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PHASE-TRANSFER REACTIONS CATALYZED BY POLYMER-SUPPORTED IMIDAZOLES

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ABSTRACT

Polymer-supported imidazoles were prepared by copolymerization of vinyl monomers containing imidazole moiety, styrene, and divinylbenzene with AIBN. The resulting polymers accelerated the reaction of octyl bromide with potassium thiocyanate, and the alkylation of an active methylene compound, benzyl cyanide, under phase-transfer conditions. The latter catalytic reaction afforded monoalkylated compound exclusively, although dialkylated compound was also obtained in monomeric alkylimidazole catalyzed reaction. Further, these polymers served as phase-transfer catalysts for the reduction of acetophenone by sodium borohydride. The relationship between the structure and catalytic activity, and the factors governing these catalytic reactions were examined.

INTRODUCTION

In a previous report, we described that polyvinylpyridines worked as phase-transfer catalysts for the reduction of carbonyl compounds by sodium borohydride, although the corresponding monomeric compounds had no activity [1]. This fact is of interest in the contribution to organic synthesis and also in the successful appearance of the polymer effect. This polymer effect was mainly understood as the cooperative function of active sites along the polymer backbone, that is, the chelation of nitrogen atoms to a sodium cation is similar to cases of polymeric analogues of dipolar aprotic solvents [2, 3].

This interaction will be enhanced by using nitrogen atoms with a higher electron density. From this point of view, we hoped that polymers containing the imidazole moiety would display a higher activity in phase-transfer reactions. This article describes the synthesis of polymer-supported imidazoles and examines the catalytic activity of these polymers in phase-transfer reactions.

EXPERIMENTAL

Materials

N-Vinylimidazole, styrene, divinylbenzene, octyl bromide, butyl bromide, benzyl cyanide, acetophenone, and solvents were used after distillation. Azobisisobutyronitrile (AIBN) was recrystallized from methanol. *N*-Benzylimidazole was prepared from the reaction of imidazole and benzyl chloride according to the literature [4]. 3-Butyl-1-methylimidazolium bromide was prepared by the reaction of *N*-methylimidazole and butyl bromide according to the literature [5]. Polyvinylpyridines were prepared by the copolymerization of 2-vinylpyridine or 4-vinylpyridine with styrene [1]. *p*-Chloromethylstyrene was kindly supplied by Seimi Chemical Co. Other reagents were obtained commercially and used without further purification.

Preparation of *N*-(*p*-Vinylbenzyl)imidazole

To a slurry of sodium hydride (60% oil suspension, 8.0 g, 0.2 mol) and *N,N*-dimethylformamide (DMF) (150 mL) was added imidazole (6.8 g, 0.1 mol) in DMF (30 mL); the mixture was stirred under nitrogen at room temperature for 1 hour. *p*-Chloromethylstyrene (15.3 g, 0.1 mol) was added dropwise to this mixture at 0°C. The mixture was filtered after it had been stirred overnight at room temperature. The residue remaining after solvent removal was poured into water and extracted with methylene chloride. After solvent removal, the product was recrystallized with hexane. The yield was 9.1 g (49%); mp 34.5°C. NMR (in CDCl₃): δ = 5.10 (s, 2H), 5.32 (dd, 1H), 5.79 (dd, 1H), 6.82 (dd, 1H), 6.95 (s, 1H), 7.15 (s, 1H), 7.37 (m, 4H), 7.60 (s, 1H) ppm. IR: $\nu_{\text{C}=\text{CH}_2}$ = 990 cm⁻¹.

Analysis. Calculated for C₁₂H₁₂N₂: C, 78.23; H, 6.56; N, 15.20%. Found: C, 78.42; H, 6.69; N, 15.24%.

