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PREPARATION OF POLYSTYRENES CONTAINING SULFONAMIDE MOIETIES AND THEIR USE AS PHASE TRANSFER CATALYSTS

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ABSTRACT

Styrenes containing sulfonamide moieties such as *N*-methyl-*N*-(*p*-vinylbenzyl)methanesulfonamide and *N,N*-dimethyl-*p*-styrene-sulfonamide were prepared. The copolymerization parameters of these monomers were obtained from copolymerization with styrene under free radical conditions. Crosslinked polymers prepared by free radical terpolymerization of the sulfonamide monomer, styrene, and divinylbenzene served as phase transfer catalysts for the reaction of *n*-octyl bromide with sodium thiophenoxide in the toluene–water system. However, the corresponding monomeric sulfonamides were practically inactive. These polymer catalysts were stable even under strongly alkaline conditions, and the recovered catalysts were used without a significant loss in activity.

INTRODUCTION

Polymeric analogs of dipolar aprotic solvents such as dimethyl sulfoxide, sulfolane, *N,N*-dimethylformamide, *N,N*-dimethylacrylamide, *N*-methylpyrrolidone, hexamethylphosphoramide, and tetramethylurea have recently been found to display catalytic activity in two-phase reactions, although the monomeric analogs are practically inactive [1–4]. We believe that the main essence of the catalytic activity of these polymers is their ability to extract alkali metal ions by means of chelation, and to activate the anions by a hydrophobic microenvironment around the active sites [5–10].

Among these polymers, polymeric carboxamides such as polymeric formamides and acetamides are not stable under strongly alkaline conditions [7, 11–13]. On the other hand, it is well known that sulfonamides are less reactive to alkaline hydrolysis than carboxamides. Moreover, Richey and Farkas recently reported that *N,N*-dialkylsulfonamides possess a significant dipolar aprotic solvent character [14].

From these facts we hoped that polymeric sulfonamides might work as phase transfer catalysts even under strongly alkaline conditions. This article describes the preparation of polystyrenes containing sulfonamide moieties and examines the catalytic activity of these polymers in phase transfer reactions.

EXPERIMENTAL

Materials

Styrene, divinylbenzene, *n*-octyl bromide, thiophenol, and solvents were used after distillation. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. *p*-Chloromethylstyrene [15] and *p*-styrenesulfonyl chloride [16] were prepared by methods described previously. The other reagents were obtained commercially and used without further purification.

Preparation of *N*-Methyl-*N*-(*p*-vinylbenzyl)methanesulfonamide (MVSA)

To a slurry of 14 g (0.35 mol) sodium hydride (60%, oil suspension) and 500 mL *N,N*-dimethylformamide (DMF) was added 28.4 g (0.26 mol) *N*-methylmethanesulfonamide in DMF (30 mL); the mixture was stirred under nitrogen at room temperature for 3 h. To this mixture 30.8 g (0.2 mol) *p*-chloromethylstyrene was added dropwise over 1 h at 0°C. After stirring for 12 h at room temperature, the mixture was filtered. The residue resulting after solvent removal was poured into 50 mL water and extracted three times with 10 mL methylene chloride. The organic layer was washed with 2% hydrochloric acid, followed by washing with water, and dried with anhyrous sodium sulfate. After solvent removal the product was recrystallized with a solution of methylene chloride and petroleum ether. The yield was 31.5 g (70%); mp 67–68°C. NMR (in $CDCl_3$): δ = 2.75 (s, 3H), 2.92 (s, 3H), 4.28 (s, 2H), 5.25 (dd, 1H), 5.74 (dd, 1H), 6.75 (dd, 1H), and 7.29 ppm (m, 4H). IR: $\nu_{C=C}$ = 920 and 980 cm^{-1}, $\nu_{S=O}$ = 1150 and 1330 cm^{-1}.

Analysis Calculated for $C_{11}H_{15}NO_2S$: C, 58.64; H, 6.71; N, 6.22; S, 14.23%. Found: C, 58.87; H, 6.88; N, 6.22; S, 14.59%.

