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Polymer Homologue of DMSO: Synthesis of Poly(ethylene sulfoxide) by Selective Oxidation of Poly(ethylene sulfide)

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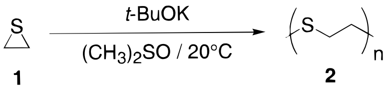
ABSTRACT: Poly(ethylene sulfoxide) having almost 100% sulfinyl groups in the main chain was synthesized by selective oxidation of poly(ethylene sulfide). Poly(ethylene sulfide), prepared by anionic ring-opening polymerization of ethylene sulfide, was reacted in a HNO_3/CH_3SO_3H system at 0 °C for 24 h to give poly(ethylene sulfoxide) in quantitative yield. The structure of the polysulfoxide obtained was confirmed by ^1H NMR, ^{13}C NMR, and IR spectra. A shorter reaction time caused insufficient oxidation, and the polymer containing sulfoxide and sulfone units was obtained when the reaction was conducted at room temperature. The resulting poly(ethylene sulfoxide) was soluble in 60% HNO_3, methanesulfonic acid, and trifluoromethanesulfonic acid, though poly(ethylene sulfide) was insoluble in any solvent at room temperature. Poly(ethylene sulfoxide) was found to be miscible with poly(vinyl alcohol). These results reflect that poly(ethylene sulfoxide) has a repeating structure of dimethyl sulfoxide, which is known as an aprotic polar solvent.

Introduction

Ethylene sulfide is known to be readily polymerized by anionic and cationic ring-opening manner to give poly(ethylene sulfide).[1] Though ethylene sulfide is an inexpensive monomer, poly(ethylene sulfide) is not of great industrial value as a material due to its insolubility.[1,2] This defect in poly(ethylene sulfide) could be improved if the solubility and/or the compatibility were to be given to the polysulfide. Introduction of sulfinyl groups into poly(ethylene sulfide) by oxidation of sulfur atoms is thought to be a good method for this purpose because the S=O bond is polarized and easily interacts with other functional molecules. The resulting polysulfoxide is regarded as a polymer homologue of dimethyl sulfoxide (DMSO), which is known as an aprotic polar solvent.[3] Many reactions such as Williamson ether synthesis are promoted by using DMSO as a solvent,[4] and DMSO dissolves several organic commodity polymers. Therefore, poly(ethylene sulfoxide) is expected to show properties based on its repeating structures such as improved solubility and miscibility with other polymers, and the polysulfoxide could then become an industrially useful polymer. In this paper, we reports the synthesis of poly(ethylene sulfoxide) by selective oxidation of poly(ethylene sulfide) and its properties.

Results and Discussion

Scheme 1



Scheme 2

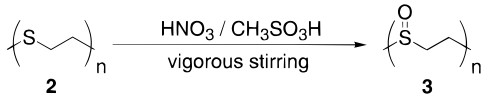


Table 1. Oxidation of Poly(ethylene sulfide) (2) to Poly(ethylene sulfoxide) (3)

entry	condition	−S−:−SO−:−SO_2−[a]	yield (%)
1	0 °C/12 h	11:89:0	quantitative
2	0 °C/24 h	0:100:0	99
3	0 °C/2 h to room temp/22 h	0:28:72	81

[a] The ratio of sulfide−sulfoxide−sulfone was determined by the integrals of methylene protons adjacent to sulfur atoms.

Poly(ethylene sulfide) (**2**) was prepared by anionic ring-opening polymerization of ethylene sulfide in DMSO by using potassium *tert*-butoxide as an initiator and obtained in 100% yield (Scheme 1).[5] The polysulfide **2** was insoluble in any solvent below 100 °C as described in the literature.[1,2] The oxidation of poly(ethylene sulfide) was then conducted in HNO_3/CH_3SO_3H system as shown in Scheme 2.[6] Though the reaction system was heterogeneous at first, the mixture became a gelatinous homogeneous solution as the reaction proceeded. The results of the oxidation are summarized in Table 1. As shown in entry 2, poly(ethylene sulfoxide) in which all sulfur atoms were oxidized to sulfoxides was obtained in 99% yield, if the reaction was conducted at 0 °C for 24 h. It is thought that no serious main chain scission occurred because the polysulfoxide was obtained in almost quantitative yield after reprecipitation into methanol. On the other hand, sulfide units were not completely reacted to sulfoxides when the reaction time was shorter (entry 1), and sulfone units were observed in the case of the reaction at room temperature (entry 3).