Preparation of Polymer-Supported Imidazoles

Soluble polymers were prepared by homopolymerization of vinyl monomers containing the imidazole moiety and copolymerization of these polymers with styrene by AIBN. Polymerization was carried out in a sealed glass tube with a thermostat maintained at 60°C. The charging of the reagents into an ampule and its sealing were undertaken by a method similar to that reported previously [6]. After polymerization, the tube was opened and its contents were poured into a large amount of poor solvent. Poly(*N*-vinylimidazole) and poly(*N*-vinylimidazole-*co*-styrene)s were purified by reprecipitation from ethanol to benzene and from benzene to ether, respectively. Poly(*N-p*-vinylbenzylimidazole) and poly(*N-p*-vinylbenzylimidazole-*co*-styrene)s were reprecipitated from chloroform to ether.

The compositions of the copolymers were calculated from elementary analysis for nitrogen.

Crosslinked polymers were prepared by copolymerization of the corresponding vinyl monomers with commercial divinylbenzene containing 45% ethylstyrene and diethylbenzene. Polymerization was carried out in the same manner used for the soluble polymers. The resulting gel was treated by Soxhlet extraction for 20 hours with chloroform and for a further 24 hours with ethanol, followed by drying of the copolymer. In the case of copolymerization of *N*-vinylimidazole, the DVB content was estimated by assuming that the reactivity of DVB is the same to that of styrene. On the other hand, in the case of the copolymerization of *N*-*p*-vinylbenzylimidazole, the divinylbenzene unit content in the copolymer was assumed to be identical to its content in the feed.

Catalytic Reactions

Reactions of octyl bromide with potassium thiocyanate and alkylation of benzyl cyanide were carried out by the same method described for the reaction catalyzed by polymeric sulfoxides [7]. The reduction of acetophenone by sodium borohydride was carried out by the method described previously [8].

Measurements

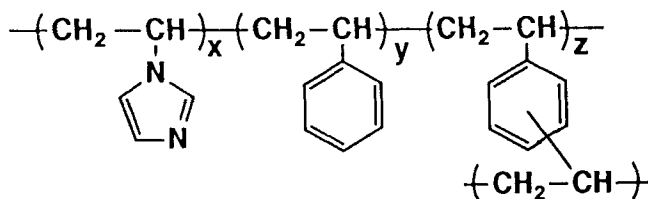
IR spectra were measured by a Hitachi R-285 spectrometer. NMR spectra were recorded by a Hitachi R-20B spectrometer using tetramethylsilane as the internal standard. Gas chromatography (Ohkura 803) was used for separations and yield determinations.

RESULTS AND DISCUSSION

In order to obtain the relation between structure and activity, polymers with well-defined structures are desirable. Therefore, we prepared polymer catalysts by the free radical terpolymerization of a vinyl monomer containing the imidazole moiety, styrene, and divinylbenzene. The monomers chosen were *N*-vinylimidazole and *N*-*p*-vinylbenzylimidazole. *N*-*p*-Vinylbenzylimidazole was prepared by the reaction of *p*-chloro-methylstyrene with imidazole in the presence of sodium hydride in DMF.

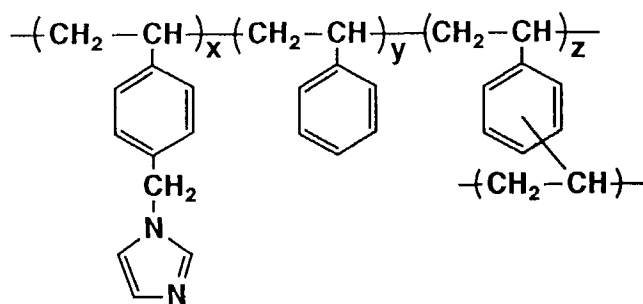


The results of the polymerization of these monomers are summarized in Table 1. The polymers, crosslinked with divinylbenzene, were crushed and separated by using sieves. The structures of the polymer catalysts used here are as follows.



1

	x	y	z
1a	100	0	0
1b	26	74	0
1c	95	0	5
1d	7	90	3



2

	x	y	z
2a	100	0	0
2b	53	47	0
2c	95	0	5
2d	51	44	5
2e	23	72	5
2f	5	90	5

Here, x, y, and z represent the content of a vinyl monomer containing the imidazole moiety, styrene, and divinylbenzene units, respectively, in mol percent.

