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Preparation of Polymeric Analogs of N,N-Dichloro-*p*-Toluenesulfonamide and Their Use for Oxidation of Alcohols, Oxidative Lactonization of Diols, and Chlorination of Carbonyl Compounds

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PREPARATION OF POLYMERIC ANALOGS OF N,N-DICHLORO-*p*-TOLUENESULFONAMIDE AND THEIR USE FOR OXIDATION OF ALCOHOLS, OXIDATIVE LACTONIZATION OF DIOLS, AND CHLORINATION OF CARBONYL COMPOUNDS

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ABSTRACT

Insoluble polystyrenes containing sulfonamide moiety were prepared by copolymerization of *p*-styrenesulfonamide and divinylbenzene with AIBN. The polymers were treated with *tert*-butyl hypochlorite to afford the polystyrenes containing N,N-dichlorosulfonamide moiety. These functional polymers were used for oxidation of alcohols, oxidative lactonization of diols, and α-chlorination of carbonyl compounds. In most cases, the carbonyl compounds, the lactones, and the α-chlorocarbonyl compounds as the corresponding products were obtained in excellent yields. The spent polymer reagents could be separated from the reaction system by simple filtration, and could be fully regenerated without loss of activity.

INTRODUCTION

Polymer-supported reagents have recently been paid much attention in organic synthesis mainly due to product separation ease, spent polymer recovery, and

reagent regeneration [1, 2]. However, the reactivity is generally lower than that of the corresponding monomeric reagents. Among these polymeric reagents, polymer-supported N-haloamides and N-haloimides such as N-bromoacrylamide [3,4], N-chloro-Nylon [5], N-bromosuccinimide [6-8] and N- chlorosuccinimide [9] have been especially studied for oxidation and halogenation agents.

Recently, we found that polymers containing N-chloroaminotriazine moiety, which can be regarded as a N- chloroamide, exhibit higher reactivity than the corresponding monomeric compounds for the oxidation of alcohols [10,11]. The reactivity enhancement by introducing active sites to polymer backbone is of interest, but such examples are few in polymeric reagent [12]. This phenomenon was realized by considering the polarity difference around the active site between the monomeric and polymeric reagents. These results prompted us to study the reactivity of other polymer-supported N-haloamides. N,N-Dichloro-*p*-toluenesulfonamide (MCSA), as a representative N-halosulfonamide, has been known to work as an effective reagent for α-chlorocarbonylation of alcohols [13]. Further, we recently found that the reagent reaction with alkanediols yields the corresponding lactones [14].

In this paper, we describe the synthesis of polymeric analogs of N,N-dichloro-*p*-toluenesulfonamide and utilization of this polymer reagent for oxidation of alcohols, oxidative lactonization of diols,and α-chlorination of carbonyl compounds.

EXPERIMENTAL

Reagents

p-Styrenesulfonamide was prepared by the method previously described [15]. 2,2'-Azobisisobutyronitrile (AIBN) was recrystalllized twice from methanol. Commercial divinylbenzene containing 45 % ethylstyrene and diethylbenzene, and solvents were used after distillation. Other reagents were obtained commercially and used without further purification.

Preparation of N,N-Dichloro-*p* -toluenesulfonamide (MCSA)

To a stirring solution of *p*-toluenesulfonamide (6.85 g, 40 mmol) and methylene chloride (100 mL) in a round- bottomed flask wrapped with aluminium foil, a solution of *tert*-butyl hypochlorite (9.06 g, 84 mmol) in methylene chloride (40 mL) was added slowly at 0°C. The reaction mixture was further stirred for 24 hours at room temperature. After evaporation of the solvent, the resulting solid was recrystallized with *n*-hexane. The yield was 4.86 g (51 %). mp 79°C ([16] 81°C).