The conversion of sulfide units to sulfoxides was monitored by ^1H NMR, ^{13}C NMR, and IR spectra. The NMR spectra were measured by using CF_3SO_3D as a solvent. In ^1H NMR spectrum of the polysulfoxide **3** in entry 2 of Table 1 (Figure 1), no peak assignable to $-SCH_2-$ (2.8 ppm) or $-S(O)_2CH_2-$ (4.1 ppm) was observed. In other entries, the ratio of sulfide−sulfoxide−sulfone was determined by the integrals of the

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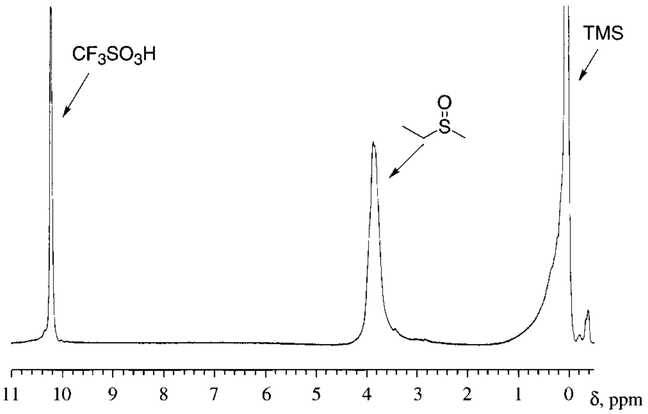


Figure 1. ^1H NMR spectrum (270 MHz) of poly(ethylene sulfoxide) (**3**) in CF_3SO_3D (Table 1, entry 2).

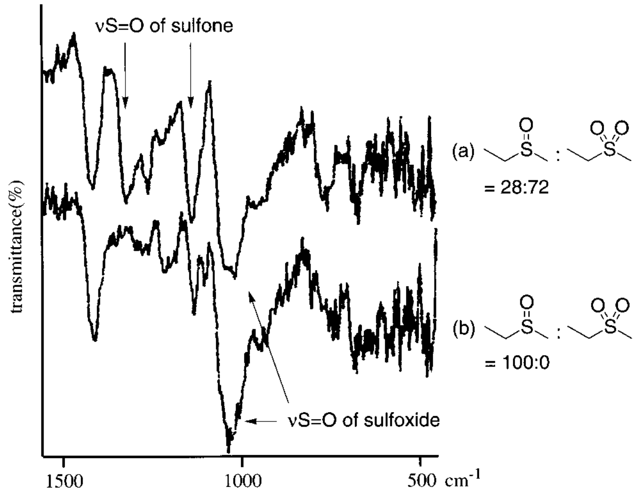


Figure 2. IR spectra of poly(ethylene sulfoxide) (**3**) with sulfoxide:sulfone = 28:72 ((a), Table 1, entry 3) and **3** with sulfoxide:sulfone = 100:0 ((b), Table 1, entry 2).

methylene protons adjacent to sulfur atoms (see the Experimental Section). There was also no peak assigned to $-SCH_2-$ (40 ppm) in ^{13}C NMR spectrum though the peaks for $-S(O)CH_2-$ and $-S(O)_2CH_2-$ could not be distinguished (one broad peak was observed around 45 ppm). IR spectra of the polymers with the ratio between sulfoxide and sulfone being 28:72 (a) and 100:0 (b) are shown in Figure 2. A large absorption of the S=O stretching band of sulfoxide was observed at 1037 cm^{-1} in both spectra. However, absorptions corresponding to S=O stretching bands of sulfone were not observed at all in Figure 2b. This result also supports the conversion of sulfides to sulfoxides without the formation of sulfone. The poly(ethylene sulfoxide) (**3**) obtained was soluble in methanesulfonic acid, trifluoromethanesulfonic acid, and 60% nitric acid at room temperature. This improved solubility reflects that polymer **3** has DMSO repeating structures. TGA traces of poly(ethylene sulfide) (**2**) and poly(ethylene sulfoxide) (**3**) are also represented in Figure 3. Though **3** decomposed at lower temperature than **2**, the rate of degradation of **3** was found to be slower than **2**. This would be explained by assuming that the small amount of sulfonium salt remaining in polymer **3** (see Scheme 3) promotes intra- and intermolecular attack of lone pairs in sulfoxides to the carbons adjacent to the salts. As a result, the decomposition starts at lower temperature and the rate of degradation of **3** decreases due to the growth of a cross-linked structure.