The catalytic activity of imidazoles was tested for the reaction of octyl bromide with potassium thiocyanate in the toluene-water system.

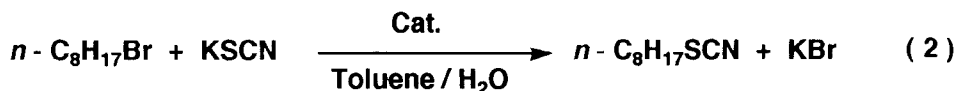
TABLE 1. Preparation of Polymer-Supported Imidazoles^a

Sample	Feed				Time, h	Polymer	
	Weight of monomer, ^b g	Weight of styrene, g	Weight of DVB, ^c mg	Weight of AIBN, mg		Yield, g	N, %
1a	1.34	0	0	25	24	1.25	
1b	1.41	1.57	0	50	44	1.86	6.70
1c	2.83	0	80	50	24	2.89	
1d	0.94	4.10	239	82	20	2.66	1.09
2a	2.95	0	0	27	24	1.78	
2b	1.47	0.89	0	27	24	1.17	10.14
2c	2.80	0	105	27	24	2.77	
2d	1.84	0.97	129	33	36	2.39	9.74
2e	1.84	2.92	262	66	36	5.16	5.22
2f	0.46	4.70	586	82	20	4.48	1.34

^aSolvent: Benzene = 10 mL, 60°C.

^bSamples 1a-1d: *N*-vinylimidazole. Samples 2a-2f: *N*-*p*-vinylbenzylimidazole.

^cDVB: Divinylbenzene containing 45% ethylstyrene and diethylbenzene.



The results are shown in Table 2.

The reaction was achieved without detectable side reactions in the presence of *N*-methylimidazole and *N*-benzylimidazole, although imidazole did not display the catalytic activity. Further, the activity of *N*-benzylimidazole was higher than that of *N*-methylimidazole. Polymers 1b and 2e also exhibited catalytic activity. These

TABLE 2. Reaction of Octyl Bromide with Potassium Thiocyanate in the Presence of Imidazoles under Phase-Transfer Conditions^a

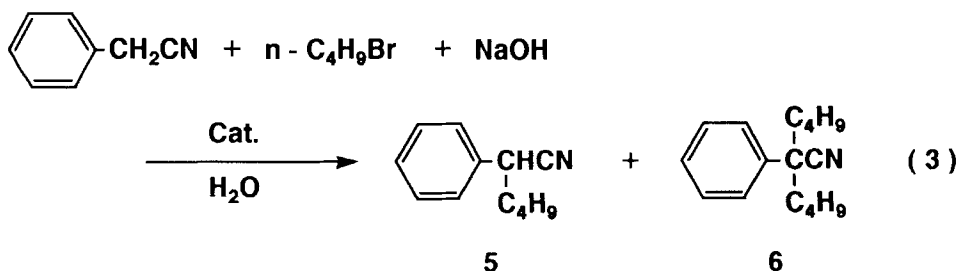
Catalyst ^b	Product yield, %
Imidazole	Trace
<i>N</i> -Methylimidazole	52
<i>N</i> -Benzylimidazole	83
1b	67
2e	61

^a100°C, time = 10 hours, [*n* - C₈H₁₇Br] = 0.55 M (in toluene); 3 mL, [KSCN] = 8.0 M (in H₂O); 5 mL.

^b0.33 mmol based on imidazole group.

results suggest that both the electron density on the nitrogen atom and the hydrophobicity of the substituent are important in catalytic activity.

Next, in order to obtain information on the stability of polymer-supported imidazoles under strongly alkaline conditions, the activity for alkylation of an active methylene compound was examined. The reaction system consisted of a toluene solution of benzyl cyanide and butyl bromide, an aqueous solution of concentrated sodium hydroxide, and imidazole catalysts.