Preparation of Poly(*p*-styrenesulfonamide-*co*-divinylbenzene) (PSA)

A solution of *p*-styrenesulfonamide (20.00 g, 113.6 mmol), commercial divinylbenzene (568 mg, 2.4 mmol), and AIBN (190 mg, 1.16 mmol) in dimethyl sulfoxide (DMSO) (140 mL) was heated at 60°C for 20 hours under nitrogen. The resulting white solid was Soxlet-extracted using methanol for 40 hours, followed drying. The yield was 20.20 g. The divinylbenzene content was assumed to be identical to that of the monomer feed.

Preparation of Poly(N,N-dichloro-*p*-styrenesulfonamide-*co*-divinylbenzene) (PCSA)

To a mixture of PSA (10.00 g, 53.8 mmol based on *p*-styrenesulfonamide unit, 60 -100 mesh) and methylene chloride (100 mL), in a round-bottomed flask wrapped with aluminium foil, a solution of *tert*-butyl hypochlorite (24.4 g, 224 mmol) in methylene chloride (160 mL) was added slowly with stirring at 0°C. The reaction mixture was further stirred for 4 days at room temperature. After filtration, the white resin was washed repeatedly with *n*-hexane and dried under reduced pressure to give PCSA (13.02 g). The elemental analysis of chlorine was 26.70%, indicating that the polymer contains 93% of N,N-dichloro-*p*-styrenesulfonamide unit.

Oxidation of Alcohols with PCSA

A typical reaction is as follows:

In a test tube with a screw cap, were placed α-phenylethyl alcohol (61 mg, 0.50 mmol), PCSA-93 (98 mg, 0.50 mmol based on dichlorosulfonamide unit), pyridine (79 mg, 1.0 mmol), and methylene chloride (2.5 mL). The mixture was stirred magnetically at room temperature for 24 hours. The resin was collected on a glass filter, and the filtrate was analyzed by gas chromatography. The yield of acetophenone was 90%. The chlorine content of the spent polymer was 15.25%, indicating that this polymer is PCSA-46. This resin was chlorinated again with *tert*-butyl hypochlorite (55 mg, 0.5 mmol) to give PCSA-89. The oxidation with PCSA-89 was carried out in the same manner to give benzaldehyde in 88% yield. The regeneration of spent polymer, and the reaction using this polymer, was carried out three times.

Oxidative Lactonization of Diols with PCSA

A typical reaction is as follows:

To a solution of 1,4-butanediol (901 mg, 10 mmol) and 50 mL of methylene chloride was added PCSA-93 (5.30 g, 20 mmol based on dichlorosulf-

onamide unit). The mixture was stirred magnetically at room temperature for 24 hours. The resin was collected on a glass filter. The solvent was removed under reduced pressure. The residue was purified by column chromatography (Wakogel C-200 eluent: methylene chloride) to give an oil (542 mg, 63%). The spectral data of the product agreed with those of an authentic sample of γ-butyro-lactone.

Chlorination of Carbonyl Compounds with PCSA

A typical reaction is as follows.:

To a solution of acetopheneone (60.1 mg, 0.5 mmol), *p*-toluenesulfonic acid (86.1 mg, 0.5 mmol) and 2.5 mL of methylene chloride was added PCSA-87 (139.2 mg, 0.5 mmol based on dichlorosulfonamide unit). The mixture was stirred magnetically at room temperature for 27 hours. The resin was collected on a glass filter, and the filtrate was analyzed by gas chromatography. The yield of phenacyl chloride was 89%.

