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Novel aprotic polar polymers

3. Synthesis and properties of poly(phenyl vinyl sulfoxide)

Toshiyuki Oyama, Junko Ozaki, Yoshiki Chujo*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University,
Yoshida, Sakyo-ku, Kyoto 606-01, Japan

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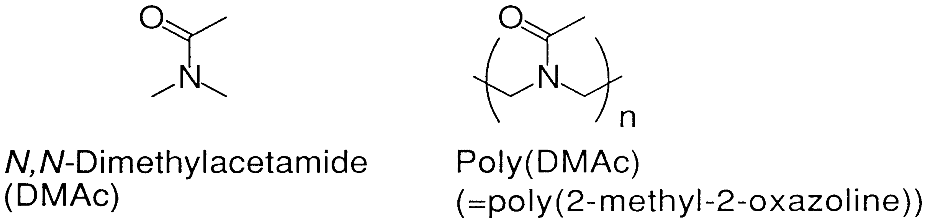
Summary

Poly(phenyl vinyl sulfoxide) **1** was prepared by anionic polymerization and its properties as a polymer homolog of dimethyl sulfoxide (DMSO) were examined. Polysulfoxide **1** was found to have good miscibility with poly(vinyl acetate) as well as poly(2-methyl-2-oxazoline) and poly(*N*-vinylpyrrolidone) by comparing glass transition temperature(s) (T_gs) of the mixture of these polymers with T_gs of the original polymers by differential scanning calorimetry.

Introduction

Aprotic polar solvent is known to show many interesting properties such as mixing with water freely and solubilizing several organic polar polymers. Increase of reaction rate of nucleophilic substitution is observed when an aprotic polar solvent is used as a reaction medium. Thus, many interesting properties based on their repeating structures are expected by preparing polymer homologs of aprotic polar solvents. The most famous example of this concept is poly(2-methyl-2-oxazoline), that is, a polymer homolog of *N*,*N*-dimethylacetamide (DMAc) (Scheme 1) (1). In fact, poly(2-methyl-2-oxazoline) shows high hydrophilicity and good miscibility with DMAc-soluble commodity polymers such as poly(vinyl chloride), poly(vinylidene fluoride) and polyamides (1). We term such polymer homologs of aprotic polar solvents “aprotic polar polymers”.

Scheme 1



In order to extend the scope of aprotic polar polymers, we have prepared aliphatic polysulfoxides as polymer homologs of dimethyl sulfoxide (DMSO) by oxidation of the corresponding aliphatic polysulfides (Scheme 2) (2). Aliphatic polysulfoxides thus obtained actually showed the properties as oxidizing reagents and the miscibility with other polymers (2,3). However, the design of polymers having sulfinyl groups as side chains is also

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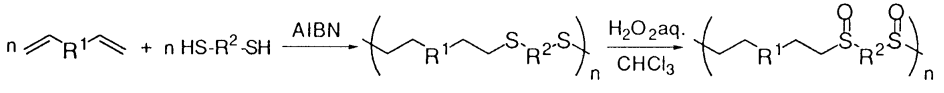
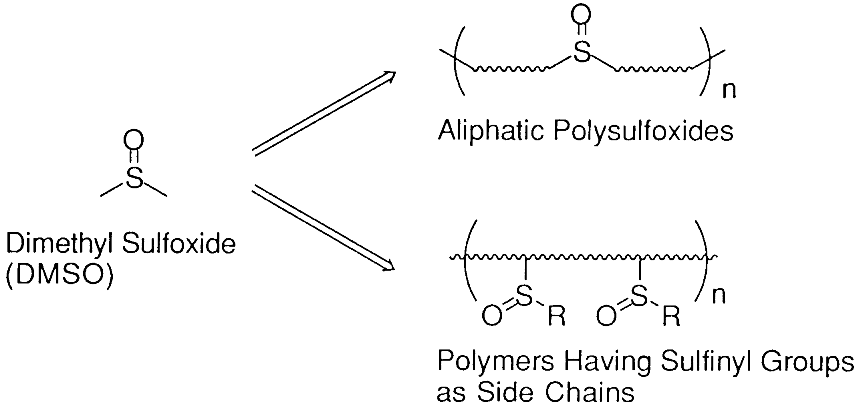
* Corresponding author

