Polymer Reagents Derived from Sodium *p*-Styrenesulfonate: *N*-Methyl-*N*-nitroso-*p*-styrenesulfonamide and *p*-Styrenesulfinic Acid Polymers

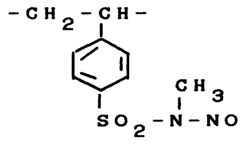
Hiroyoshi KAMOGAWA* and Tomoo KITAMURA
Department of Applied Chemistry, Yamanashi University, Kofu 400

(Received July 25, 1988)

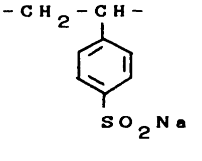
N-Methyl-*N*-nitroso-*p*-styrenesulfonamide (**1**) was synthesized starting with sodium *p*-styrenesulfonate (**3**). Monomer **1** and sodium *p*-styrenesulfinate (**2**), also synthesized starting with **3**, were polymerized and polymer of **2** was converted to corresponding free acid (**9**). The function of polymer of **1** as the reagent attaching the CH_2 group to the carbonyl carbon by insertion and that of polymer **9** as the catalyst for cis→trans isomerization were investigated for various compounds, including cyclohexanone and benzaldehyde and ethyl oleate. The effects of these polymer reagents as compared with those of the corresponding model compounds were discussed.

Sodium *p*-styrenesulfonate, now commercially available, is a versatile reagent for the syntheses of a variety of polymer reagents.[1—4] In the present article, we wish to report the synthesis of *N*-methyl-*N*-nitroso-*p*-styrenesulfonamide (**1**) polymer as a novel polymer reagent, together with *p*-styrenesulfinic acid polymer as a novel polymer catalyst, both being derived from sodium *p*-styrenesulfonate.

Thus, monomer **1** and sodium *p*-styrenesulfinate (**2**) were synthesized and homo- and copolymerized with *N*-vinyl-2-pyrrolidone (VP), respectively, to afford soluble polymers in appropriate solvents. VP was employed here to get copolymers soluble in reaction solvents.



Polymer of 1



Polymer of 2

The CH_2 insertion and cis→trans isomerization reactions with polymer of **1** and the acid form of polymer of **2** were investigated, respectively.

Results and Discussion

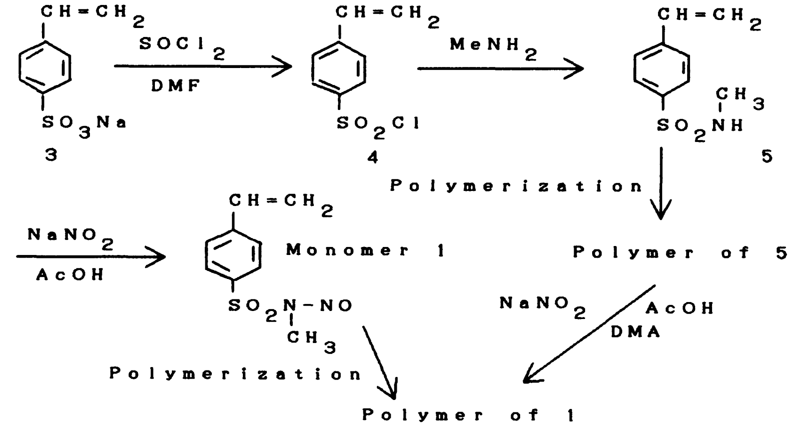
Monomer **1** was synthesized starting with sodium *p*-styrenesulfonate (**3**) in the following manner (Eq. 1).

Compound **4** was synthesized from **3** in a high yield (91%) at 20 °C or below, without danger of polymerization.[1] Addition of an excess of methylamine to **4** provided **5** in a moderate yield (64%). Compound **5** in acetic acid was treated with aqueous sodium nitrite to afford crude monomer **1**. Reprecipitation from benzene–hexane by cooling followed by silica-gel column chromatography provided the purified monomer **1** in 62% yield. Analytical data (^{1}H NMR, IR, mass, and CHN) were all satisfactory.