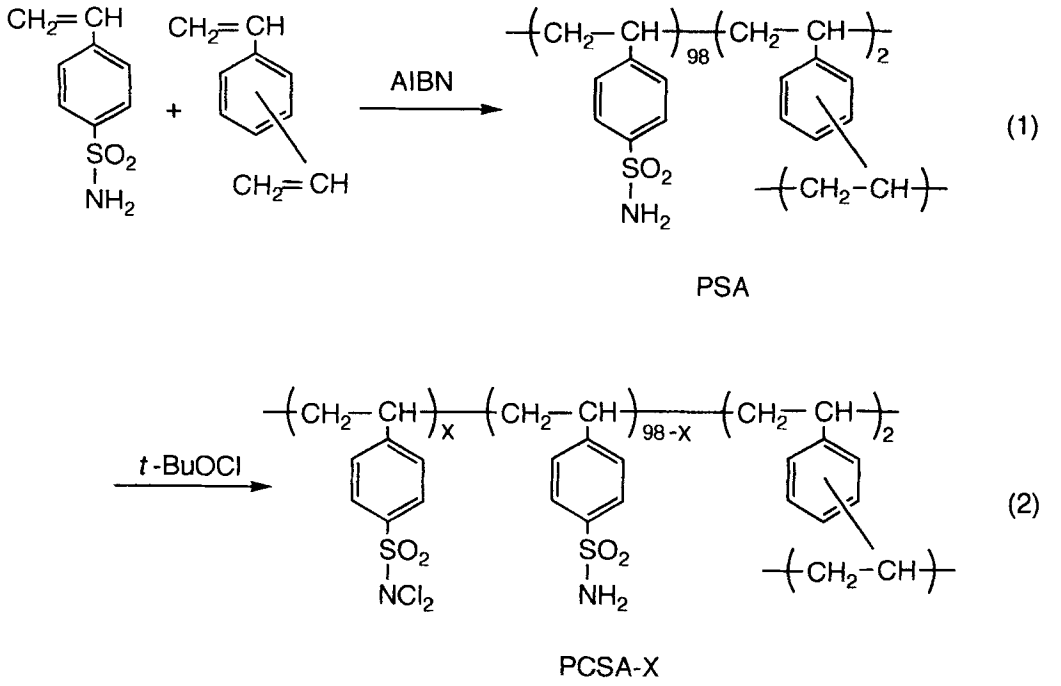
Measurements

IR spectra were measured with a Hitachi-285 spectrometer. GC (Carbowax 20 M, 5%, 2 m, and Silicone SE-30 10%, 2 m) was used for separations and yield determinations.

RESULTS AND DISCUSSION

Preparation of N, N-dihalogeno-poly(styrene-*co*-divinylbenzene)sulfonamides from a sulfonate cation-exchange resin have been reported by Bogoczek, et al. [17] However, the conversion of functional groups to dichlorosulfonamide groups was not high. Therefore, we prepared crosslinked polystyrene containing N,N-dichlorosulfonamide moiety (PCSA) according to Scheme 1.

Gel-type poly(*p*-styrenesulfonamide) crosslinked with 2 mol % divinylbenzene (PSA) was prepared by the copolymerization of the corresponding vinyl monomers with AIBN. The resulting polymer was crushed and sieved to 60 - 100 mesh. Then, the polymer particle was treated with *tert*-butyl hypochlorite in methylene chloride to afford poly(*p*-N,N-dichlorostyrenesulfonamide-*co*-divinylbenzene) (PCSA-x). Here, x represents the percent of dichlorosulfonamide unit in copolymer. The structure of PCSA-x was confirmed by the elemental analysis and the comparison with a model compound, N,N-dichloro-*p*-toluenesulfonamide (MCSA) by IR spectroscopy. The disappearance of characteristic absorption band



Scheme 1

of the amino group at 3380 cm^{-1} indicated that most of the amino group were converted to dichloroamino groups. PCSA is remarkably stable odorless solid, and can be stored for long time at room temperature in the dark.

First, the usefulness of PCSA as an oxidant of alcohol was examined. α-Phenylethyl alcohol was allowed to react with PCSA-93 containing equimolar amounts of dichlorosulfonamide unit to hydroxy groups with stirring in methylene chloride at room temperature. The time-conversion of the oxidation product, acetophenone, is shown in Figure 1. As can be seen from the figure, the acetophenone yield reached about 80% after 2 hours. But, after that, the yield decreased rapidly accompanying the production of chlorination product of acetophenone, phenacyl chloride, and phenacyl chloride was obtained in 54% yield after 18 hours. While, in the reaction with the monomeric analogue, N,N-dichloro-*p*-toluenesulfonamide (MCSA), the yield of actophenone increased gradually and the yield of side product, phenacyl chloride, was very low (Table 1). Thus, it is of interest that the oxychlorination rate was enhanced by using the polymeric reagent. Similar phenomenon that the reactivity was enhanced by anchoring the active site to polymer