Scheme 2

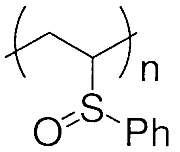


R^1 = $-CH_2CH_2-$, $-CH_2OC_6H_4OCH_2-$, $-C_6H_4-$,
R^2 = $-(CH_2)_n-$ (n=2, 4, 6, 8)

Scheme 3. Possible Designs for Polymer Homologs of DMSO.



possible as the polymer homologs of DMSO as shown in Scheme 3. These new polysulfoxides may have more excellent properties as aprotic polar polymers because their functional groups are stuck out from the main chain and can easily interact with solvents or functional groups of other polymers. Here, we chose poly(phenyl vinyl sulfoxide) **1** as the polymer having sulfinyl groups at side chains (4). The monomer (phenyl vinyl sulfoxide) is easily available and polysulfoxide **1** is already known as the precursor for the synthesis of polyacetylene (4). If polysulfoxide **1** has the properties as the polymer homolog of DMSO, the polymer **1** can be very versatile polymer having many possibilities not only as the precursor but as compatibilizer, polymer solvent and so on. In this paper, synthesis and examination of properties of poly(phenyl vinyl sulfoxide) **1** such as oxidizing ability and miscibility are described.



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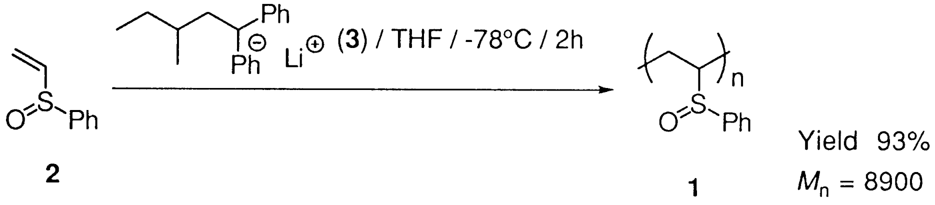
Results and discussion

Poly(phenyl vinyl sulfoxide) **1** as the polysulfoxide having sulfinyl groups at side chains was prepared according to Scheme 4 (4c,4d). Anionic polymerization of phenyl vinyl sulfoxide **2** by using (3-methyl-1, 1-diphenylpentyl)lithium **3** as an initiator afforded the corresponding polysulfoxide **1** in 93% yield. The number average molecular weight of the polymer **1** was 8900 when 1.7mol% of the initiator was used.

Figure 1 shows ^{1}H-NMR spectrum of poly(phenyl vinyl sulfoxide) **1**. Methylene protons were observed around 1.6ppm, methyne proton adjacent to sulfinyl group was

Scheme 4. Anionic Polymerization of Phenyl Vinyl Sulfoxide **2**.



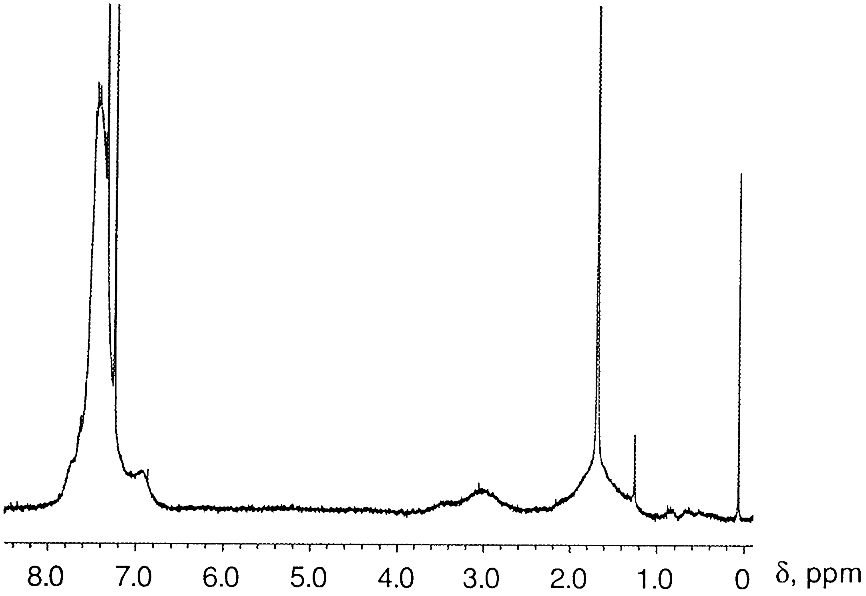
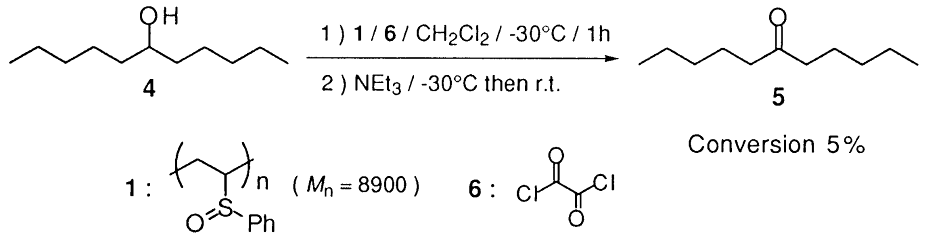