Preparation of *N,N*-Dimethyl-*p*-styrenesulfonamide (DMSA)

To a solution of *p*-styrenesulfonylchloride (19.5 g, 0.45 mol) in chloroform (300 mL) was introduced dimethylamine which was produced by the reaction of dimethylamine hydrochloride (98 g, 1.2 mol) and 50% aqueous sodium hydroxide (200 g) at 0°C. The mixture was stirred for 12 h at room temperature, and the resulting solid was filtered off. Evaporation of the solvent from the filtrate gave a white solid. The solid was recrystallized with ethanol and further recrystallized twice with petroleum ether. The yield was 51 g (54%); mp 62–63°C (literature [17], 63–63.5°C). NMR (in $CDCl_3$): $\delta = 2.69$ (s, 6H), 5.42 (dd, 1H), 5.86 (dd, 1H), 6.80 (dd, 1H), and 7.63 ppm (m, 4H).

Polymerization Procedure

Polymerization was carried out in a sealed tube with shaking thermostated at 60°C. Charging of the reagents into an ampule and sealing of the ampule were undertaken according to a method reported previously [18]. The tube was opened after polymerization, and its contents were poured into a large amount of methanol to precipitate the polymer. The resulting polymer was purified by reprecipitation from methylene chloride into methanol. Copolymer composition was evaluated from the sulfur content.

Preparation of Catalysts

A procedure similar to that described below was used for preparing all the polymers employed in this article. A mixture of MVSA (2.25 g), styrene (1.04 g), commercial divinyl-benzene containing 45% ethylbenzene and diethylbenzene (52.1 g), AIBN (33 mg), and benzene (15 mL) was charged into a glass tube which was then degassed under vacuum by the conventional freezing-and-thawing technique and sealed off under vacuum. The tube was heated at 60°C for 48 h. The resulting gel was isolated by filtration. The gel was extracted in a Soxhlet for 30 h by using chloroform as the solvent and then dried. The yield of copolymer (3c) was 1.68 g. The copolymer composition was evaluated from the sulfur content. The divinylbenzene content of the copolymer was assumed to be identical to its content in the feed.

Kinetics

A typical rate experiment was carried out as follows. To a 50-mL round-bottomed flask equipped with a reflux condenser was added 0.55 *M* *n*-octyl bromide, 0.25 *M* *n*-dodecane as internal standard in toluene (5 mL), and a catalyst containing 0.5 mmol sulfonamide unit. The mixture was heated at 100°C for 1 h with stirring. Then 2.0 *M* sodium thiophenoxide in water (15 mL) was added at zero time. The reaction was followed by GLC analysis (Silicone SE-30 20% over Celite 545 at 140°C), and the results were corrected by calibration with standard mixtures. The pseudo-first-order rate constants ($k_{\mathrm{obs.}}$) were obtained by plotting the logarithm of the substrate concentration against time and by determining the slope of the straight line. The measurement was repeated at least twice, and the reproducibility was found to be ±10%.

Swelling of the Polymer Catalysts

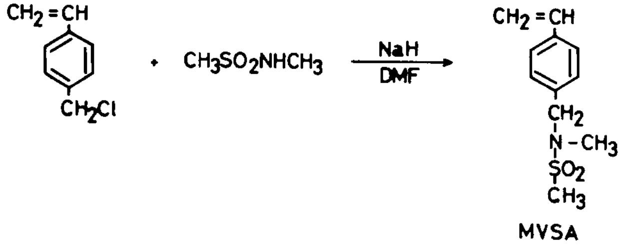
Dry resin (0.5 g) was suspended in 20 mL solvent. The mixture was stirred magnetically for 1 h at room temperature. The external liquid was removed by filtration in a preweighed sintered glass crucible, following the established procedure [19].

