in the presence of AsF_3 than without AsF_3. The speculation has been that AsF_3 may act as a plasticizer, serving to increase the rate of AsF_5 diffusion into the film. With the polymer backbone more flexible and separated from adjacent polymer chains, there could also be enhanced formation of dibenzothiophene units. This intramolecular bridging is believed to enhance the conductivity of the polymer by increasing the planarity of the polymer chains. Similar processes are plausible in the case of SO_3. As shown in Figure 1, SO_3 was also much faster acting than the rate reported with AsF_5 alone. It is possible that in addition to oxidizing the polymer, the sulfur trioxide was promoting cross-link formation for coupling of the rings. The evacuation step presumably removed excess SO_3, but the fact that the conductivity was unchanged on evacuation showed that the doping reaction was both fast and irreversible.

The effect of air exposure on the conductivity has been investigated by exposing some of the samples listed in Table I to air while still attached to the electrodes. In general, a film of moisture formed quickly on the polymer surface. If this moisture film shorted the electrodes, the sample gave a spurious reading of high conductivity that decreased on subsequent evacuation. In other cases (Figure 4), the conductivity dropped on exposure to air and continued to do so after evacuation. This behavior is more likely an accurate reflection of the response of the doped material since immersing the sample in water brought about a more substantial, and irreversible, drop in conductivity. Moisture could affect the conductivity in several ways: by solvating the charge carriers, by causing further

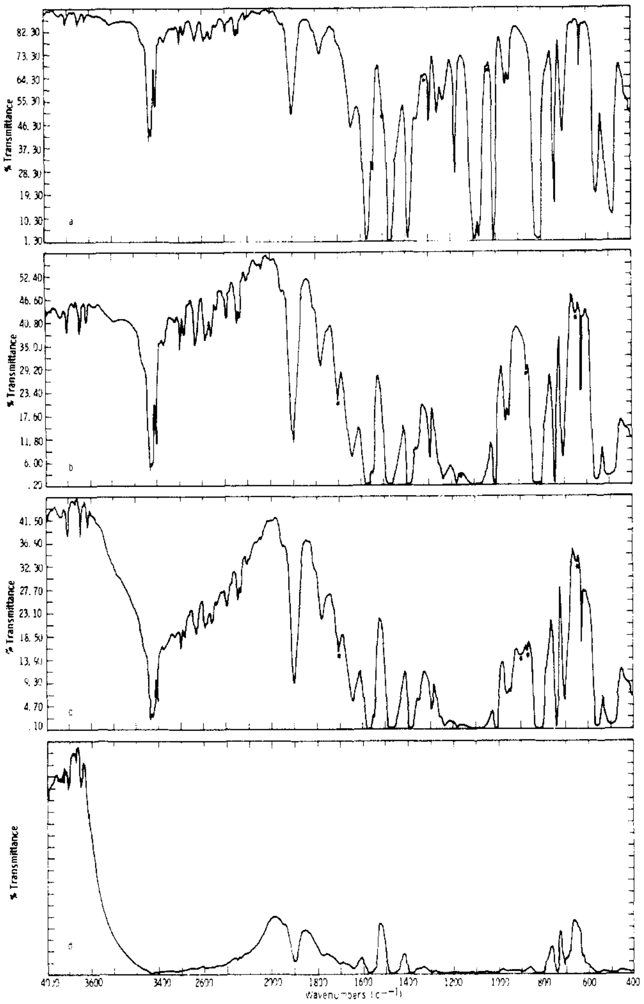

Figure 5. Infrared spectra of PPS-SO_3: (a) undoped; (b) $[(C_6H_4S)(SO_{0.93})_{0.03}]_n$; (c) $[(C_6H_4S)(SO_{0.90})_{0.09}]_n$; (d) $[(C_6H_4S)(SO_{0.80})_{0.49}]_n$. Absorptions marked with asterisks increase during doping.

cross-linking of the polymer chains, thereby reducing the conjugation length, or (in excess) by dissolving the charged dopant species.

Infrared Spectra. Transmission infrared spectra of doped and undoped PPS films are given in Figure 5. Completely doped samples (Figure 5d) showed an intense absorption below 3600 cm^{-1}, attributed to free carriers. A similar absorption has been reported in the IR spectra of several other conductive polymers as well as AsF_5-doped PPS.[3] The frequency at which the free carrier absorption occurs is different for different polymers but is generally in the range 250–2500 cm^{-1}.