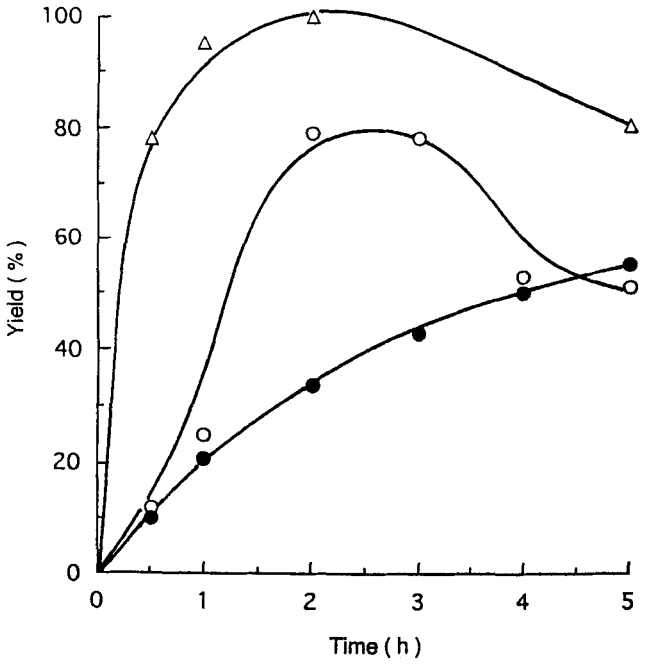


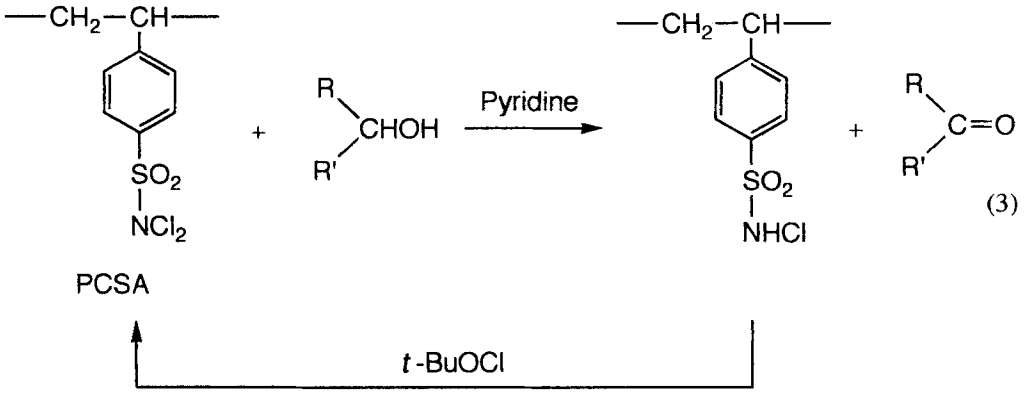
Figure 1. Relation between time and yield of the product, acetophenone for the reaction of α–phenylethyl alcohol with MCSA (Δ) , PCSA (O) without pyridine, and PCSA (●) in the presence of pyridine. α–Phenylethyl alcohol = 0.5 mmol, dichlorosulfonamide unit = 0.5 mmol, pyridine = 1.0 mmol, CH_2Cl_2 = 2.5 mL.