Monomer **2** was synthesized also starting with **3**, as described in a previous paper.[2]

Monomer **1** was polymerized with α,α′-azobisisobutyronitrile (AIBN) in *N*,*N*-dimethylformamide (DMF) with 72% conversion to afford polymer of **1**, which was soluble in a ternary mixture of *N*,*N*-dimethylacetamide (DMA), ethanol, and water and suitable for the investigation of its function.

Polymer of **1** could also be prepared by means of the polymer reaction using the copolymerization product



(1)

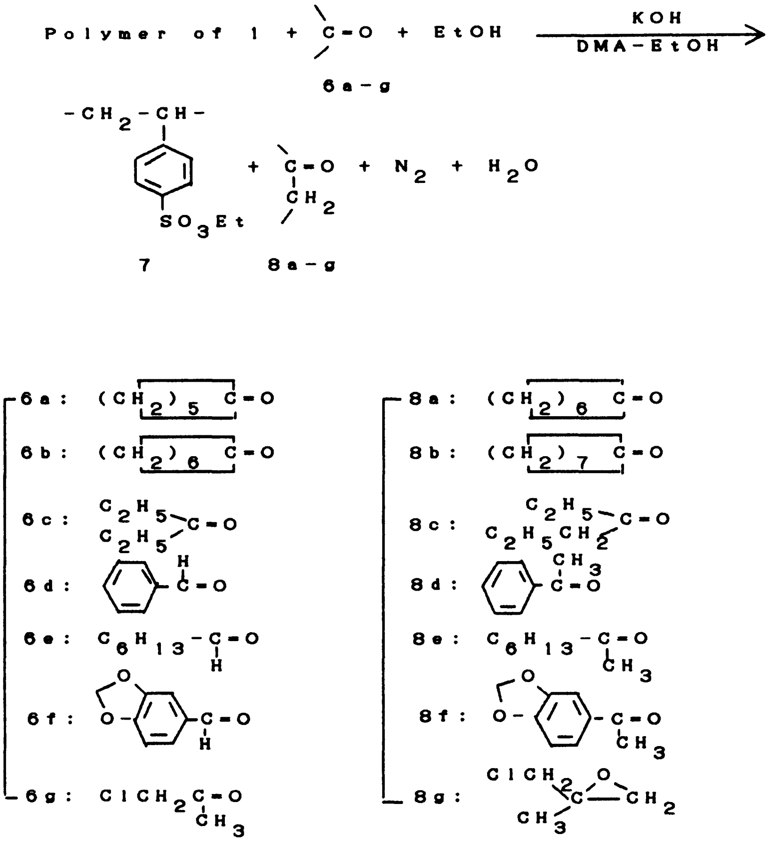
of **5** with VP in DMF (conversion, 70%) and consisting of nitrosation in a mixture of DMA, acetic acid, and water (conversion, 62%), as shown in Eq. 1.

Polymer of **2** was prepared by the copolymerization of **2** with VP in ethanol (conversion, 88%). Polymer of **2** in aqueous solution was converted to its acid form by acidification with concd HCl to produce polymer **9**, which was soluble in dioxane, the cis–trans reaction solvent, and immediately used as catalyst.

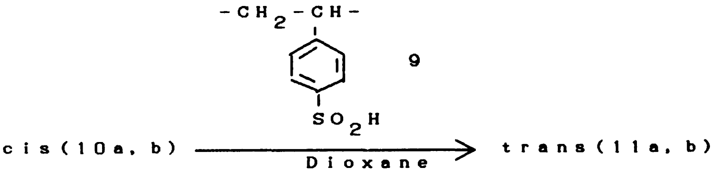
The functions adopted for homopolymer of **1** and polymer **9** were the same as those for the corresponding low-molecular-weight compounds, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide and *p*-toluenesulfinic acid (Eqs. 2 and 3).[5,6] However, separations of polymers **7** and **9** from products were easier.

