

Synthesis of Polystyrenes Having 2-Pyridylthio Group and Their Use as Phase Transfer Catalysts for the Reduction of Carbonyl Compounds by Sodium Borohydride

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ynopsis

p-(2-Pyridylthiomethyl)styrene (PTMS) and *p*-(2-pyridylthioethyl)styrene (PTES) were prepared from the reactions of 2-pyridinethiol with *p*-chloromethylstyrene and with *p*-bromomethylstyrene, respectively. These monomers are readily polymerized in the presence of AIBN. From the copolymerization of PTMS with styrene, $Q_{PTMS} = 1.19$ and $e_{PTMS} = 0.24$ were obtained. The resulting polymers can extract alkali metal ions such as sodium and potassium cations. The extraction ability increases with increasing the density of active sites in polymers. Further these polymers serve as phase transfer catalysts for the reduction of carbonyl compounds by sodium borohydride.

INTRODUCTION

2-Pyridylthio group is a unique chelating ligand which is composed of nitrogen and thioether donor groups.¹ This action has been widely applicable to organic synthesis.²⁻⁵ Recently we have reported that polymers containing pyridylthio group along the main chain serve as phase transfer catalysts.⁶ The relationship between the activity and structure in polymeric phase transfer reagents has been investigated in detail, and the activity is found to depend markedly on many factors such as molecular weight, microenvironment around the active site, flexibility,⁷⁻¹⁰ etc. However, it was difficult to examine these factors on the catalysts mentioned above because these were prepared by condensation polymerization.¹¹ Therefore, in order to investigate these factors and further to improve the catalytic activity of polymers containing pyridylthio group, it is necessary to prepare the polymers containing this group by polymerization of corresponding vinyl monomers or copolymerization with other vinyl monomers.

In this article, we describe synthetic method of desirable polymers, interaction of alkali metal ions with the polymers, and utilization of the polymers as phase transfer catalysts for the reduction of carbonyl compounds by sodium borohydride.

EXPERIMENTAL

Reagents

Styrene, azobisisobutyronitrile (AIBN), 2-octanone, acetophenone, propiophenone, and benzaldehyde were obtained commercially and used after ordinary purification. 2-Pyridinethiol was prepared according to the Albert and Barlin's method¹² in 37% yield. *p*-Chloromethylstyrene was prepared by the same method reported previously.¹³ *p*-Bromoethylstyrene was prepared by the Braun's method.¹⁴ 2-Ethylthiopyridine¹¹ and 2-benzylthiopyridine¹¹ were prepared from the reaction of 2-chloropyridine with the corresponding thiolate anion in DMF. Solvents were used after distillation. Other reagents were obtained commercially and used without further purification.

SYNTHESIS OF *p*-(2-PYRIDYLTHIOMETHYL)STYRENE (PTMS)

To a solution of sodium ethoxide (1.36 g, 20 mmol) in ethanol (50 mL) was added 2-pyridinethiol (2.2 g, 20 mmol) slowly with stirring. Then, *p*-chloromethylstyrene (2.3 g, 15 mmol) was added to the solution at 0°C and refluxed for 5 h in the presence of *t*-butyl catechol (0.1 g). The reaction mixture was poured into 100 mL of water and extracted three times with 30 mL of ether and dried with sodium sulfate. After removal of the solvent, the residue was separated by column chromatography (silica gel, benzene) to give a oily product (1.67 g, 49%). IR: 750, 850, 910, 1120, 1415, 1455, 1510, and 1585 cm^{-1} . NMR (CDCl_3): δ = 4.40 (s, 2H), 5.15 (dd, 1H), 5.65 (dd, 1H), 6.75 (dd, 1H), 7.25 (m, 7H), and 8.40 ppm (d, 1H).

ANAL.: Calc for $\text{C}_{14}\text{H}_{13}\text{NS}$: C, 73.97%; H, 5.76%; N, 6.16%; S, 14.10%. Found: C, 73.79%; H, 6.03%; N, 5.77%; S, 14.32%.