At intermediate doping levels (Figure 5b,c) there were absorptions at 1700, 1160, 900, 870, and 650 cm^{-1} that were not observed in the undoped film (Figure 5a). Those absorptions were not correlated uniquely with absorptions due to sulfates, sulfites, bisulfates, thiosulfates, pyrosulfates, or metabisulfates.[16] Depending on the other pendant groups present, S=O stretches occur from 950 to 1200 cm^{-1} and S–O stretches occur from 500 to 700 cm^{-1}, so the absorption at 1160 cm^{-1} is presumably due to S=O moieties and the 600-cm^{-1} peak to S–O groups. The other absorptions (1700, 900, and 870 cm^{-1}) suggested sulfonation of the rings. Methanesulfonic acid has a strong absorption at 1700 cm^{-1} due to the S–O stretch in SOH and at 900 cm^{-1} due to the S–O stretch in SOC, and both such absorptions are observed in doped PPS. Such linkages in the polymer suggested sulfonation of the polymer and possibly cross-link formation. Sulfonation of the polymer was a distinct possibility under these conditions since sulfonation of aromatics is generally done by reaction with fuming H_2SO_4, SO_3 being the active reagent. If there had been sulfonation of the polymer, there should be absorptions near 900 cm^{-1} due to the SOC stretch and at 1700 cm^{-1} if there were SOH present, possibly formed by the presence of trace amounts of water. We regarded as unlikely the possibility of sulfone or sulfoxide formation from the bridging sulfide linkages. Such an occurrence would also produce S–O and S=O linkages. During thermal cure of PPS in oxygen, infrared spectra show aryl ether linkages but no oxidized sulfur bridges.[17]

Table II
X-ray Diffraction Reflections in Poly(phenylene sulfide)

hkl	*d*,[a] Å	*d*,[b] Å
002	5.10	
110	4.72	4.69
102	4.41	
200	4.36	
111	4.30	4.31
112	3.49	3.48
211	3.27	3.25
212	2.86	
020	2.81	2.80
113	2.77	
021	2.70	2.70
004	2.56	
311	2.48	2.49
213	2.42	
220	2.34	
312	2.30	
114	2.25	2.26
023	2.16	
223	1.94	1.99
006	1.71	1.76

[a] From ref 18. [b] From this work, Figure 6.

It is generally held that high conductivity is the result of delocalization of charge carriers along polymer chains. That process is enhanced when a polymer can adopt a planar configuration. PPS is not planar initially because of bending of the polymer chain at the sulfur atoms. In the case of AsF_5-doped PPS, the planarity is enhanced by cross-linking, forming dibenzothiophene units in the chain.[3a] That change is indicated in the infrared spectrum by an increased absorption at 850 cm^{-1} due to out-of-plane vibrations of isolated hydrogens and a corresponding decrease in the absorption at 800 cm^{-1}, associated with two adjacent hydrogens. There was an increased absorption at 870 cm^{-1} in the SO_3-doped material. In order to determine the effect of doping on the polymer structure, some samples were compensated with NH_3 and extracted with water. The conductivity of compensated samples had returned to the value before doping, but the infrared spectra of compensated samples were essentially the same as before compensation. Apparently the structural changes on doping were irreversible in the case of SO_3.

X-ray Diffraction. Considerable work has been done on the structure of PPS and changes during heating. In previous work, undoped PPS films were found to crystallize on annealing at 204 °C for approximately 2 h.[7] Evidence for crystallization on annealing was provided by DTA, X-ray diffraction, and infrared spectroscopy. The effect of crystallization appeared in the tensile strength, viscosity, etc. The X-ray diffraction pattern has been assigned in an orthorhombic unit cell with cell parameters $a = 8.67$ Å, $b = 5.61$ Å, $c = 10.26$ Å by Tabor et al.[18] Each unit cell contains two monomer units. The S atoms of an individual chain are arranged in zigzag fashion with a 110° angle at the S atom. A comparison of the diffraction patterns of annealed samples by Tabor and this work is

Table III
Elemental Analyses of $[(C_6H_4S)(SO_x)_y]_n$

		calcd				found			
P_{SO_3}, torr	composition	% C	% H	% S	% O	% C	% H	% S	% O
30	$[(C_6H_4S)(SO_{3.0})_{0.065}]_n$	63.57	3.55	30.12	2.75	63.93	3.53		
60	$[(C_6H_4S)(SO_{3.0})_{0.24}]_n$	56.58	3.16	31.21	9.04	56.54	3.37	31.11	8.99
110	$[(C_6H_4S)(SO_{3.2})_{0.35}]_n$	52.92	2.96	31.79	12.34	54.71	3.12	28.51	13.66