Measurements

IR spectra were measured by a Jasco IR-2 spectrometer. NMR spectra were recorded by a Hitachi R-20B spectrometer using tetramethylsilane as the internal standard. Gas chromatography (Ohkura 803) was used for separations and yield determinations.

RESULTS AND DISCUSSION

In order to obtain polymers with well-defined structures, we first carried out the preparation of vinyl monomers having sulfonamide moieties. The monomers chosen as representative aliphatic and aromatic sulfonamide monomers were *N*-methyl-*N*(*p*-vinylbenzyl)methanesulfonamide (MVSA) and *N,N*-dimethyl-*p*-styrenesulfonamide (DMSA), respectively. MVSA was prepared by the reaction of *p*-chloromethylstyrene with *N*-methylmethanesulfonamide in the presence of sodium hydride in DMF. DMSA was prepared by the reaction of sodium *p*-styrene-sulfonate with thionyl chloride, followed by treatment with dimethylamine. The structures were confirmed by elemental analysis and spectroscopic data.



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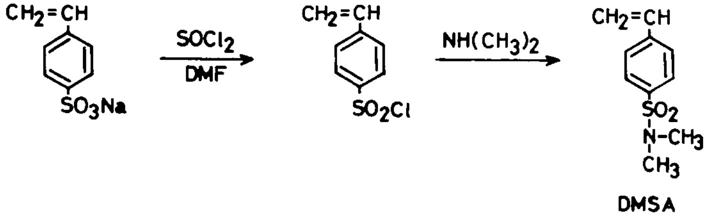

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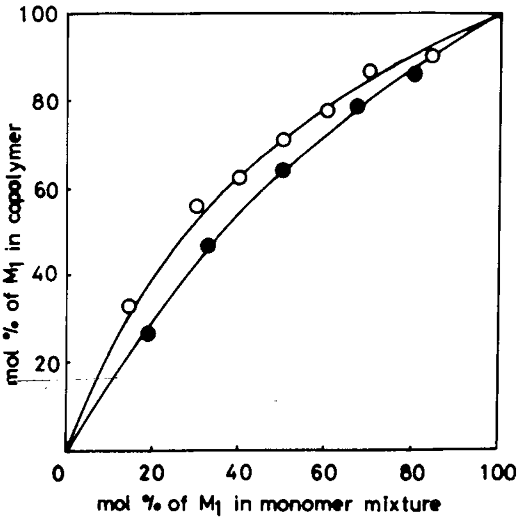
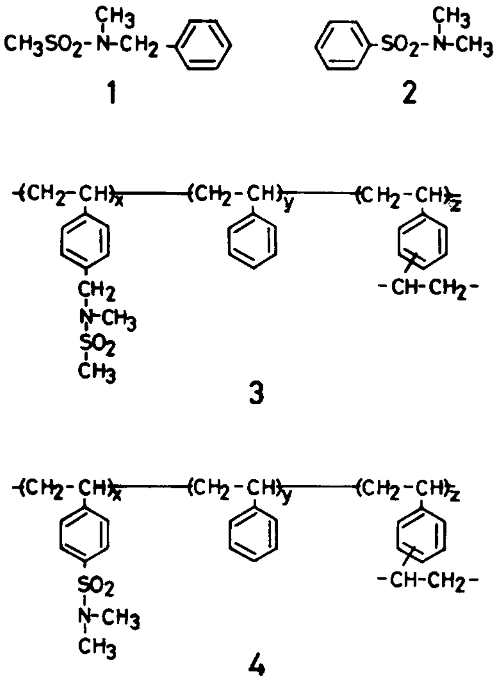


FIG. 1. Monomer–copolymer composition curves of DMSA (M_1)-styrene (M_2) (○) and MVSA (M_1)-styrene (M_2) (●).

The monomers were readily polymerized by AIBN at 60°C. In order to clarify the reactivity of these monomers for radical polymerization, copolymerization with styrene was carried out. All copolymerizations were carried out to less than 10% conversion. The monomer–copolymer composition curves are shown in Fig. 1.