The results are summarized in Table 3.

Similar to the case of the substitution reaction with potassium thiocyanate, imidazole did not display catalytic activity for alkylation, but this reaction was catalyzed effectively by the *N*-alkylated imidazoles (*N*-methylimidazole and *N*-benzylimidazole) to afford monoalkylation product 5 and dialkylation product 6. Further, copolymers 1b and 2b also worked as highly efficient catalysts, although homopolymers 1a and 2a were practically inactive. The difference of this catalytic

TABLE 3. Butylation of Benzyl Cyanide Catalyzed by Imidazoles

Catalyst ^a	Product yield, %	
	Monobutylation (5)	Dibutylation (6)
Imidazole	Trace	0
<i>N</i> -Methylimidazole	65	15
<i>N</i> -Benzylimidazole	85	15
1a	Trace	0
1b	95	5
1c	28	Trace
1d	89	Trace
1d ^b	87	Trace
2a	10	Trace
2b	93	7
2c	51	Trace
2d	76	Trace
2d ^b	38	Trace

^aReaction conditions: Room temperature, time = 24 hours, $\text{C}_6\text{H}_5\text{CH}_2\text{CN}$ = 8.5 mmol, $n\text{-C}_4\text{H}_9\text{Br}$ = 10 mmol, 50% NaOH aq = 13.65 g, catalyst = 1.7 mmol based on imidazole group.

^bReused catalyst.

activity is probably due to the solubility of the polymers; that is, the homopolymers aggregated in the reaction system but the copolymers were soluble in toluene.

Gel-type polymers crosslinked with divinylbenzene also exhibited catalytic activity, and the activity increased with an increase in the styrene content of the resin. This tendency has been observed with polymer-supported ammonium and phosphonium salts as phase-transfer catalysts [9, 10]. It should be noted that these resins catalyzed alkylation to give monoalkylation products exclusively, in contrast to monomeric imidazoles and soluble polymers containing the imidazole moiety. This may be caused by the steric hindrance of the polymer backbone and the restriction of active site mobility by crosslinking. These polymers were recovered by filtration alone. The recovered catalyst 1d was used without a significant loss of activity, but the activity of recovered catalyst 2d was decreased slightly. This result can be understood as due to the decomposition of catalyst through abstraction of the acidic hydrogen in the benzylic position of catalyst 2d under strongly alkaline conditions.

In order to obtain information about the true catalytic species for these reactions, time conversions of alkylations catalyzed by *N*-methylimidazole and the corresponding imidazolium salt 3-butyl-1-methylimidazolium bromide were examined. As can be seen from Fig. 1, the activity of the imidazolium salt is higher than that

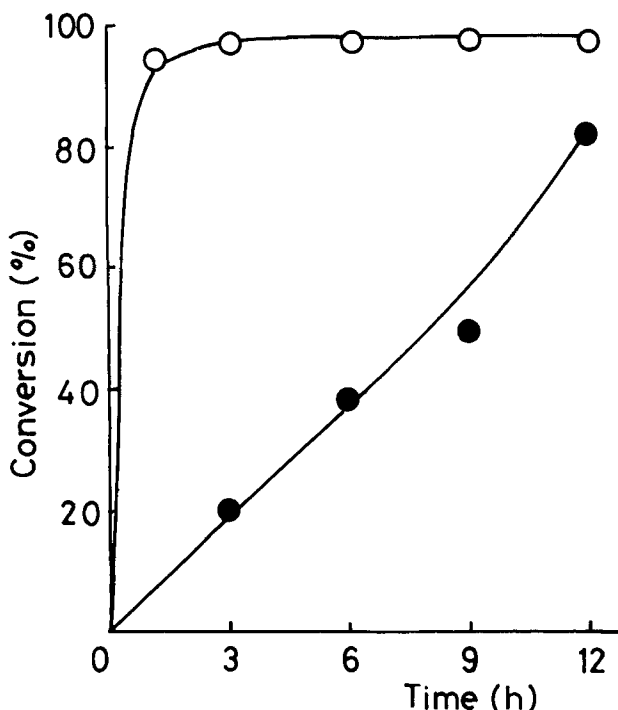


FIG. 1. Time-conversion curves in the formation of alkylation products for the reaction of benzyl cyanide and butyl bromide in the presence of *N*-methylimidazole and 3-butyl-1-methylimidazolium bromide: (●) *N*-methylimidazole, (○) 3-butyl-1-methylimidazolium bromide.