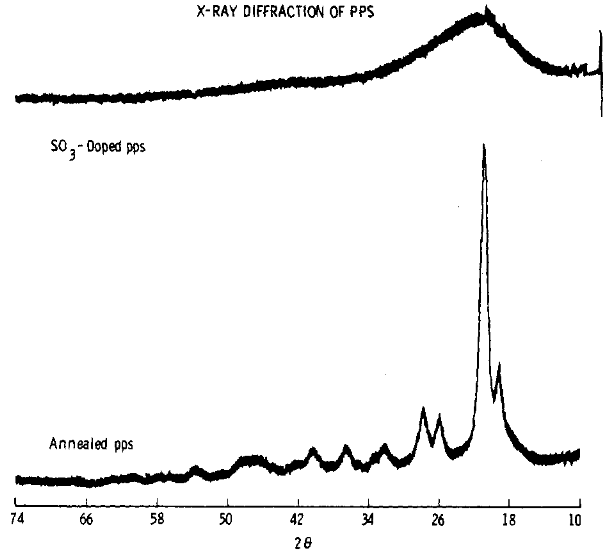

Figure 6. X-ray diffraction patterns of PPS.

given in Table II. The results of this work are consistent with the earlier data.

As mentioned above, it is generally held that in order for a polymer system to be highly conductive, there has to be extensive orbital overlap along or between polymer chains. That circumstance is more likely if the polymer chains are planar. One rationalization for the enhanced conductivity observed in AsF_5-doped PPS is that the intramolecular cross-linking observed in the infrared spectrum after doping makes the polymer chains more nearly coplanar.[3a] X-ray diffraction studies of doped films have shown that oriented films, which have a similar diffraction pattern to the annealed films, lose their crystallinity after doping.[3b,19] The extensive disorder induced on doping is probably the result of cross-linking as well as the insertion of dopant ions between chains. The diffraction patterns of the doped material show only a very broad reflection at $2\theta = 18°$ in AsF_5-doped films. The patterns are similar to those of amorphous or unoriented films, indicating substantial loss in crystallinity on doping. Moreover, the result is the same after doping whether the starting material is crystalline or amorphous. Results for SO_3-doped films are given in Figure 6 and show similar loss in crystallinity on doping. Likewise, the SO_3-doped films were amorphous regardless of the crystallinity of the starting material. The only effect of the crystallinity of the starting material is on the rate of doping. Doping of amorphous samples occurs more quickly than doping of crystalline samples.

Elemental Analysis. The doped polymer apparently was especially thermally stable, as it was much more difficult to get complete combustion of doped samples than undoped samples. Results for typical samples are given in Table III. An O/S ratio in the dopant species near 3 gave the most consistent results in each case. The calculation was made by solving simultaneously for x and y in the formula $[(C_6H_4S)(SO_x)_y]_n$ using the analytical data. An average of the best results for x and y was then used for the compositions given in the table. Since the oxygen content is the one that varies the most with different compositions, a close match in oxygen content was preferred when a choice had to be made, as in the case of the 110-torr sample shown in the table. The elemental analysis is thus consistent with an O/S ratio near 3, but confirmation by other methods would be required to be certain.

Mass Spectroscopy. Mass spectra were recorded of the gas mixture after the doping reaction had occurred, in hopes of finding whether there was any oxygen or SO_2 present. Standard samples of SO_2, SO_3, and O_2 were investigated first to see if these gases could be detected alone and when mixed. Results showed that in fact, the difference in mass spectra between authentic samples of SO_2 and SO_3 was barely detectible. The peak at mass 80 (SO_3) was very small whereas the peak at mass 64 (SO_2) was predominant in both cases. There has been no spectrum reported for SO_3. Perhaps there is an equilibrium like

$$SO_3 \rightleftarrows SO_2 + {}^1/_2O_2$$

which would shift to the right under the high-vacuum conditions of the mass spectrometer. In that case, even a sample containing SO_3 would give a mass spectrum like that of SO_2. In any event, this technique did not prove useful in detecting small amounts of O_2 or SO_2 in the gas mixture following the doping reaction.

Raman Spectroscopy. Raman measurements were attempted on samples of doped powder and film, but without success. Apparently the laser radiation decomposed the sample before a scattering spectrum could be collected.