Figure 1. ^{1}H-NMR Spectrum of Poly(phenyl vinyl sulfoxide) **1**.

seen between 2.6 and 3.6ppm, and protons of phenyl group were found around 7.5ppm as previously reported (4b). In IR spectrum, characteristic absorptions for sulfoxide and phenyl groups were observed (see an experimental section).

DMSO is known as an organic oxidizing reagent for oxidation of alkyl halide, alcohols and sulfonates to the corresponding aldehydes or ketones (5-9). We prepared aliphatic polysulfoxides as the polymer homologs of DMSO and revealed, in previous paper, that they oxidized primary or secondary alcohol to the corresponding aldehyde or ketone (2). In order to estimate the ability of poly(phenyl vinyl sulfoxide) as a polymer homolog of DMSO, the oxidation of alcohol to carbonyl compound by using polysulfoxide **1** and oxalyl chloride as an activator (Swern oxidation) was examined. In Swern oxidation, abstraction of α-hydrogen of sulfoxide is necessary, while polysulfoxide **1** has only one α-hydrogen on its main chain (10, 11). Thus, it is anticipated that effective oxidation by poly(phenyl vinyl sulfoxide) **1** is more difficult than the oxidation by aliphatic polysulfoxides. The result is shown in Scheme 5 and, in fact, it was found that polymer **1** had poorer ability of oxidizing alcohols to the corresponding carbonyl compounds than

Scheme 5. Swern Oxidation of 6-Undecanol by Polysulfoxide **1**.



DMSO itself and aliphatic polysulfoxides.

Miscibility with other organic polymers is another important property expected as polymer homologs of DMSO. DMSO is known as a solvent for many organic polymers, especially having polar groups. Similarly, it became clear that aliphatic polysulfoxides have good miscibility with other polymers such as ones having amide groups as side chains (3). On the other hand, miscibility of the polymers having sulfinyl groups at side chains is expected to be higher than the polymers containing sulfoxides in the main chain due to higher degree of freedom of sulfinyl groups. Here, we examined the miscibility of poly(phenyl vinyl sulfoxide) **1**, which shows the glass transition temperature at -17°C, with other organic polymers by a differential scanning calorimetry (DSC) method. Samples for DSC analyses were prepared as described in an experimental section. The resulting sample looked homogeneous and was subjected to DSC analysis at heating rate of 15°C/min. The degree of miscibility was estimated by comparing the glass transition temperature(s) of the mixture of two polymers with those of the original polymers.

Table 1. Miscibility of Polysulfoxide **1** (T_g = -17°C) with Other Polymers.

entry	**1** (wt %)	the other polymer (wt %)		results [a) b)]
1	50	50	Poly(2-methyl-2-oxazoline) M_n=8500, T_g = 67°C	T_g = 33°C
2	20	80		T_g = 20, 42°C
3	80	20		T_g = 18, 54°C
4	50	50	Poly(*N*-vinylpyrrolidone) M_n=10000, T_g = 108°C	T_g = 20°C
5	20	80		T_g = 25, ---°C[c)]
6	80	20		T_g = 20, 48°C
7	50	50	Poly(vinyl acetate) M_n=83000, T_g = 22°C	T_g = 2.6°C
8	20	80		T_g = -12, 20°C
9	80	20		T_g = -23, 18°C
10	50	50	Poly(vinyl chloride) M_n=27000, T_g = 75°C	T_g = 0, 42°C
11	20	80		T_g = 11, 49°C
12	80	20		T_g = -13, 24°C

a) Two polymers were dissolved in the cosolvent and then reprecipitated.
b) Glass transition temperature was determined by DSC.
c) Glass transition temperature was not observed due to decomposition of **1**.