Conversion from **6a**—**e** to **8a**—**e** and the extent of cis→trans isomerization were determined gas-chromatographically for the purified reaction mixtures, except for **6f**—**8f** and **6g**—**8g** mixtures, in which no standard samples of **8f**,**g** were available and the reaction products (**8f** and **8g**) were identified by IR, mass, and ^{1}H NMR and determined by ^{1}H NMR.

It can be seen in Table 1 that cyclic ketones such as **6a** and **6b** provided particularly low conversions under these conditions, presumably due to the poor accessbility of these bulky ketones to the functional portions of polymer molecules. *N*-Methyl-*N*-nitroso-*p*-toluenesulfonamide, the corresponding low-molecular-weight compound, afforded results similar to those observed for polymer of **1**. **8g**, a different kind of



(2)



(3)

10a: Ethyl oleate
10b: cis-2-Octene

11a: Ethyl elaidate
11b: trans-2-Octene

Table 1. Function of Polymer of **1** According to Eq. 2[a]

Reactant	Product	Conversion/%
6a	**8a**	13(20[b])
6b	**8b**	17(23[b])
6c	**8c**	35(38[b])
6d	**8d**	35
6e	**8e**	65(65[b])
6f	**8f**[c]	67[d]
6g	**8g**[c]	57[d]

a) As for experimental conditions, see Experimental Section. b) For reference sample, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide. c) The identity of the product was determined only by ^{1}H NMR, IR, and mass spectra. d) Determined by ^{1}H NMR.

Table 2. Function of Polymer **9** According to Eq. 3[a]

Reactant	Product	Conversion/%
10a	**11a**	80(83[b])
10b	**11b**	83(88[b])

a) As for experimental conditions, see Experimental section. b) For reference sample, *p*-toluenesulfinic acid, as catalyst.

product from others, was the same as that obtained from **6g** with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide.[5]

Recycle of polymer of **1** could be carried out by the alkaline hydrolysis of polymer **7** to polymer containing **3** units, followed by conversion to polymer containing **1** units, which showed an enough function. This recycle could be repeated at least three times.

Table 2 also shows the results with polymer **9** according to Eq. 3. Conversions obtained with polymer **9** were also similar to those with the corresponding low-molecular-weight compound, *p*-toluenesulfinic acid. In this case, polymer **9** was not appreciably changed during the reaction and could be reused, if properly stored.

It is concluded from these results that, in the cases of the styrene polymers containing *N*-methyl-*N*-nitrososulfonamide and sulfinic acid functional groups, polymers bahave in reactions almost similarly to the corresponding low-molecular-weight reagents, but with more readiness of the separation of products from reagents as well as the possibility of recycling.

Experimental

The infrared (IR), ^{1}H NMR, and mass spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX60 spectrometer, and a Hitachi M808MS spectrometer, respectively, under standard conditions. Elemental analyses were made with a Perkin-Elmer 240 instrument. Gas chromatography was carried out with a Hitachi 164 gas chromatograph fitted with a SE-30 column under helium stream (30 ml min^{-1}).

_N_-Methyl-_p_-styrenesulfonamide (5). A large excess of aqueous methylamine (25%; 10 ml, 80 mmol) was added dropwise to a stirred solution of *p*-styrenesulfonyl chloride (**4**; 4.4 g, 20 mmol), prepared from sodium *p*-styrenesulfonate (**3**) according to the method described in a previous report,[1] in ether (40 ml), cooled with an ice bath. Stirring was continued further for one hour, the resulting reaction mixture was extracted with ether (160 ml), and the organic layer was rinsed with water and dried over anhydrous sodium sulfate, followed by concentration on a rotary evaporator below 40 °C to leave a fluid in 64% yield. Found: C, 54.70; H, 5.65; N, 6.91%. Calcd for $C_9H_{11}NSO_2$: C, 54.75; H, 5.58; N, 7.09%. IR ($CHCl_3$) 3400 (NH), 1320, 1140 (SO_2), 990, 910 (vinyl) cm^{-1}. ^{1}H NMR (CCl_4) δ=2.5 (d, 3H, Me), 5.1—5.9 (m, 3H, CH_2=+NH), 6.7 (q, 1H, CH=), 7.5 (q, 4H, ArH). MS m/z 197 (M^+).