SYNTHESIS OF (2-PYRIDYLTHIOETHYL)STYRENE (PTES)

PTES was prepared by the same method in the case of PTMS by the use of *p*-bromoethylstyrene instead of *p*-chloromethylstyrene. Yield was 47%. IR: 900, 1405, 1550, 1570, 1620, and 2950 cm^{-1} . NMR (CDCl_3): δ = 2.95 (t, 2H), 3.35 (t, 2H), 5.20 (dd, 1H), 5.65 (dd, 1H), 6.75 (dd, 1H), 7.25 (m, 7H), 8.42 ppm (d, 1H).

ANAL.: Calc for $\text{C}_{15}\text{H}_{15}\text{NS}$: C, 74.65%; H, 6.26%; N, 5.80%; S, 13.28%. Found: C, 74.92%; H, 6.11%; N, 5.43%; S, 13.25%.

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 ampoule and its sealing were undertaken according to a similar method reported previously.¹⁵

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 the reprecipitation from benzene to methanol. The conversion was calculated from the weight of the dried polymer obtained.

Copolymerization was carried out by the same method as mentioned previously.¹³ The composition of the copolymers was calculated from their elemental analysis of sulfur.¹⁶ The monomer reactivity ratio was obtained by the Fineman–Ross method.

EXTRACTION

To a 20 mL of benzene solution of the polymer containing 6.25×10^{-3} mmol of pyridylthio group was added 5 mL of an aqueous picric acid solution (5×10^{-5} mol/L) containing excess metal hydroxide (1×10^{-2} mol/L). The mixture was stirred magnetically for 1 h at 20°C. After separation, the aqueous solution was analyzed on the picrate absorption at 355 nm ($\epsilon = 14400$) by spectrophotometry.

REDUCTION OF CARBONYL COMPOUNDS

To a 30 mL of round bottomed flask were charged a solution of ketone (1.5 mmol) in 4 mL of benzene, 1% aqueous sodium hydroxide (0.1 mL), sodium borohydride (1.2 mmol), and a pyridylthio compound (0.1 mol eq). The mixture was stirred magnetically at room temperature for a given time. Then, the solution was acidified by 10% HCl to pH 5–6, and poured into petroleum ether to precipitate the polymer. The organic layer was analyzed by GLPC.

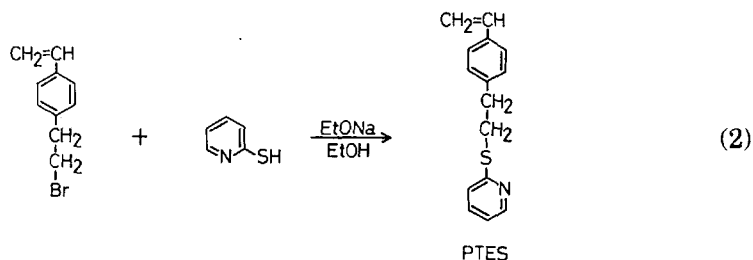
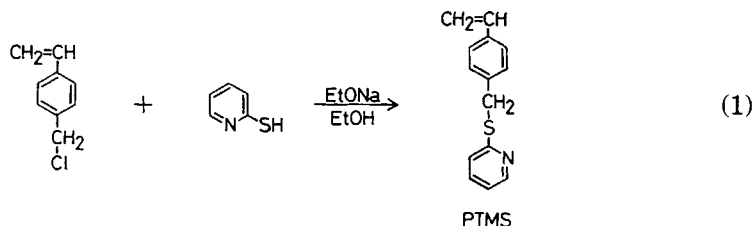
MEASUREMENTS

IR spectra were recorded on a JASCO IRA-2 Spectrometer. The separation was performed by the use of gas–liquid partition chromatography (Hitachi 063). The internal standard method was used in yield determinations. The column used included 20% Carbowax 20 M (1 m \times 6 mm) on Celite 545. NMR spectra were recorded by Hitachi R-20B spectrometer by using tetramethylsilane as an internal standard. UV spectra were taken by Hitachi 124 spectrometer.