The monomer reactivity ratios were computed for the copolymerization of MVSA according to the Fineman–Ross method as $r_{MVSA} = 1.55$, $r_{St} = 0.60$. From these values the resonance stabilization factor Q and the electrical factor e were calculated as $Q_{MVSA} = 1.34$ and $e_{MVSA} = -0.43$. These values are very similar to those of *p*-chloromethylstyrene [15]. Similarly, the copolymerization parameters of DMSA were calculated as $r_{DMSA} = 1.22$, $r_{St} = 0.20$, $Q_{DMSA} = 1.99$, and $e_{DMSA} = 0.41$. This large Q value can be understood by the fact that the sulfur-oxygen bond in sulfones has a double-bond character [20].

Based on the copolymerization parameters obtained above, insoluble polymer catalysts 3 and 4 were prepared by the copolymerization of the corresponding vinyl monomers. (Table 1). The catalysts used here are shown in Scheme 1.



SCHEME 1.

TABLE 1. Preparation of Crosslinked Polymeric Sulfonamides[a]

	Feed						Copolymer	
Sample	Amide, g	St, g	DVB,[b] mg	AIBN, mg	Benzene, mL	Yield, g	S, %	Composition x:y:z[c]
3a	2.25	0	48	33	15	2.05		98:0:2
3b	2.25	0.52	72	33	15	1.75	12.30	75:23:2
3c	2.25	1.04	96	33	15	1.68	9.32	47:51:2
3d	2.25	2.08	144	50	15	2.86	7.62	35:63:2
3e	2.25	5.21	248	66	10	6.41	4.36	17:81:2
4a	2.11	0	48	33	15	1.33		98:0:2

(continued)

TABLE 1. (continued)

	Feed						Copolymer	
Sample	Amide, g	St, g	DVB,[b] mg	AIBN, mg	Benzene, mL	Yield, g	S, %	Composition x:y:z[c]
4b	2.75	0.66	93	33	15	1.98	12.80	73:25:2
4c	4.22	2.08	192	66	15	3.72	10.39	52:46:2
4d	1.89	3.24	192	66	10	2.41	7.21	31:67:2
4e	1.41	3.47	192	66	10	2.81	4.87	19:79:2
4f	1.69	1.15	92	33	10	1.68	10.39	55:40:5
4g	1.69	1.04	87	33	10	1.55	9.86	49:41:10

[a] Reaction conditions: temperature = 60°C, time = 48 h.

[b] DVB: Divinylbenzene containing 45% ethylbenzene and diethylbenzene.

[c] x, y, and z represent the content of sulfonamide monomer, St, and DVB units, respectively, in mol %.

The catalytic activity of insoluble polymeric sulfonamides was tested for the reaction of *n*-octyl bromide with sodium thiophenoxide in the toluene–water system at 100°C.

$$\text{n-}C_8H_{17}Br + C_6H_5SNa \xrightarrow[\text{Toluene}/H_2O]{\text{Cat.}} \text{n-}C_8H_{17}SC_6H_5 + NaBr \qquad (3)$$

Reaction rates were determined by using a large excess of aqueous sodium thiophenoxide (11 mol of thiophenoxide/mol of *n*-octyl bromide); the reactions were monitored by following the disappearance of *n*-octyl bromide from the organic phase.

Under these conditions the reaction followed pseudo-first-order kinetics up to 70% conversion. In spite of the complexity of these systems, the reproducibilities of the kinetic measurements and material balance were good. The reaction rates for this reaction in the presence of several sulfonamides are summarized in Table 2.

TABLE 2. Phase Transfer Reaction of *n*-Octyl Bromide with Sodium Thiophenoxide Catalyzed by Sulfonamides[a]

Catalyst	$10^5 \times k_{obs.}$ (s^{-1})
None	6.3
1	8.3
2	6.9
3a	32.3
4a	16.5

[a] Reaction conditions: temperature = 100°C; [n-$C_8H_{17}Br$] = 0.55 *M* (in toluene), volume = 5 mL; [C_6H_5SNa] = 2.0 *M* (in H_2O), volume = 15 mL, Catalyst = 0.5 mmol based on sulfonamide unit; particle size of polymer catalyst = 60–100 mesh; stirring speed = 1000 rpm.

