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Minoru Senga[a]; Shuji Kondo[a]; Kazuichi Tsuda[a]
[a] Nagoya Institute of Technology Gokisocho, Showa-ku Nagoya, Japan

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# Synthesis and Free-Radical Polymerization of a Vinyl Monomer Containing Sulfilimine Structure

MINORU SENGA, SHUJI KONDO, and KAZUICHI TSUDA

Nagoya Institute of Technology
Gokisocho, Showa-ku
Nagoya 466, Japan

## ABSTRACT

N-Tosyl-S-methyl-S-4-vinylphenylsulfilimine (VPSI) was synthesized by the reaction of methyl 4-vinylphenyl sulfide and chloramine-T in 58% yield. This monomer was readily homopolymerized in DMSO by AIBN at 60°C. The polymer obtained was soluble in chloroform and DMSO, but insoluble in petroleum ether, benzene, ether, acetone, methanol, and water. The inherent viscosity of this homopolymer was 0.71 dL/g in DMSO. This sulfilimine monomer copolymerized with styrene, methyl methacrylate, acrylonitrile, and acrylamide under radical conditions. From the results of copolymerization with styrene, copolymerization parameters were obtained as $r_{VPSI} = 0.95$, $r_{St} = 0.25$, $Q_{VPSI} = 1.54$, $e_{VPSI} = 0.40$. Further, this homopolymer was treated with hydrochloric acid to give sulfoxide polymer.

## INTRODUCTION

Considerable attention has recently been given to sulfoxide polymers as functional polymers [1-5]. Sulfilimine and sulfoxide have an isoelectric semipolar bond, and both have electrophilic sulfur and nucleophilic oxygen or nitrogen adjacent to a sulfur atom [6]. Therefore,

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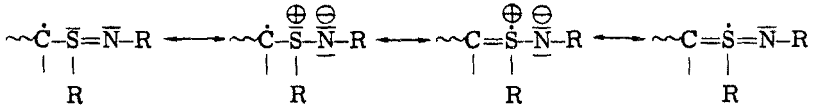
sulfilimine polymer is expected to work as a functional polymer as well as a sulfoxide polymer.

In 1974, Kise et al. [7] first reported the preparation of sulfilimine polymer by the reaction of poly(4-vinylbenzyl alkyl sulfide) with chloramine-T. Further, they prepared the sulfilimine polymer by the radical polymerization of N-tosyl-S-alkyl-S-vinylbenzylsulfilimine. Preparation of S-vinylsulfilimine and polymerization by n-butyllithium was carried out by Okawara et al. [8]. This reaction was performed in 30% yield, accompanied by some monomeric products.

However, the polymerizability of sulfilimine monomer under radical conditions has not yet been studied.

The substituent effect of the sulfilimine group in radical polymerization is interesting in relation to 3d orbital resonance because the lone pair of sulfilimine sulfur in a propagating species can participate in electron sharing resonance as well as with divalent sulfur as shown by



$$\sim\!\sim\underset{|}{\overset{\bullet}{C}}-\underset{\substack{|\\ R}}{\bar{S}}=\bar{N}-R \longleftrightarrow \sim\!\sim\underset{|}{\overset{\bullet}{C}}-\underset{\substack{|\\ R}}{\overset{\oplus}{\bar{S}}}-\overset{\ominus}{\underline{\bar{N}}}-R \longleftrightarrow \sim\!\sim\underset{|}{C}=\underset{\substack{|\\ R}}{\overset{\oplus}{\dot{S}}}-\overset{\ominus}{\underline{\bar{N}}}-R \longleftrightarrow \sim\!\sim\underset{|}{C}=\underset{\substack{|\\ R}}{\dot{S}}=\bar{N}-R \qquad (1)$$

In general, participation of 3d orbital resonance in radical polymerization is assumed because of the Q value. Therefore, in order to clarify this effect, a vinyl monomer which has a ylide sulfur at the vinylic position or the 4-position of styrene is desirable. Although N-tosyl vinylsulfilimine has been reported [8], we did not use this compound because the free-radical polymerization of a vinyl sulfonium salt carrying bulky groups at vinylic position does not correctly reflect the resonance effect in the Q value [9].

We therefore prepared N-tosyl-S-methyl-S-4-vinylphenylsulfilimine (VPSI) and studied the free-radical polymerization of this sulfilimine monomer. Interconversion of polysulfilimine to sulfoxide polymer was also examined.