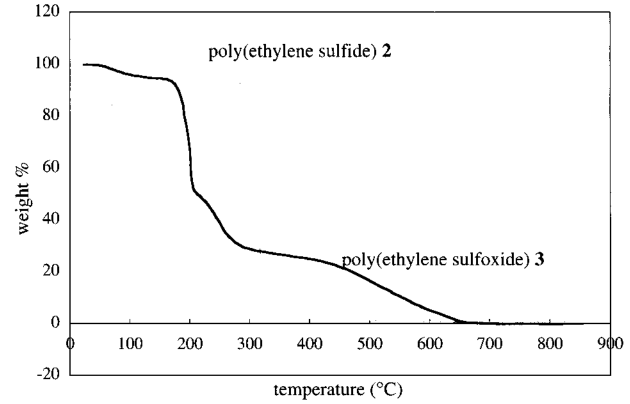
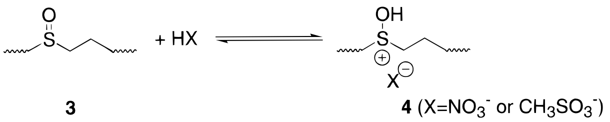
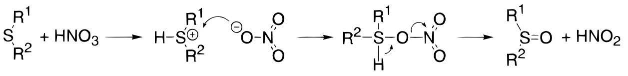


Figure 3. TGA traces of poly(ethylene sulfide) (**2**) and poly(ethylene sulfoxide) (**3**) in air.

Scheme 3



Scheme 4



The reason poly(ethylene sulfide) was oxidized to the corresponding polysulfoxide without the formation of sulfone is speculated to be as follows: Poly(ethylene sulfide) is known to be insoluble in any solvent due to its high crystallinity, and poly(ethylene sulfoxide) was found to be soluble in methanesulfonic acid and nitric acid probably because of its aprotic polar sulfinyl groups and reduced crystallinity. Therefore, the oxidation of the polysulfide to the polysulfoxide would be promoted as sulfur atoms in the polysulfide are converted to sulfinyl groups. On the other hand, the sulfoxide formed in the reaction is thought to be in equilibrium with the corresponding sulfonium salt **4** due to the weak basicity of sulfoxide (Scheme 3).[7] The oxidation of sulfides to sulfoxides (and of sulfoxides to sulfones) by nitric acid in methanesulfonic acid is thought to proceed as shown in Scheme 4. In this oxidation, it is important that a lone pair on a sulfur atom attacks a proton to give a sulfonium cation. However, the sulfonium salt **4** formed in the reaction is difficult to perform the nucleophilic attack since the sulfur atom of **4** is cationic. Thus, the sulfonium salt would be expected to be resistant to oxidation, and as a result, the oxidation of sulfoxides to sulfones is considered to be difficult in this system.[6-8]

Poly(ethylene sulfoxide) (**3**) is expected to exhibit miscibility with other polar polymers because it has sulfoxide groups in its repeating structures,[1b] and the industrial value of the poly(ethylene sulfoxide) (and poly(ethylene sulfide)) would be improved if miscibility of the polysulfoxide could actually be realized. Thus, the miscibility of **3** (T_g = 31 °C) with poly(*N*-vinylpyrrolidone) and with poly(vinyl alcohol) was investigated by comparing the glass transition temperatures of the mixture of two polymers with those of the original polymers. The glass transition temperatures were determined by differential scanning calorimetry (DSC) method at heating rate of 10 °C/min. The results are summarized in Table 2. Large shifts of T_gs were observed in the systems of poly(ethylene sulfoxide) (**3**)

Table 2. Miscibility of Poly(ethylene sulfoxide) (3) (T_g = 31 °C)

entry	**3** (wt %)	the other polymer (wt %)		obsd T_g (°C)[a]
1	20	80	poly(*N*-vinylpyrrolidone) $M_n = 10\,000$, $T_g = 93$ °C	34, *b*
2	50	50		30, 80
3	80	20		42, 82
4	20	80	poly(vinyl alcohol) $M_n = 10\,000$, $T_g = 104$ °C	38, 60
5	50	50		69
6	80	20		40

[a] Glass transition temperatures were determined by differential scanning calorimetry (DSC) method (second heating scan). [b] Not observed.

with poly(vinyl alcohol) as shown in entries 4−6. In particular, only one glass transition temperature was observed between those of the original polymers when the weight ratios between **3** and poly(vinyl alcohol) were 50:50 and 80:20 (entries 5 and 6). These results indicate that poly(ethylene sulfoxide) actually has good miscibility with poly(vinyl alcohol), probably via hydrogen bonds between two polymers.[9] The lower miscibility of **3** with poly(*N*-vinylpyrrolidone) would be due to weaker electrostatic interaction between polar groups of two polymers.