Conclusions

Sulfur trioxide doping of PPS produces a material with a maximum conductivity of approximately 10^{-4} S/cm. The maximum conductivity was reached after 40–60-min exposure to SO_3. The temperature dependence of the conductivity was consistent with one-dimensional hopping. On exposure to air, there was an irreversible reaction with moisture that caused a drop in conductivity, as is the case in AsF_5-doped samples. The reaction was slower in SO_3-doped films than in AsF_5-doped films. In addition to changing the electronic structure of the polymer, SO_3 also changed the polymer itself, possibly by sulfonation or cross-link formation or both. Infrared spectra of lightly doped samples suggested sulfonation and possibly cross-linking during doping. Although the spectra also showed the presence of SO_x species, it was impossible to identify uniquely which anion or anions were present. Elemental analyses were consistent with the dopant anions being SO_3^{2-}. X-ray diffraction of films before and after doping showed that doping induced substantial disorder in the polymer, possibly the result of incorporation of dopant between polymer chains or of cross-linking. Similar results have been reported for AsF_5 doping.

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Registry No. SO_3, 7446-11-9; Ryton V-1, 25212-74-2.

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Solution Studies of Cellulose in Lithium Chloride and *N*,*N*-Dimethylacetamide

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ABSTRACT: The dissolution process and some solution properties of cellulose in mixtures of lithium chloride (LiCl) and *N*,*N*-dimethylacetamide (DMAc) are discussed. Dilute solution properties were measured by viscometry, low-angle laser light scattering and quasi-elastic light scattering. The following Mark–Houwink–Sakurada (MHS) equation and the relationship between the intrinsic viscosity and the *z*-average radius of gyration $\langle S^2\rangle_z^{1/2}$ were established: $[\eta] = (1.278 \times 10^{-4})M_w^{1.19}$ (cm^3/g) and $\langle S^2\rangle_z^{1/2} = (6.48 \times 10^{-10})M_w^{0.74}$ (cm) for cellulose in 9% LiCl/DMAc at 30 °C. On the basis of the light-scattering and viscosity data, the conformation parameter $\sigma = 6.71$, the characteristic ratio $C_\infty = 91.9$, and the persistence length $q = 252 \times 10^{-8}$ (cm) were calculated. Estimations of the MHS equation and the chain dimensions reveal that the LiCl/DMAc solvent greatly enhances the stiffness of the cellulose backbone. Liquid crystalline behavior is observed for solutions at the solubility limit (~15%) by the appearance of an anisotropic phase induced by shearing.

Introduction

In the past, facile characterization and derivatization of unmodified cellulose has been hampered by the lack of suitable nondegrading solvents. The initial discovery in our laboratories of cellulose solubility in lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc) solutions led to the preparation of a number of derivatives[1–4] and the study of the mechanism of dissolution.[5] Recently, we reported evidence for lyotropic mesomorphicity at concentrations approaching the solubility limit.[6] In this work, we present details of solution behavior, an estimation of the molecular dimensions, and additional evidence for a lyotropic liquid crystalline phase in this solvent system.

While a number of cellulose derivatives form lyotropic mesophases,[7] unmodified cellulose has been less suitable due to its poor solubility. Cellulose apparently requires highly interactive solvents for complete dissolution. Mesomorphic solutions of cellulose have been reported by Chanzy and Peguy[8] utilizing a water/*N*-methylmorpholine *N*-oxide solvent system and by Patel and Gilbert[9] in mixtures of trifluoroacetic acid and chlorinated alkanes. By comparison, LiCl/DMAc is apparently nondegrading to cellulose and could be of significance in future commercial developments.

The LiCl/DMAc solvent has been utilized to form films and fibers of chitin,[10] cellulose,[11,12] and aromatic polyamides.[13–18] The implications of enhanced physical properties of cellulose films and fibers formed from liquid crystalline solutions, applications of a variety of cellulose characterization techniques, and the demonstrated utility for homogeneous solution reactions have prompted our continuing investigations.

Experimental Section

Cellulose Sources. The cellulose samples used in this study were from several different sources and representative of a large molecular weight range. PC-1 and PC-3 are catalog no. 0230 and 4853 from Polysciences, Inc. PC-2, PC-5, and PC-6 are catalog no. 1529, 1525, and 1528, respectively, from the J. T. Baker Chemical Co. PC-4 is cellulose powder CF1 from Whitman, Ltd. PC-7 is a regenerated viscose cellulose yarn. PC-8 and PC-9 are buckeye cotton 505 and buckeye cotton ER-6500 from the James River Corp. All samples are unfractionated, and no information