## EXPERIMENTAL

### Preparation of VPSI

A solution of methyl 4-vinylphenyl sulfide (1.65 g, 10 mmol) in 20 mL of methanol was added to a solution of chloramine-T (3.10 g, 11 mmol) in 20 mL of methanol at room temperature. The mixture was permitted to stand at 50°C for 3 h and poured into a cold, dilute sodium hydroxide solution. The oily product was extracted with 30 mL of chloroform. The chloroform layer was washed with water, dried, and the solvent was removed. The residue was then washed with ether. The crude product was recrystallized by an acetone/n-hexane mixture. The yield was 1.94 g (58%), mp 94-95°C; $\lambda_{max}$ = 261 nm ($\epsilon$ = 22,500) in ethanol.

Analysis: Calculated for $C_{16}H_{17}NO_2S_2$: C, 60.17; H, 5.33; S, 20.06%. Found: C, 60.51; H, 5.17; S, 19.84%.

### Other Reagents

Styrene, methyl methacrylate, and acrylonitrile, used as comonomers, were purified by ordinary methods and distilled under nitrogen just before polymerization. Acrylamide was purified by recrystallization from benzene. 2,2'-Azobisisobutyronitrile (AIBN) used as an initiator was recrystallized twice from methanol. Other reagents and solvents were used after purification.

### Polymerization Procedure

Polymerization was carried out in a sealed glass tube with shaking in a thermostat maintained at constant temperature. The charging of the reagents into an ampule and its sealing were undertaken according to a similar method reported previously [10].

After polymerization for a given time, the tube was opened and its content was poured into a large amount of methanol to precipitate the polymer formed. The resulting polymer was purified by reprecipitation from methylene chloride into excess ether. Conversion was calculated from the weight of the dry polymer obtained.

Copolymerization was carried out by the same method as mentioned previously. The composition of the copolymers was calculated from elementary analysis of sulfur by the Wagner method using arsenazo III as an indicater. Monomer reactivity ratios were obtained by the Fineman-Ross method.

### Conversion of Poly(VPSI) to Poly(methyl 4-vinylphenyl Sulfoxide)

The sulfilimine polymer poly(VPSI) (0.48 g) was stirred with 35% of hydrochloric acid (10 mL) in 35 mL of dioxane. The mixture was stirred for 5 d at 55°C. Then a 10% sodium carbonate solution was added until the pH of the solution became 8-9. The resulting solid was washed several times with water and dried in vacuum. The yield was 0.26 g. The IR spectrum of this polymer is shown in Fig. 1.

Analysis: Calculated for $(C_9H_{10}OS)_n$: C, 65.06; H, 6.02; S, 19.94%. Found: C, 65.44; H, 6.24; S, 20.20%.

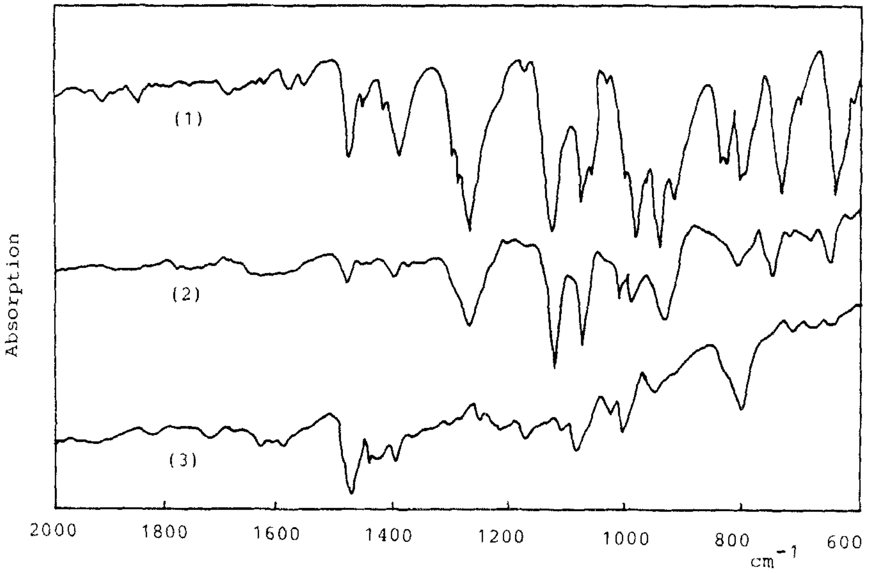


FIG. 1. IR spectra of (1) VPSI, (2) poly(VPSI), and (3) poly(methyl 4-vinylphenyl sulfoxide) obtained from the hydrolysis of poly(VPSI).