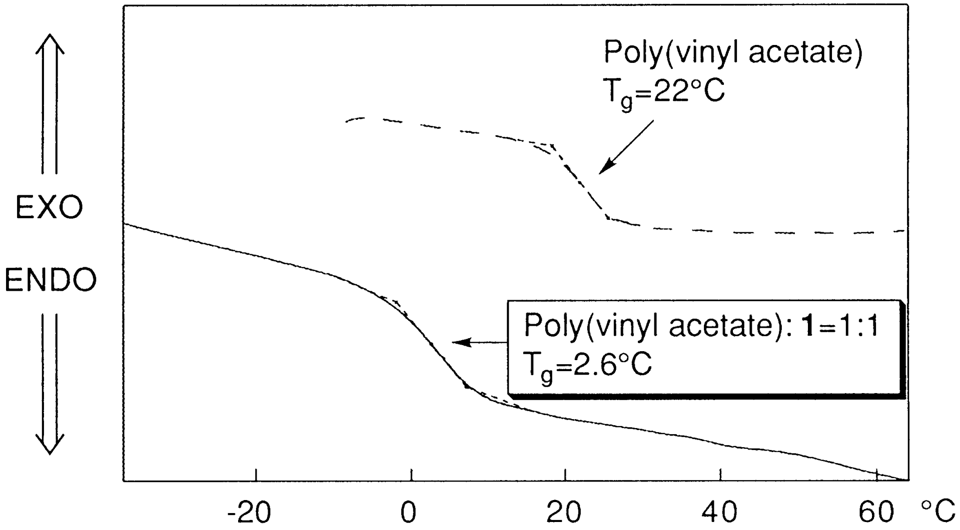


Figure 2. DSC Thermograms of Poly(vinyl acetate) and 1:1 Mixture of Poly(vinyl acetate) with Polysulfoxide **1**.

The results of changes of glass transition temperatures are shown in Table 1. In entries 1, 4 and 7, when the ratio of polysulfoxide **1** to poly (2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone) or poly(vinyl acetate) was 1:1, one glass transition temperature was observed between those of the original polymers. These results show that polysulfoxide **1** has high miscibility with poly(2-methyl-2-oxazoline), poly(*N*-vinylpyrrolidone) and poly(vinyl acetate). It is worth noting that poly(phenyl vinyl sulfoxide) **1** showed good miscibility not only with the polymers having amide groups but also with the polymer containing ester groups, though aliphatic polysulfoxides have good miscibility only with polymers having amide groups as side chains (3). Figure 2 shows DSC thermograms of poly(vinyl acetate) and 1:1 mixture of poly(vinyl acetate) with poly(phenyl vinyl sulfoxide) **1**. Only one glass transition temperature was observed at 2.6°C in DSC thermogram of the mixture. From these thermograms, it is obvious that these two polymers are highly miscible. Thus, it is thought that polysulfoxide **1** has better miscibility than aliphatic polysulfoxides, probably because polysulfoxide **1** has sulfinyl groups as side chains and, as a result, these sulfinyl groups can easily interact with functional groups of the other polymer.

In conclusion, though ability as oxidizing reagent is poorer than DMSO and aliphatic polysulfoxide, poly(phenyl vinyl sulfoxide) **1** prepared by anionic polymerization showed better miscibility with the polymers having amide or ester groups as side chains. These results showed that poly(phenyl vinyl sulfoxide) **1** can be used as a novel polymer homolog of DMSO, besides utilization as the precursor of polyacetylene (4). Good miscibility of polysulfoxide **1** also revealed that polymer homologs of aprotic polar solvent having functional groups as side chains are better designs for synthesis of aprotic polar polymers. Preparations of polymer homologs of other aprotic polar solvents such as hexamethylphosphoramide (HMPA) and *N*,*N*-dimethylacetamide (DMAc) having polar groups at side chains are in progress.

