Polysulfoximines, a Novel Class of Sulfur-Containing Polymers

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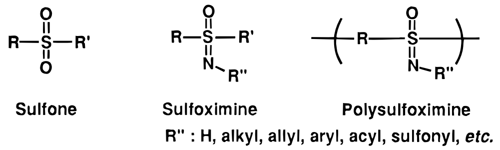
Introduction. Sulfide and sulfone groups are major main chain functional groups in sulfur-containing polymers hitherto reported, although many organic sulfur-based functional groups are known.[1] In fact, sulfur-containing polymers such as polysulfone and poly(*p*-phenylene sulfide) are used as high-performance engineering plastics. Sulfoximine,[2] a mononitrogen analog of sulfone, is a well-known sulfur-containing compound showing sulfone-like properties which are often affected by substituents at the nitrogen atom. Therefore, the chemical and physical properties of “polysulfoximines” are of particular interest due to their rigid and unsymmetrical structure, but there have been no polysulfoximines synthesized previously, so far as we know. Recently, we have succeeded in preparing polysulfoximines by a self-polycondensation utilizing a catalytic Friedel−Crafts reaction.[3] This paper preliminarily communicates the synthesis and characterization of the first polysulfoximine (**1**).



Results and Discussion. A sulfonimidoyl chloride was prepared as a monomer to utilize in the synthesis of a polysulfoximine by Friedel−Crafts reaction analogous to the synthesis of a polysulfone using an arenesulfonyl chloride.[4] Benzene- (**2a**) and 4-phenoxybenzenesulfonimidoyl chlorides (**2b**) were obtained in 17% and 76% yields, respectively, by the reactions of the corresponding arenesulfinyl chlorides (**3**) with anhydrous chloramine T.[5] Whereas benzenesulfinyl chloride (**3a**) was prepared by the reaction of diphenyl disulfide with chlorine in the presence of acetic anhydride (99% yield), 4-phenoxybenzenesulfinyl chloride (**3b**) was derived from diphenyl ether via a four-step reaction sequence (62% overall yield), as depicted in Scheme 1. The monomers **2** were somewhat moisture-sensitive products which were purified by recrystallization (**2a**) or chromatography (**2b**) and characterized by the IR absorptions (ν_{S-O} and ν_{S-N}) in addition to the NMRs.[6]

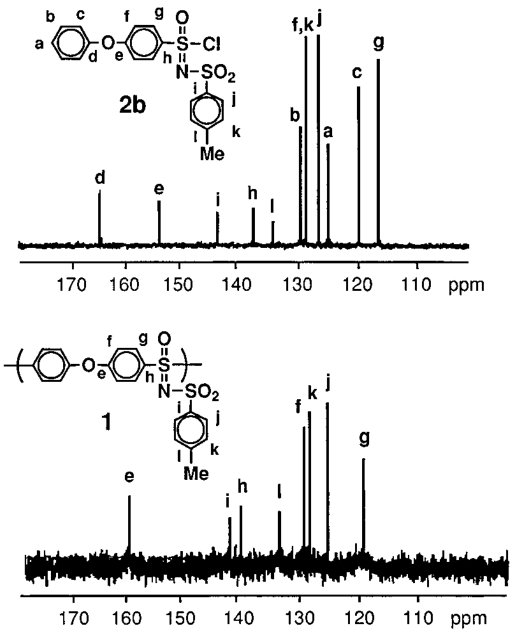
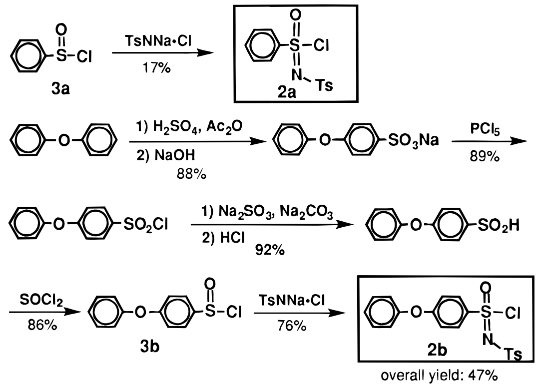
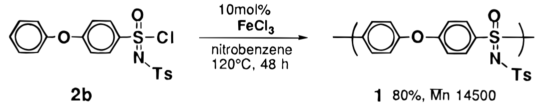


Figure 1. ^{13}C NMR spectra (aromatic region) of monomer **2b** and polysulfoximine **1** ($CDCl_3$, 27 °C for **2b**, and dimethyl sulfoxide-d_6, 81 °C, for **1**). Chemical shifts of methyl carbon signal: 21.6 ppm (**2b**) and 20.4 ppm (**1**).

Scheme 1



Scheme 2



Although treatment of **2a** with Lewis acids such as aluminum chloride and ferric chloride yielded no polymeric product, probably because of the lowered reactivity due to the poor electron density of the benzene ring, similar treatment of **2b** afforded methanol-insoluble polymer in high yield (Scheme 2). In that reaction, a mixture of **2b** and 10 mol % of ferric chloride ($FeCl_3$) in nitrobenzene (0.5 M) was heated at 120 °C for 48 h under a nitrogen stream to remove hydrogen chloride evolved during the reaction. The isolated polymeric product (80% yield, $\bar{M}_n$ 14 500) was determined to be polysulfoximine **1** by IR, NMR, and GPC analyses.[7]

The ^{13}C NMR spectrum of **1** showed only eight carbon signals, although that of **2b** revealed 12 carbon signals, as shown in Figure 1 where all aromatic signals were assigned for polymer **1** (bottom) and monomer **2b** (top), respectively. This reduction in the number of carbon signals can be clearly explained by the successive regioselective condensative addition of the monomer **2b** by the $FeCl_3$-catalyzed Friedel−Crafts self-condensation reaction which equalizes the two phenyl groups of the main chain repeating unit. Namely, it indicates that the Friedel−Crafts self-condensation reaction exclusively occurred at the *para* position of the phenoxy group of **2b**.[8]