### Instruments

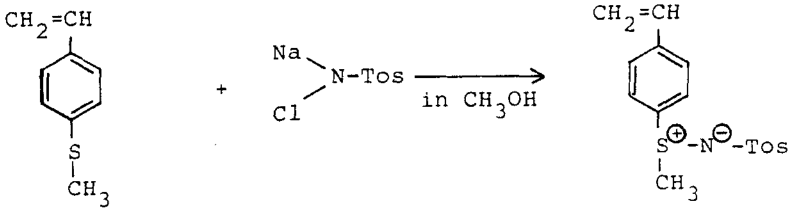
IR spectra were recorded on a Jasco IRA-2 spectrometer. NMR spectra were recorded in $CDCl_3$ on a 60 MHz Hitachi R-20B spectrometer using tetramethylsilane as an internal standard. UV spectra were measured by Hitachi 124 spectrometer.

## RESULTS AND DISCUSSION

### Preparation of Sulfilimine Monomer (VPSI)

Many methods for the preparation of sulfilimine have been developed [11]. In this work, we employed the reaction of sulfide with chloramine-T because of the ease of the workup procedure and the stability of the resulting compound. Monomer VPSI was prepared as shown in Eq. (2) where Tos = p-toluenesulfonyl.

The monomer was obtained as a white solid in 58% yield. This compound is stable in air at room temperature for several months. The IR spectrum of VPSI is shown in Fig. 1, in which characteristic absorption



bands are observed at 950 ($\nu_{S=N}$) and 920 cm$^{-1}$ (terminal methylene). Figure 2 shows the NMR spectrum of VPSI with signals at $\delta$ = 2.35 (methyl protons), 2.85 (S-methyl protons), 5.39 and 5.81 (methylene protons), 6.72 (methylene proton), and 7.0-7.9 ppm (phenyl protons). These spectral results confirm the structure of VPSI.

## Polymerizations of VPSI

Polymerizations of VPSI were carried out under various conditions, and the results are shown in Table 1. VPSI polymerized readily by

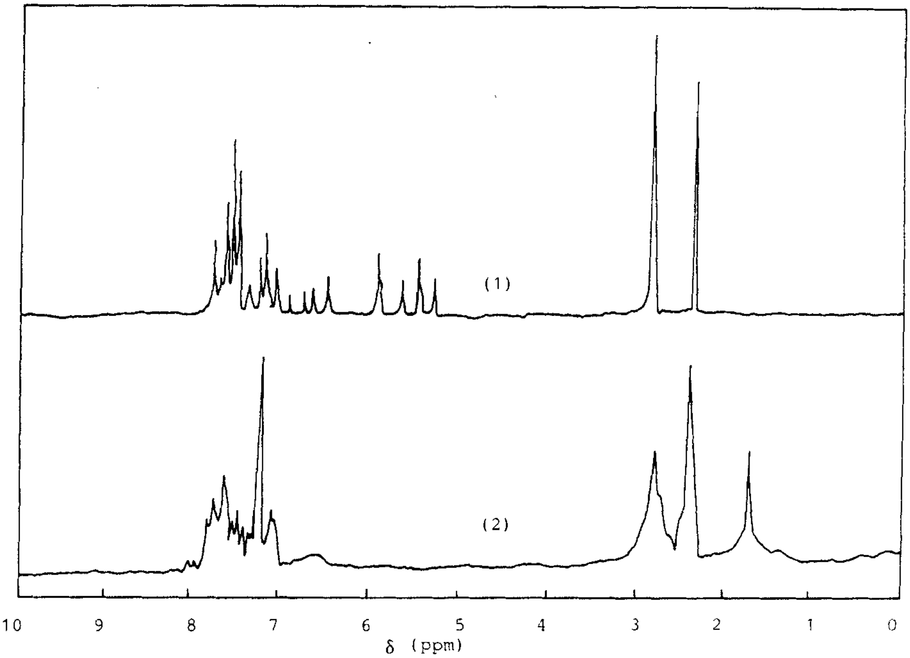


FIG. 2. NMR spectra of (1) VPSI and (2) poly(VPSI).