Experimental section

General. All DSC analyses were carried out on a Seiko DSC200 instrument by using about 10mg of exactly weighed samples. ^{1}H-NMR spectra were obtained with a JEOL JNM-EX270 spectrometer (270MHz) in chloroform-*d*. IR spectra were recorded on a Perkin Elmer 1600 spectrometer. Gel permeation chromatographic analyses were carried out on a Tosoh UV-8011 and RI-8000 (Shodex K-803L column) by using chloroform as an eluent after calibration with standard polystyrene samples.

Unless otherwise noted, the materials were obtained from commercial sources and used after distillation under nitrogen. Tetrahydrofuran (THF) was distilled under nitrogen from sodium diphenylketyl and redistilled under argon from lithium aluminum hydride before use. Phenyl vinyl sulfoxide was distilled from CaH_2. *sec*-Butyllithium (solution in cyclohexane) was purchased from Kanto Chemical Co. Poly(vinyl acetate) and poly(*N*-vinylpyrrolidone) were obtained from Aldrich Chemical Co. Poly(2-methyl-2-oxazoline) was prepared by ring-opening polymerization of 2-methyl-2-oxazoline as described in reference (1).

Synthesis of poly(phenyl vinyl sulfoxide) (1). Poly(phenyl vinyl sulfoxide) **1** was prepared as described in reference (4). Under argon atmosphere, *sec*-butyllithium (solution in cyclohexane, 1.13N) was slowly added to a solution of 1,1-diphenylethylene (73.5μl, 0.42mmol) in 17.5ml of THF until the red color of solution remained at least for 15 min. Then, another 0.37ml (0.42mmol) of *sec*-butyllithium was added and the solution was cooled to -78°C. Phenyl vinyl sulfoxide (3.37ml, 25.2mmol) was added to the solution and the mixture was stirred at -78°C for 2 hours. The reaction was quenched by addition of methanol. Then the solution was allowed to warm to room temperature and poured into large amount of diethyl ether to give a pale brown solid. By subsequent filtration and freeze-drying, 3.57g (93%) of poly(phenyl vinyl sulfoxide) **1** was obtained. **1**: ^{1}H-NMR(δ, ppm) 1.3-2.2($-CH_2-$, br, 2H), 2.8-3.6(-CH-, br, 1H), 6.9-7.8($-C_6H_5$, br, 5H); IR(neat) 3054, 2919, 1655, 1477, 1443, 1086, 1043, 998, 749, 691cm^{-1}. In order to avoid gradual change to polyacetylene, the obtained polymer was stored under -20°C (4).

Oxidation of 6-undecanol by poly(phenyl vinyl sulfoxide) (1). To a solution of **1** (0.274g, 1.8mmol of S=O unit) in dichloromethane (5ml) was added oxalyl chloride (78.5ml, 0.90mmol) at -30°C. The mixture was stirred for 10 minutes and a solution of 6-undecanol (0.103g, 0.6mmol) in dichloromethane (1ml) was added. Stirring was continued for additional 1 hour. Triethylamine (0.418ml, 3.0mmol) was added and the reaction mixture was stirred for 20 minutes and then allowed to warm to room temperature. Aqueous ammonium chloride was added and the mixture was extracted with CH_2Cl_2. The organic layers were combined, washed with saturated aqueous NaCl solution and dried over anhydrous $MgSO_4$. The solvent was evaporated, and the resulting residue was dissolved in chloroform and poured into large amount of n-hexane to give a pale brown solid. The supernatant was collected and evaporated to give the mixture of 6-undecanone with the reactant (6-undecanol). By comparing the integral of the peak at 2.38ppm corresponding to methylene protons adjacent to carbonyl group of 6-undecanone with that of the peak at 3.59ppm corresponding to methyne proton next to hydroxyl group in ^{1}H-NMR spectrum of the mixture, conversion and yield of this reaction were found to be 5% and 93%, respectively.

Differential scanning calorimetry analyses. Samples for DSC analyses were prepared as follows: A mixture (0.10g) of polysulfoxide **1** with commodity polymer at a desired ratio was dissolved in small amount of chloroform. The solution was then reprecipitated into large amount of n-hexane to give a pale brown solid. After filtration and freeze-drying of the mixture, the resulting solid was dried *in vacuo* and the sample was obtained as a pale brown powder or gum. In samples with poly(vinyl chloride), *N*,*N*-dimethylformamide was used as a solvent and the mixture was reprecipitated into methanol.

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