RESULTS AND DISCUSSION

Preparation of *p*-(2-Pyridylthiomethyl)styrene (PTMS) and *p*-(2-Pyridylthioethyl)styrene (PTES)

Though various vinyl monomers having 2-pyridylthio group are possible to design, we chose the following two monomers, PTMS and PTES, in terms of the compounds with high polymerizability and with no functional group except for 2-pyridylthio group. These monomers are prepared from the reaction of 2-pyridinethiol with *p*-chloromethylstyrene or *p*-bromoethylstyrene in moderate yields. The structure was confirmed by spectroscopic data and elemental analysis:



FREE RADICAL POLYMERIZATION OF PTMS AND PTES

PTMS was successfully polymerized in benzene with AIBN at 60°C to yield a white solid with an inherent viscosity of 0.13 dL/g. It was soluble in chloroform, benzene, DMSO, and DMF, but insoluble in *n*-hexane, methanol, and water. Similarly, PTES was readily polymerized in benzene to give polyPTES quantitatively.

In order to clarify the reactivity of PTMS for radical copolymerization, copolymerization with styrene was carried out. The results are summarized in Table I and the monomer-copolymer composition curve is shown in Figure 1. The monomer reactivity ratio computed according to the Fineman-Ross method was $r_{\text{PTMS}} = 0.50$ $r_{\text{St}} = 0.60$. From these values, the resonance stabilized factor Q and the electrical factor e were calculated as $Q = 1.19$ and $e = 0.24$. These values are similar to those of *p*-alkyl styrenes such as *p*-chloromethylstyrene¹³ and *p*-bromoethylstyrene.¹⁴

TABLE I
Copolymerization of PTMS with Styrene^a

M_1^b	Time (h)	Temp (°C)	Conv. (%)	S (%)	m_1^c
0.13	2	60	3.8	5.06	0.19
0.28	2	60	6.6	7.35	0.32
0.42	2	60	6.4	9.21	0.44
0.56	2	60	4.3	10.12	0.51
0.70	2	60	6.9	11.87	0.63
0.85	2	60	5.7	12.33	0.71

^a [PTMS] + [St] = 1.0M. [AIBN] = 1.0×10^{-2} M. Solvent: benzene (10 mL).

^b Mole fraction of PTMS in monomer mixture.

^c Mole fraction of PTMS in copolymer.

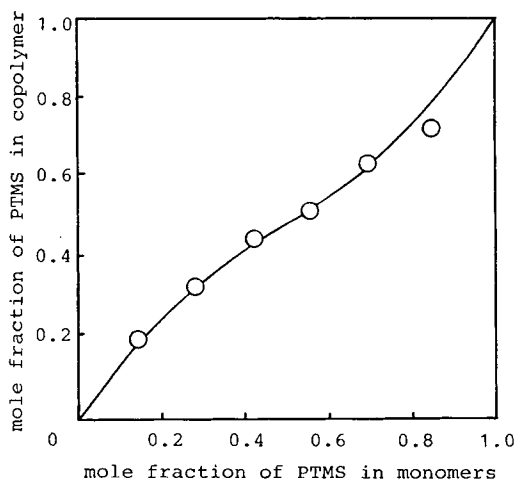
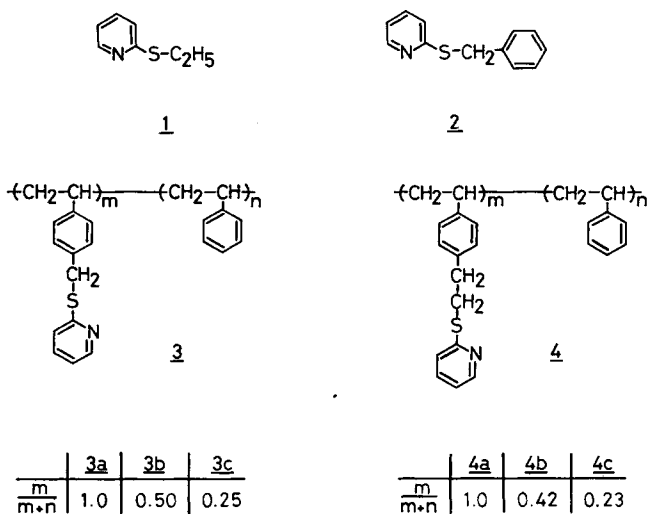


Fig. 1. Monomer-copolymer composition curve of PTMS (M_1) and styrene (M_2).