_N_-Methyl-_N_-nitroso-_p_-styrenesulfonamide (1). A solution of sodium nitrite (0.84 g, 12 mmol) in water (2 ml) was added dropwise to a stirred solution of **5** (2.0 g, 10 mmol) in acetic acid (10 ml) containing a small quantity of water in an ice bath. Stirring was continued further for one hour. The reaction mixture was poured into aqueous sodium hydrogencarbonate (excess) containing ice, immediately followed by extraction with ether. The organic layer was washed thoroughly with water, dried over anhydrous sodium sulfate, and concentrated on the rotary evaporator to give crude **1**, which was reprecipitated from benzene (or ether)–hexane by cooling down to −20 °C, then subjected to silica-gel column chromatography to afford a purified fluid in 62% yield. Single spot by TLC. Found: C, 47.58; H, 4.46; N, 12.23%. Calcd for $C_9H_{10}N_2SO_3$: C, 47.79; H, 4.42; N, 12.40%. IR ($CHCl_3$) 1560, 1490 (N=O), 1360, 1110 (SO_2), 980 (vinyl) cm.$^{-1}$ ^{1}H NMR ($CDCl_3$) δ=3.2 (s, 3H, Me), 5.8 (q, 2H, CH_2=), 6.7 (q, 1H, CH=), 7.9 (q, 4H, ArH). MS m/z 196 (M^+—NO).

Preparation of Polymer of 1. (a) By Homopolymerization. A solution of monomer **1** (0.5 g) and purified α,α'-azobisisobutyronitrile (AIBN; 0.03 g) in DMF (1 ml) was put into a glass ampule, which was evacuated and sealed in the conventional manner. The ampule was then let stand at 50 °C for 72 h to effect polymerization. The content of the ampule was poured into a large amount of ether to afford precipitate in 72% conversion. $[\eta]$=0.06 dl g^{-1} (DMF, 25 °C). IR for polymer of **1** deposited on a KRS cell indicated the absorptions characteristic of the *N*-methyl-*N*-nitrososulfonamide portion of polymer, together with those at 2930—2860 cm^{-1} attributable to the vinyl polymer backbone.

(b) By Polymer Reaction Using Polymer of 5. Alternatively, polymer of **1** was prepared by a polymer reaction applied to polymer of **5**.

(i) Polymer of 5. A solution of **5** (1.0 g, 5 mmol), VP (10.0 g, 92 mmol), and AIBN (0.5 g) in DMF (20 ml) was gently stirred at 80 °C for 48 h under a nitrogen atmosphere. The resulting solution was diluted with DMF and poured into ether to afford precipitate in 70% conversion. $[\eta]$=0.21 dl g^{-1} (DMF, 25 °C). IR was satisfactory and the **5** to VP ratio in copolymer was 1:5.5 from the result of elemental analysis.

(ii) Polymer Reaction. To the stirred solution of polymer of **5** (5 g), prepared above, in a mixture of DMA (10 ml) and acetic acid (5 ml) cooled with an ice bath was added dropwise a solution of sodium nitrite (0.42 g, 6 mmol) in water (1 ml), followed by stirring for 2 h. The reaction mixture was precipitated into ether to afford a sticky solid. IR was satisfactory and the conversion calculated from the results of elemental analysis was 62%.

Preparation of Polymer 9. (a) Polymer of 2. A solution of sodium *p*-styrenesulfinate (**2**; 0.2 g), prepared also starting with **3** as reported in a previous paper,[2] VP (1.0 g), and AIBN (0.06 g) in ethanol (2 ml) was put into an ampule, which was evacuated and sealed in the conventional manner and let stand at 70 °C for 72 h. The resulting viscous solution was precipitated into ether to afford polymer of **2** in 88% conversion. $[\eta]$ in water at 25 °C was 0.78 dl g^{-1} and the **2**/VP ratio in copolymer was 0.17 from elemental analysis.