TABLE 1. Polymerization of VPSI in DMSO[a]

| Initiator (mol/L) | Temperature (°C) | Time (h) | Yield (%) | $\eta^b$ |
|---|---|---|---|---|
| AIBN ($1 \times 10^{-2}$) | 60 | 20 | 96 | 0.71 |
| UV | 20 | 20 | 25 | 1.30 |
| UV/AIBN ($1 \times 10^{-2}$) | 20 | 20 | 55 | 0.80 |

[a] Polymerization conditions: [VPSI] = 1 mol/L.
[b] Inherent viscosity was measured in DMSO at 30°C.

AIBN at 60°C in DMSO to yield a white solid with an intrinsic viscosity of 0.71 dL/g. It was soluble in chloroform and DMSO, but insoluble in petroleum ether, benzene, ether, acetone, methanol, and water. The IR and NMR spectra of the polymer are shown in Figs. 1 and 2, respectively.

In the IR spectrum, the characteristic absorption band at 920 $cm^{-1}$, based on the vinyl group, disappeared. In the NMR spectrum the peaks at 5.39, 5.81, and 6.72 ppm, based on olefinic protons, disappeared, and a new peak at 1.73 ppm, based on a methylene proton, was observed. It is therefore clear that VPSI polymerized by an ordinary vinyl polymerization mechanism.

VPSI polymer was also obtained by photopolymerization and AIBN photosensitized polymerization.

## Copolymerization with Several Vinyl Monomers

VPSI was copolymerized with methyl methacrylate, styrene, acrylamide, and acrylonitrile in the presence of AIBN at 60°C. The copolymers obtained were confirmed by IR spectra. The results are summarized in Table 2.

In order to clarify the substituent effect of sulfilimine in radical polymerization, copolymerization of VPSI with styrene in DMSO was investigated in detail. The results are shown in Table 3. The composition of the copolymers was calculated from their sulfur content. Figure 3 shows the monomer-copolymer composition curve.

The monomer reactivity ratio was computed from the copolymerization of VPSI and styrene according to the Fineman-Ross method as $r_{VPSI} = 0.95$, $r_{St} = 0.25$. From these values of the monomer reactivity ratio for this copolymerization, the resonance stabilization factor Q and the electrical factor e were calculated as $Q_{VPSI} = 1.54$, $e = 0.40$. Q and e values of compounds analogous to VPSI are shown in Table 4.

As can be seen from Table 4, the Q value of VPSI is a little larger

TABLE 2. Copolymerization of VPSI with Several Vinyl Monomers at 60°C (solvent: DMSO)

| Comonomer[a] | Time (h) | Conversion (%) | $m_1$[b] |
|---|---|---|---|
| Methyl methacrylate | 20 | 75.4 | 0.57 |
| Styrene | 0.75 | 4.7 | 0.62 |
| Acrylamide | 20 | 76.9 | 0.78 |
| Acrylonitrile | 20 | 81.4 | 0.64 |

[a] Equimolecular VPSI and comonomer were used.
[b] Mole fraction of VPSI in copolymer.

TABLE 3. Copolymerization of VPSI ($M_1$) and Styrene ($M_2$)[a]

| $M_1$[b] | Time (min) | Conversion (%) | S (%) | $m_1$[c] |
|---|---|---|---|---|
| 0.113 | 90 | 4.77 | 8.32 | 0.186 |
| 0.197 | 75 | 4.20 | 12.33 | 0.381 |
| 0.346 | 60 | 7.57 | 14.65 | 0.469 |
| 0.438 | 60 | 9.18 | 16.32 | 0.586 |
| 0.485 | 45 | 4.65 | 16.74 | 0.622 |
| 0.639 | 40 | 6.51 | 17.64 | 0.704 |
| 0.789 | 30 | 6.49 | 18.90 | 0.841 |

[a] Copolymerizations were carried out in DMSO; $[M_1] + [M_2] = 1$ mol/L, $[AIBN] = 1 \times 10^{-3}$ mol/L.
[b] Mole fraction of $M_1$ in monomer mixture.
[c] Mole fraction of $M_1$ in copolymer.

than that of styrene and smaller than that of the corresponding sulfide. The larger Q value of 4-alkylthiostyrene than those of styrene and 4-alkoxystyrene is the result of 3d-orbital resonance [9]. Therefore, these results indicate that the sulfilimine group participates slightly in the electron-sharing resonance of the propagating species as shown in Eq. (1).