As can be seen from Table 2, this reaction is accelerated by polymeric sulfonamides 3a and 4a, but is not catalyzed by monomeric sulfonamides 1 and 2. A similar result has been found for polymeric formamides, acetamides, sulfoxides, and sulfones [4]. It is of interest to note that polymeric sulfonamides show the same reactivity as polymeric analogs of dipolar aprotic solvents in phase transfer catalysis.

In order to obtain information about the effect of experimental factors, we first examined the dependence of rate on the stirring speed. As can be seen from Table 3, the rate increased upon increasing the stirring speed up to almost 800 rpm, and remained constant beyond this value. Therefore, reactions were carried out by stirring at 1000 rpm to minimize

TABLE 3. Dependence of Reaction Rate on the Stirring Speed, Particle Size, and Degree of Crosslinking for the Phase Transfer Reaction of *n*-Octyl Bromide with Sodium Thiophenoxide[a]

Catalyst	Stirring speed, rpm	Particle size, mesh	Crosslinking, %	$10^5 \times k_{obs.}$ (s^{-1})
3a	0	60–100	2	17.4
3a	500	60–100	2	28.0
3a	800	60–100	2	31.7
3a	1000	60–100	2	32.3
3a	1200	60–100	2	32.0
3a	1000	100–200	2	36.6
3a	1000	200–300	2	37.8
4c	1000	60–100	2	43.1
4f	1000	60–100	5	39.8
4g	1000	60–100	10	35.7

[a] Other experimental conditions are the same as in Table 2.

the influence of diffusion. In addition, catalytic reactivity increased with a decrease of particle size of the polymer catalyst, indicating the importance of the surface area of catalyst.

The dependence of the rate of reaction on the degree of crosslinking is also shown in Table 3 (4c, 4f, 4g). A high degree of crosslinking should restrict the flexibility and swellability of the polymer chains, which would slow the diffusion of the reactants to active sites and should result in lower reaction rates. As expected, a slight decrease in the rate was observed in the range from 2 to 10% crosslinking.

The effect of organic solvent on the reaction rate was investigated by using *n*-decane, toluene, and chlorobenzene (Table 4). The degree of catalytic activity decreases in the order of chlorobenzene > toluene > *n*-decane. This order is in agreement with the order of swelling (Table 5), and it indicates the importance of diffusion of reagents in the polymer particles.

These results show that this catalytic reaction can be accelerated by an appropriate choice of such experimental parameters as stirring speed, particle size, degree of crosslinking, and solvent.

Previously we found that the catalytic activity of polymeric analogs of dimethylsulfoxide was remarkably affected by the microenvironment around the active site. In order to obtain information on this point for polymeric sulfonamides, the relation between activity and copolymer composition was investigated. The results are shown in Fig. 2.

Interestingly, the catalytic activity in both 3 and 4 decreases when the

TABLE 4. Phase Transfer Reaction of *n*-Octyl Bromide with Sodium Thiophenoxide Catalyzed by 3a in Several Solvents[a]

Solvent system	$10^5 \times k_{obs.}$ (s^{-1})
Chlorobenzene–H_2O	58.1
Toluene–H_2O	32.3
Decane–H_2O	27.6

[a] Other experimental conditions are the same as in Table 2.

TABLE 5. Swelling of Crosslinked Polymeric Sulfonamide 3a in Several Organic Solvents[a]

Solvents	Swelling, solvent (g)/ polymer (g)
Chlorobenzene	1.72
Toluene	0.55
Decane	0.13

[a]Experimental conditions are shown in the Experimental section.