(b) Polymer 9. A solution of polymer of **2** (0.5 g) prepared above in a small amount of water was acidified with concd HCl to afford precipitate, which was dried under reduced pressure (yield, 29%) and employed immediately for the reaction indicated in Eq. 3.

Function of Polymer of 1 According to Eq. 2. To a solution of polymer of **1** (0.5 g, 2 mmol), prepared by homopolymerization of monomer **1** as described above, in DMA (5 ml) were added with vigorous stirring ethanol (5 ml) and a carbonyl compound (**6a—g**; 2 mmol). To the resulting solution cooled in an ice bath, a solution of potassium hydroxide (0.2 g) in water (5 ml) was further added dropwise, followed by 3-h stirring of the resulting alkaline mixture below 20 °C. The reaction mixture was poured into an ice-water mixture, followed by ether extraction and conventional work up to afford a sample for gas chromatography. Polymer **7** remaining after the ether extraction as insoluble residue was hydrolyzed with 1 mol l^{-1} NaOH at 20 °C overnight to afford polymer of **3**, which was subjected to a reaction sequence analogous to that in Eq. 1 to recover polymer of **1**.

The position of peaks and their areas in the gas chromatograms of samples (column temperature: 80—100 °C) were compared with those of standard compounds to determine the **6a—e**→**8a—e** conversions. The results thus obtained are satisfactory and shown in Table 1. In the cases of **6f—g**→**8f—g** combinations, no standard compounds of **8f** and **8g** were available, so that quantitative comparison was not made by GC, but made by ^{1}H NMR. Conversions using a low-molecular-weight compound, *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, instead of polymer of **1**, were also determined and compared with the results obtained with polymer.

The result of recycle or polymer was 12 (1st), 10 (2nd), and 10% (3rd) in conversion for **6a**→**8a** in Table 1.

Function of Polymer 9 According to Eq. 3. A solution of polymer **9** (2.4 g, 2 mmol as $-SO_2H$), prepared above and a cis compound (**10a,b**; 2 mmol) in dry dioxane (10 ml) was heated under nitrogen stream. Reaction temperatures and times were 100 °C and 1 h and 70 °C and 6 h, respectively. Upon cooling, the reaction mixture was diluted with hexane to precipitate polymer **9**, which was removed by filtration and ready to another use. The filtrate was washed twice with sat. aq. NaCl, dried over anhyd. $MgSO_4$, and concentrated on a rotary evaporator to leave a sample for gas chromatography. The comparison of the positions and areas of peaks in the gas chromatogram with those for the corresponding standard compound was successfully done and provided the **10a,b**→**11a,b** conversion. The results thus obtained are shown in Table 2, in which the results with *p*-toluenesulfinic acid instead of polymer **9** are also given. Column temperatures were 210 and 80 °C for samples **10a** and **10b**, respectively.

The result of recycle of polymer was 75 (1st), 74 (2nd), and 70% (3rd) in conversion for **10a**→**11a** in Table 2.

References

1) H. Kamogawa, A. Kanzawa, M. Kadoya, T. Naito, and M. Nanasawa, *Bull. Chem. Soc. Jpn.*, **56**, 762 (1983).

2) H. Kamogawa and K. Maeda, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 1393 (1984).

3) H. Kamogawa, Y. Haramoto, Y. Misaka, Y. Asada, Y. Ohno, and M. Nanasawa, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 1517 (1985).

4) H. Kamogawa and T. Sueki, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 1963 (1985).

5) C. D. Cutsche, "Organic Reactions, VIII," Wiley, New York (1954), p. 365.

6) T. W. Gibson and P. Strassburger, *J. Org. Chem.*, **41**, 791 (1976).