On the other hand, Otsu et al. [12] previously reported that a linear relationship exists between log Q and $\lambda_{max}$ for the $\pi$-$\pi^*$ transition of vinyl monomers. According to their proposal, the $\lambda_{max}$ of VPSI is expected to be a little longer than that of 4-methoxystyrene because the Q value of VPSI is a little larger than that of 4-methoxy-

TABLE 4. Q Value and $\lambda_{max}$ of p-Substituted Sulfur-Containing Styrenes

| Substituent | Q | $\lambda_{max}$ | Ref. |
|---|---|---|---|
| $-H$ | 1.0 | 249 | 13 |
| $-OCH_3$ | 1.36 | 275 | 13 |
| $-SCH_3$ | 2.58 | 283 | 9 |
| $-SOCH_3$ | 1.19 | 262 | 5 |
| $-S^{\oplus}(CH_3)_2$ | 1.63 | 262 | 9 |
| $-\underset{\displaystyle CH_3}{\underset{\vert}{S^{\oplus}}}-N^{\ominus}-Tos$ | 1.54 | 261 | This work |

$^a\lambda_{max}$ was measured in ethyl alcohol.

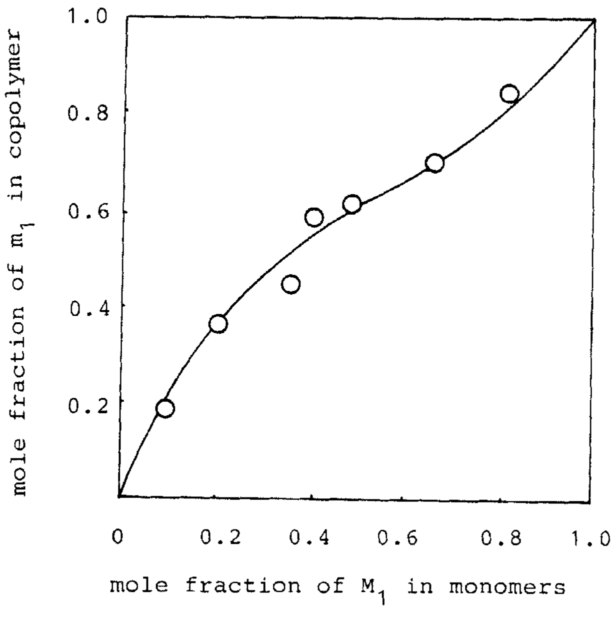


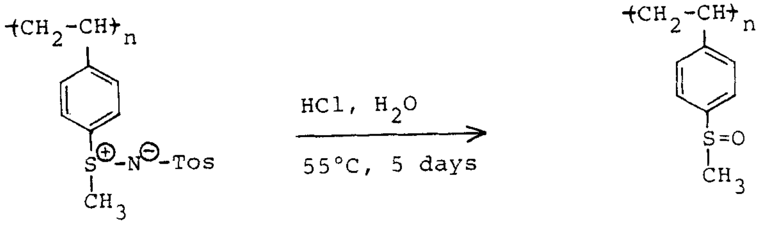
FIG. 3. Monomer-copolymer composition curve of VPSI ($M_1$) and styrene ($M_2$).

styrene. However, as can be seen from Table 4, $\lambda_{max}$ of VPSI is similar to that of 4-sulfinylstyrene which does not have electron-sharing participation in the propagating species.

From the data of Q value and $\lambda_{max}$ of these monomers, it may be concluded that the sulfur of VPSI participate slightly in 3d orbital resonance in radical polymerization. The positive e value of VPSI is reasonable because of the strong electron-withdrawing character of the sulfilimine group.

## Conversion of VPSI to Poly(methyl 4-Vinylphenyl Sulfoxide)

Previously Cram et al. [14] reported that N-tosyl-S diphenylsulfilimine was treated with hydrochloric acid to give diphenyl sulfoxide quantitatively. Therefore, this reaction was applied to VPSI polymer. Treatment of VPSI with hydrochloric acid for 5 d yielded Polymer II. The IR of Polymer II shows a new absorption at 1040 cm$^{-1}$ based on sulfoxide, but does not show the characteristic absorption band of S=N at 950 cm$^{-1}$ (Fig. 1). Further, the IR spectrum is in good agreement with that of poly(methyl 4-vinylphenyl sulfoxide) [5] which was prepared by the radical polymerization of the corresponding vinyl monomer. This result indicates that the sulfilimine structure was completely hydrolyzed to sulfoxide as follows:



(II)

On the other hand, N-tosyl-S-methyl-S-phenyl sulfilimine as a model compound of VPSI was not hydrolyzed under these condition. The significant difference of the reactivity between the polymer and the model compound is interesting. This point is being studied in our laboratory.

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