In summary, poly(ethylene sulfoxide) (**3**) was prepared by selective oxidation of poly(ethylene sulfide) by using HNO_3/CH_3SO_3H system in almost 100% yield. Sulfide units in the polymer were found to be oxidized to sulfoxides quantitatively without the formation of sulfone units from ^1H NMR, ^{13}C NMR, and IR spectra of the product. The resulting poly(ethylene sulfoxide) (**3**) showed good miscibility with poly(vinyl alcohol) due to hydrogen bonds between two polymers. Though poly(ethylene sulfide) was insoluble in any solvent around room temperature, poly(ethylene sulfoxide) was soluble in nitric acid and methanesulfonic acid at ambient temperature. Further studies about application of poly(ethylene sulfoxide) such as its use as a component of composite materials and as an compatibilizer are in progress.

Experimental Section

General Data. ^1H NMR and ^{13}C NMR spectra were obtained with a JEOL JNM-EX270 spectrometer (270 MHz for ^1H NMR and 67.9 MHz for ^{13}C NMR) in trifluoromethanesulfonic acid-*d* by using tetramethylsilane (TMS) as an internal standard (0 ppm). IR spectra were recorded on a Perkin-Elmer 1600 spectrometer. All DSC analyses were carried out on a Seiko DSC200 instrument by using about 10 mg of exactly weighed samples at heating and cooling rate of 10 °C/min. TGA traces were measured on a Shimadzu TG-30 and TGC-30 at a rate of 10 °C/min in air.

Unless otherwise noted, the materials were obtained from commercial sources. Dimethyl sulfoxide (DMSO) was distilled under nitrogen from CaH_2. Potassium *tert*-butoxide was purchased from Nacalai Tesque, Inc. and used as received. Poly(*N*-vinylpyrrolidone) was obtained from a commercial source and used without further purification. Poly(vinyl alcohol) was used after reprecipitation into acetone.

Synthesis of Poly(ethylene sulfide) (2). To a mixture of DMSO (100 mL) with potassium *tert*-butoxide (18.7 mg, 0.166 mmol) was added dropwise ethylene sulfide (9.9 mL, 166 mmol) with cooling in a water bath. As the addition was started, a white precipitate appeared immediately. The mixture was then stirred at room temperature overnight, and the reaction was quenched by adding methanol. The precipitate was collected by suction filtration, and the resulting polymer was washed by methanol and dried at 90 °C in vacuo to give poly(ethylene sulfide) (**2**) in a quantitative yield. IR (KBr): 2930, 1426, 1185, 1144, 722, 693, 671 cm^{-1}.

Oxidation of Poly(ethylene sulfide) (2) to Poly(ethylene sulfoxide) (3). General Procedure. In a 100 mL three-necked flask equipped with a mechanical stirrer was placed 60% nitric acid (12.0 mL, 0.158 mol), and the reaction was cooled to 0 °C. Then, methanesulfonic acid (18.9 mL, 0.291 mol) was added and the mixture was stirred for 10 min. To this solution was added poly(ethylene sulfide) (**2**) (0.50 g, 8.32 mmol) in one portion with vigorous stirring. The polymer turned brown as soon as it was added to the solution, and the mixture became a gelatinous homogeneous solution as the reaction proceeded (2−3 h). The mixture was vigorously stirred at 0 °C (or a desired temperature) for 24 h (or a desired period), and the reaction was quenched by pouring a large amount of methanol into the reaction flask. The resulting precipitate was collected by suction filtration and washed repeatedly with methanol. The white solid was dried at 65 °C in vacuo to afford poly(ethylene sulfoxide) (**3**) having 100% sulfoxide groups in 99% yield. ^1H NMR (δ, ppm): (2.78 ($-CH_2S$-, br)), 3.82 ($-CH_2S(O)$-, br, 4H), (4.10 ($-CH_2S(O)_2$-, br)). ^{13}C NMR (δ, ppm): (40.0), 44−46 (br). IR (KBr): 2966, 2908, 1625, 1409, 1273, 1213, 1130, 1101, 1037 cm^{-1}. Anal. Calcd for $(C_2H_4OS)_n$: C, 5.30; H, 31.56. Found: C, 5.22; H, 30.33.

Differential Scanning Calorimetry Analyses. The samples for DSC analyses were prepared as follows: A mixture (0.10 g) of poly(ethylene sulfoxide) (**3**) with poly(vinyl alcohol) or with poly(*N*-vinylpyrrolidone) at a desired ratio was dissolved in methanesulfonic acid at room temperature. The solution was then reprecipitated into a large amount of methanol to give a white solid. After filtration and freeze-drying of the mixture, the resulting solid was dried in vacuo and used for DSC analyses. The midpoint of the T_g peak in the thermogram of the second heating scan was adopted as the value of the glass transition temperature.

References and Notes

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