EXTRACTION OF SODIUM AND POTASSIUM CATIONS

The polymers and the corresponding monomeric analogue employed in the extraction studies are as follows:



Since polymers 3 and 4 are readily dissolved in benzene and methylene chloride, phase transfer of metal ions from water into these organic solvents should be possible if 3 and 4 are effective phase transfer reagents. In order to assess the ability of these polymers as phase transfer catalysts, we have determined the extent of transfer of picrate salts from water to benzene in the presence of polymers 3 and 4 and monomeric analogs 2-ethylthiopyridine 1 and benzylthiopyridine 2 (Table II).

TABLE II
Extraction of Picrate by Pyridylthio Compounds^a

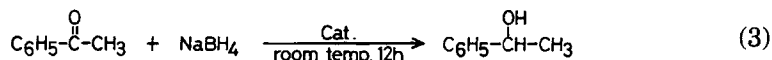
Compounds	Extraction (%)	
	Na ⁺	K ⁺
1	0.0	0.0
2	0.0	0.0
3a	6.2	7.4
3b	3.7	3.7
3c	1.8	2.5
4a	5.4	6.0
4b	4.9	4.5
4c	4.0	4.1

^a [Picrate] = $5.0 \times 10^{-5}M$ (in H₂O) 5 mL. [Compound]/[picrate] = 25. Benzene, 20 mL.

As can be seen from the table, polymers **3** and **4** extract sodium and potassium ions, but the monomeric compounds do not do so to any detectable degree. The extraction ability increases with increasing density of active sites in polymers. These results can be explained by a mechanism involving chelation of a metal ion with several pyridylthio groups. Similar phenomenon has been observed in polymeric sulfoxides, sulfones, and formamides.¹⁶⁻¹⁹ Though K⁺ seems to be extracted somewhat larger than Na⁺, clear selectivity to alkali metal ions was not found. Furthermore, Table II shows that polymer **4a** extracts cations more effectively than **3a**. These results can be explained by considering the difference of polymer flexibility. In polymer **4** the active site can be approached more easily than in polymer **3** due to the methylene group spacer.

CATALYSIS FOR THE REDUCTION OF CARBONYL COMPOUNDS BY SODIUM BOROHYDRIDE

The catalytic activity of these polymers was tested for the reduction of acetophenone by sodium borohydride. These reactions were carried out in benzene-water solutions and the results are shown in Table III:



The reactions in the presence of **3a** and **4a** afforded 1-phenethyl alcohol in 31% and 43% yield, respectively, but not catalyzed by **1** and **2**. It should be noted that the catalytic activity of these polymers is superior to their monomeric analogue. Furthermore, the catalytic activity of **4** increases with increasing density of active sites, in agreement with the cation extraction ability.

Based on above results, we are convinced that the 2-pyridylthio group coordinate to the metal cation at the water benzene interface, and the anion is transferred to organic phase where it attacks the substrate.

Moreover, these polymers can serve as phase transfer catalysts for the reduction of other carbonyl compounds such as 2-octanone, propiophenone, and benzaldehyde (Table IV).

TABLE III
Reduction of Acetophenone by Pyridylthio Compounds at Room Temperature for 12 h^a

Cat.	Yield (%)
None	Trace
1	Trace
2	Trace
3a	31
4a	43
4b	41
4c	18

^a [Cat.]/[ketone] = 0.1. [Ketone] = 1.5 mmol, [NaBH₄] = 1.2 mmol. Solvent: benzene (4 mL), 1 wt % NaOH (aq) (0.1 mL).

TABLE IV
Reduction of Carbonyl Compounds by Polymers Containing Pyridylthio Group^a

Substrate	Cat.	Time (h)	Yield (%)
2-Octanone	None	12	Trace
	3a	12	63
	4a	12	10
Propiophenone	None	30	Trace
	3a	30	24
	4a	30	10
Benzaldehyde	None	5	37
	3a	5	93
	4a	5	91

^a [Cat.]/[substrate] = 0.1. [Substrate] = 1.5 mmol, [NaBH₄] = 1.2 mmol. Solvent: benzene (4 mL), 1 wt % NaOH (aq) (0.1 mL).

In addition, these polymers were readily recovered quantitatively by reprecipitating from the benzene solution with petroleum ether.

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