TABLE 4. Reduction of Acetophenone by Sodium Borohydride in the Presence of Imidazoles under Phase-Transfer Conditions^a

Catalyst ^b	Time, h	Yield of product, %
—	24	14
<i>N</i> -Methylimidazole	24	36
<i>N</i> -Benzylimidazole	24	27
1b	12	61
2c	12	66
2d	24	78
2e	24	55
2f	24	23
Poly(2-vinylpyridine) ^c	12	33
Poly(4-vinylpyridine) ^d	12	47

^aReaction conditions: 50°C, C₆H₅COCH₃ = 1.5 mmol, NaBH₄ = 1.2 mmol, benzene = 4 mL, 1% NaOH aq = 0.1 mL.

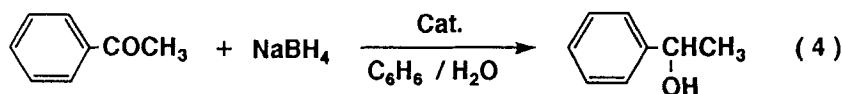
^bCatalyst = 0.15 mmol based on imidazole group.

^cCopolymer containing 30% styrene units.

^dCopolymer containing 50% styrene units.

of *N*-methylimidazole. Further, 3-butyl-1-methylimidazolium bromide was found in the reaction mixture of *N*-methylimidazole and butyl bromide. In addition, polymer catalyst 1b, recovered after the alkylation of benzyl cyanide, also showed characteristic absorption bands based on the imidazolium salt at 1150 and 1565 cm⁻¹ [5]. These results strongly indicate that the activity can be attributed to the “*in-situ*” formation of imidazolium salt.

It was of interest to investigate whether or not imidazoles themselves work as phase-transfer catalysts. We tested the catalytic activity for the reduction of carbonyl compounds with sodium borohydride, because there is no possibility of the formation of imidazolium salts in this system. Acetophenone was chosen as the carbonyl compound. This reaction was carried out in benzene-water solution.



The results are shown in Table 4.

The reaction in the presence of polymer-supported imidazoles afforded 1-phenylethyl alcohol in moderate yield, and the activity was higher than that of polyvinylpyridines, as expected. However, imidazole and *N*-benzylimidazole slightly accelerated this reaction. It should be noted that the activity of polymeric catalysts is superior to that of the monomeric analogues.

Furthermore, the activity increased with an increase of active site density, except for 2c. Similar results have been observed in substitution reactions catalyzed by polymer-supported tetramethylureas [11] and in the reduction of carbonyl compounds catalyzed by polyvinylpyridines [1]. Therefore, the above results can be understood by the following mechanism. Initially, a sodium cation is coordinated

with the nitrogen atoms at the interface in an imidazole and transferred into the organic phase together with the anion as the counterion. The resulting anion attacks the substrate at the organic layer in the polymer.

CONCLUSION

N-Alkylated imidazoles and polymer-supported imidazoles served as phase-transfer catalysts for the reaction of octyl bromide with potassium thiocyanate and the alkylation of benzyl cyanide with butyl bromide in the presence of sodium hydroxide. In these cases the true catalytic species are mainly alkylated imidazolium salts produced *in situ* in the reaction system. Further, polymer-supported imidazoles show a higher selectivity compared with the corresponding monomeric imidazoles for the alkylation reaction. The reduction of carbonyl compounds with sodium borohydride was also accelerated by these catalysts, indicating that alkylated imidazoles themselves work as phase-transfer catalysts.

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