TABLE 1. Oxidation of Alcohols with N,N-Dichloro-*p*-toluemesulfonamide (MCSA) and Its Polymer Analog (PCSA) at Room Temperature [a]

Run	Alcohol	Reagent	Additive	Time,h	Product	Yield,%
1	α-Phenylethyl alcohol	MCSA	none	2	Acetophenone	99
2	α-Phenylethyl alcohol	PCSA-93	none	2	Acetophenone	80
					α-Chloroacetophenone	7
3	α-Phenylethyl alcohol	PCSA-93	none	18	Acetophenone	29
					α-Chloroacetophenone	54
4	α-Phenylethyl alcohol	PCSA-93	Pyridine	24	Acetophenone	90
5	1-Octanol	PCSA-93	Pyridine	24	Octanol	12
6	2-Octanol	PCSA-93	Pyridine	24	2-Octanone	56
7	Cyclohexanol	PCSA-93	Pyridine	24	Cyclohexanone	52
8	Benzyl alcohol	PCSA-93	Pyridine	24	Benzaldehyde	86
9	Benzhydrol	PCASA-93	Pyridine	7	Benzophenone	99

[a] Reaction conditions. alcohol = 0.5 mmol, dichlorosulfonamide unit = 0.5 mmol, pyridine = 1.0 mmol, CH_2Cl_2 = 2.5 mL, room temperature

backbone was observed for the oxidation of alcohols with polymer-supported chloroaminotriazine [11]. This oxychlorination was prevented by adding pyridine, and acetophenone was obtained exclusively even after 24 hours.



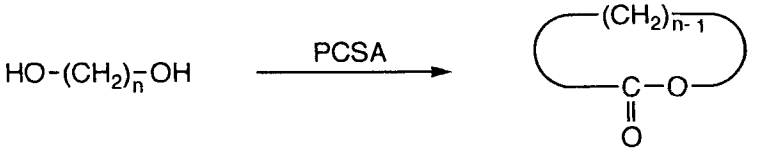
(3)

After the reaction, the resulting polymer was separated from the reaction mixture by filtration. From the elemental analysis, the recovered polymer structure was identified as PCSA-46. This polymer was again chlorinated with *tert*-butyl hypochlorite to generate PCSA-89. Further, the oxidation with the regenerated polymer reagent was examined. The results are shown in Table 2. Although the regeneration of the reagent was repeated three times, the activity of the reagent was almost unchanged.

The reaction of PCSA with other alcohols was carried out in the presence of pyridine under the same conditions, and the results are also shown in Table 1.

The reaction of the primary alcohol, 1-octanol, occurred slowly to yield octanal. With benzyl alcohol, the oxidation product, benzaldehyde, was obtained in high yield at moderate rate. Secondary alcohols such as cyclohexanol, α–phenyl-ethyl alcohol, and benzhydrol were oxidized rapidly to the corresponding ketones in excellent yields.

Next, the availability of this polymer reagent for the lactone synthesis from alkanediols was examined, and the results are shown in Table 2.



(4)

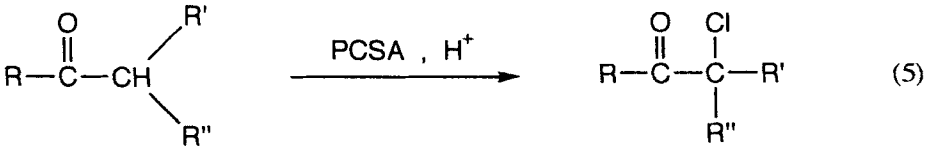
TABLE 2. Regeneration of the Spent Polymer Reagent and Reuse for the Reaction with α–Phenylethyl Alcohol[a]

Run	Polymer reagent	Product yield,%	Spent polymer	Regenerated polymer[b]
1	PCSA-93	90	PCSA- 46	PCSA-89
2	PCSA-89	88	PCSA- 42	PCSA-90
3	PCSA-90	85	PCSA- 43	PCSA-92
4	PCSA-92	91	PCSA- 43	PCSA-87

a) Reaction conditions, α–phenylethyl alcohol = 0.5 mmol, dichlorosulfonamide unit = 0.5 mmol, pyridine = 1.0 mmol, CH_2Cl_2 = 2.5 mL, room temperature
b) Spent polymer was treated with excess t-butyl hypochlorite.