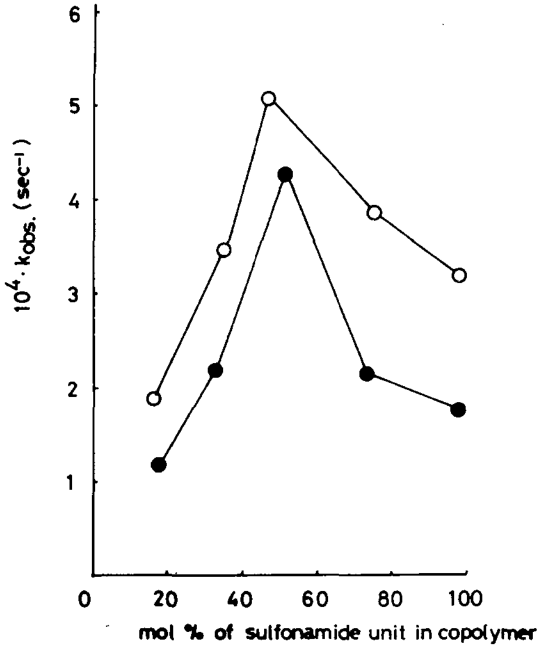


FIG. 2. Dependence of pseudo-first-order rate constants ($k_{obs.}$) on copolymer composition for the phase transfer reaction of *n*-octyl bromide with sodium thiophenoxide. Catalyst: (○) 3 crosslinked with 2% DVB; (●) 4 crosslinked with 2% DVB.

solfonamide unit of the copolymers increases from 50 to approximately 98%, which is related to the number of active sites of sodium ion content. However, above this range of composition, the active sites self-associate to form a hydrophilic microenvironment which greatly slows the reaction. Furthermore, the activity of 3 is generally higher than that of 4, which might be related to the difference in the strength of the interaction with sodium cation due to the electon density of oxygen in the sulfonamide moieties.

In closing, it should be noted that when polymer catalyst 3a was recovered from the reaction by filtration, it could be used directly without a significant loss in activity (Table 6). These polymers are also effective as catalysts for the reaction of *n*-octyl bromide with lithium iodide, sodium iodide, potassium iodide, sodium cyanide, potassium cyanide, and potassium thiocyanate (Table 7). The catalytic activity of 3c is comparable to that of benzyltriethylammonium chloride, but it is lower than that of tetrabutylammonium hydrogen sulfate and 18-crown-6.

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TABLE 6. Catalytic Activity of Reused Catalyst 3a for the Reaction of *n*-Octyl Bromide with Sodium Thiophenoxide[a]

Number of recycles	$10^5 \times k_{obs.}$ (s^{-1})
–	32.5
1	30.5
2	27.1

[a] Experimental conditions are the same as in Table 2.

TABLE 7. Phase Transfer Reaction of *n*-Octyl Bromide with Several Nucleophilic Reagents Catalyzed by Polymeric Sulfonamides[a]

Reagents	Catalyst	Time, h	Yield of product, %
LiI	3a	48	79
NaI	3a	24	64
NaI	3a	48	99
NaI	4a	24	41
KI	3a	48	99
KI	4a	48	70
NaCN	3a	24	99
NaCN	4a	24	99
KCN	4a	24	99
KSCN	3a	10	43
KSCN	3c	10	67
KSCN	4a	10	29
KSCN	BETAC[b]	10	64
KSCN	TBAHS[c]	10	94
KSCN	18-Crown-6	10	83

[a] Reaction conditions: temperature = 100°C; *n*-$C_8H_{17}Br$ = 1.65 mmol; [LiI, NaI, KI] = 4.0 mol/L (in H_2O), 5 mL; [NaCN, KCN, KSCN] = 8.0 mol/L (in H_2O), 5 mL; catalyst = 0.3 mmol based on sulfonamide unit (60–100 mesh).

[b] Benzyltriethylammonium chloride.

[c] Tetrabutylammonium hydrogen sulfate.

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