It has been reported that treatment of *N*-tosylsulfoximine (*N*-Ts derivative) with concentrated sulfuric acid

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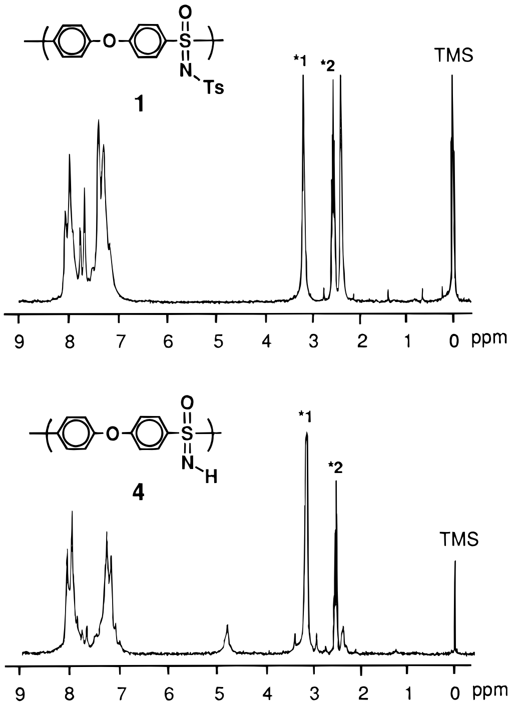
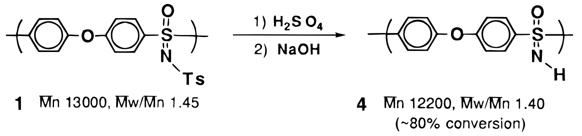


Figure 2. ^{1}H NMR spectra of polysulfoximine **1** (*N*-tosyl derivative) and "free" polysulfoximine **4** (*N*-H derivative) (dimethyl sulfoxide-d_6, 81 °C, for **1** and **4**): (*1) signal of water; (*2) signal of dimethyl sulfoxide.

Scheme 3



followed by neutralization with sodium hydroxide gives "free" sulfoximine (*N*-H derivative).[9] When polymer **1** was similarly treated according to this procedure at room temperature, the corresponding polymer containing the "free" sulfoximine moiety (**4**) was obtained. Since the molecular weight of **4** ($\bar{M}_n$ 12 200, $\bar{M}_w/\bar{M}_n$ 1.40) was nearly equal to that of **1** ($\bar{M}_n$ 13 000, $\bar{M}_w/\bar{M}_n$ 1.45), main chain fission did not take place under the conditions employed. The ^{1}H NMR spectrum of **4** clearly suggested disappearance of the tosyl moiety (7.7 ppm) in addition to appearance of an N−H group (4.8 ppm) in Figure 2, being consistent with the IR results (disappearance of absorptions at 1320 and 1160 cm^{-1} of the SO$_2$ group and appearance of an absorption at 3310 cm^{-1} for the N−H group). Further, from the signal ratio of the tosyl group in the ^{1}H NMR spectrum of **4**, ca. 80% of the *N*-tosyl group was removed while the residual 20% of it remained unreacted.

Glass transition temperatures of **1** and **4** measured by differential scanning calorimetry (DSC) were almost equal, 335 and 333 °C, respectively. Thermogravimetric analyses revealed that "free" *N*-H polymer **4** was much more thermally stable than **1**, judging from their 10 and 20% weight loss temperatures ($T_{d_{10}}$, $T_{d_{20}}$).[10] The thermal stability of **4** seems to be comparable to that of poly(ether−sulfone) ($T_{d_{20}}$ 550 °C).

Thus, this work presents the synthesis and properties of polysulfoximines, a novel class of sulfur-containing polymers. Detailed studies on the polysulfoximines and related polymers are continuing.

References and Notes

(1) Review see: Spassky, N.; Sepulchre, M.; Sigwalt, P. In *Handbook of Polymer Synthesis;* Kricheldorf, H. R., Ed.; Marcel Dekker, Inc.: New York, 1992; Part B, Chapter 16, p 991 (see also references (reviews) cited therein).

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(6) Satisfactory elemental analysis data were obtained for **2b**, of which spectral data are as follows: IR (NaCl, cm^{-1}) 3098, 3069, 1578, 1485, 1342, 1287, 1254, 1165, 1109, 1088, 733, 696; ^{1}H NMR (CDCl$_3$, δ) 8.0−7.9 (m, 4H), 7.5−7.3 (m, 5H), 7.1−7.0 (m, 4H), 2.43 (s, 3H).

(7) The molecular weight of **1** was determined by GPC (DMF eluent, polystyrene standards). IR data of **1** (KBr, cm^{-1}): 3065, 2924, 2857, 1580, 1483, 1319, 1242, 1159, 1088, 1059, 1009, 870, 831.

(8) Therefore, Friedel−Crafts reactions which may occur at a few other possible positions of both **2b** and the product **1** would be completely suppressed under the conditions, probably by some electronic and/or steric factors.

(9) Furukawa, N.; Omata, T.; Yoshimura, T.; Aida, T.; Oae, S. *Tetrahedron Lett.* **1972**, 1619. *Idem. J. Org. Chem.* **1976**, *41*, 1728.

(10) Thermogravimetric analyses data: $T_{d_{10}}$ 358°C, $T_{d_{20}}$ 396 °C for **1** and $T_{d_{10}}$ 376 °C, $T_{d_{20}}$ 506 °C for **4**.

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