When 1,4-butanediol was treated with PCSA in methylene chloride at room temperature for 6 hours, γ-butyrolactone was produced in 58% yield. δ–Valerolactone was also obtained from the corresponding diol, 1,5-pentanediol. Lactones of four- or seven-membered rings were not produced from the corresponding diols. These lactones are probably formed via hemiacetals, as in the case of N, N-dichlorobenzenesulfonamide [14].

Further, the results of the reaction with α–phenylethyl alcohol mentioned above indicates that PCSA works not only as oxidant but also as a chlorinating agent of carbonyl compounds. Therefore, the reaction of PCSA with acetophenone was examined under the same conditions as in the case of alcohols. But, the reaction did not occur even after 24 hours. While, when this reaction was carried out in the presence of acids such as hydrochloric acid and *p*-toluenesulfonic acid, the desired product phenacyl chloride was obtained quantitatively. These results suggest that this chlorination occurs through the addition of positive chlorine to the enol derived from acetophenone in the presence of acid. The results of the reaction with other carbonyl compounds are summarized in Table 3.



(5)

As expected, the reaction with propiophenone gave the α–chlorination product quantitatively. This high selectivity was also observed for the reaction of

TABLE 3. Oxidative Lactonization of Alkanediols with MCSA and PCSA[a]

Run	Diol	Reagent	Time, h	Product	Yield, %
1	1,4-butanediol	MCSA	4	γ-butyrolactone	90
2	1,4-butanediol	CSA-93	4	γ-butyrolactone	63
3	1,5-pentanediol	MCSA-93	24	δ–valerolactone	59
4	1,5-pentanediol	PCSA-93	24	δ–valerolactone	50
5	1,3-pentanediol	PCSA-93	24	mixture	
6	1,6-hexanediol	PCSA-93	24	mixture	

[a] Reaction conditions, diol = 10 mmol, dichlorosulfonamide unit = 20 mmol, CH_2Cl_2 = 50 mL, room temperature

TABLE 4. Chlorination of Carbonyl Compounds with MCSA and PCSA[a]

Run	Carbonyl compound	Reagent	Additive	Time(h)	Product	Yield(%)
1	Acetophenone	MCSA	none	27	Phenacyl Chloride	0
2	Acetophenone	MCSA	TosOH	27	Phenacyl Chloride	77
3	Acetophenone	PCSA-87	none	27	Phenacyl Chloride	0
4	Acetophenone	PCSA-87	HCl	27	Phenacyl Chloride	57
5	Acetophenone	PCSA-87	TosOH	27	Phenacyl Chloride	89
6	Propiophenone	PCSA-87	TosOH	180	α–Chloropropiophenone	99
7	Cyclohexanone	PCSA- 87	TosOH	7	α–Chlorocyclohexanone	67
8	Octanonal	PCSA 87	TosOH	6	α–Chlorooctanal	11
9	2-Octanone	PCSA-87	TosOH	27	3-Chloro-2-octanone	43
					1-Chloro-2-octanone	18

[a] Reaction conditions. carbonyl compound = 0.5 mmol, dichlorosulfonamide unit = 0.5 mmol, HCl , TosOH (*p*-toluenesulfonic acid) = 0.5 mmol, CH_2Cl_2 = 2.5 mL, room temperature

cyclohexanone and octanal. The reaction with 2-octanone yielded two α-chlorination products.

For the reaction with alkanediols and carbonyl compounds, the spent polymers were also separated by filtration, and were regenerated and used without loss of reactivity.

CONCLUSION

Polymer-supported N,N-dichlorosulfonamide was prepared by the chlorination of the corresponding polymeric sulfonamide with t*ert*-butyl hypochlorite. This polymer reagent was stable in the dark, and was useful for oxidation of

primary and secondary alcohols, oxidative lactonization of alkanediols, and α-chlorination of aldehyde and ketones. The spent polymer could be separated by only filtration, and regenerated with treatment with *tert*-butyl hypochlorite.

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