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POLYSTYRENE-SUPPORTED DIMETHYLFORMAMIDES AS PHASE TRANSFER CATALYSTS IN SOLID–SOLID–LIQUID SYSTEM

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ABSTRACT

Polymer-supported dimethylformamides were prepared by copolymerization of *N*-methyl-*N*-(*p*-vinylbenzyl)formamide, styrene, and divinylbenzene with AIBN. These polymers displayed catalytic activity for the reaction of alkyl bromides with alkali metal thiocyanates and potassium acetate in a solid–solid–liquid triphase system, although the corresponding monomeric formamides were inactive. The catalytic activity depended remarkably on the copolymer composition. Further, the catalytic reaction was affected by some experimental parameters such as stirring speed, particle size, degree of crosslinking, and solvent. A plausible catalytic reaction mechanism consisting of collisional contact between the solid catalysts and reagents was proposed.

INTRODUCTION

In previous reports [1, 2], we described that soluble and insoluble polymeric tetramethylureas worked as phase transfer catalysts in liquid–liquid and solid–solid–liquid systems as well as polymer-supported oligo(oxyethylene)s [3–10]. However, the monomeric analogues were inactive. These results are of interest in both a successful appearance of polymer effect and a contribution to the field of organic synthesis. The essence of this polymer effect was thought to be a cooperative function of active sites. Furthermore, the availability as a catalyst in a solid–solid–liquid system is attractive from practical standpoints [11, 12].

Polymeric dimethylformamides were found to display higher activity than the corresponding polymeric tetramethylureas in liquid–liquid phase transfer reactions [13, 14]. The activity depended remarkably on copolymer composition, indicating the importance of a cooperating effect of active sites and hydrophobic microenvironment around the active sites in catalytic activity. Therefore, we think it important to examine the catalytic activity of polymeric formamides in solid–solid–liquid systems from the viewpoint of structure and catalytic activity.

In this paper we describe the catalytic activity of polystyrene-supported dimethylformamides for reactions of alkyl bromides with alkali metal thiocyanates and with alkali metal acetates in the absence of water. Further, the experimental parameters governing these catalytic activities were examined.

EXPERIMENTAL

Materials

1-Bromooctane, benzyl bromide, commercial divinylbenzene containing 45% ethylbenzene and diethylbenzene, and solvents were used after distillation. Alkali metal thiocyanates and acetates were dried for 24 hours at 100°C under reduced pressure before use. Polymer catalysts were prepared by the same method described previously [15]. Other reagents were obtained commercially and used without further purification.

Phase Transfer Reactions

In a test tube (30 mm × 100 mm) with a stopper were placed 1.65 mol/L toluene solution of 1-bromooctane, 0.8 mol/L toluene solution of cyclohexylbenzene (2 mL), and a solid catalyst (0.66 mmol based on amido unit) together with a 15-mm magnetic stir bar. The mixture was stirred at 100°C for 1 hour. Then 10 mmol of an alkali metal thiocyanate was added at zero time. The reaction was followed by GLC analysis (Ohkura 802, Carbowax 20 M over Celite 545 at 160°C), and the results were corrected by calibration with standard mixtures. Initial rates were calculated from the gradients of 1-bromooctane decay curves. The reaction of benzyl bromide with alkali metal acetates was carried out by the same method as the substitution reaction of thiocyanates except for the amount of catalyst. GLC: Silicone SE-30 over Celite 545 at 140°C.

RESULTS AND DISCUSSION

Polymer catalysts were prepared by free-radical polymerization of the corresponding vinyl monomers (Table 1). The structures are shown in Scheme 1. Here x, y, and z represent the mole percent of the corresponding vinyl monomer units, respectively. Polymer catalysts were crushed and separated with sieves before use.

TABLE 1. Preparation of Polystyrene-Supported Dimethylformamides[a]

	Feed composition[b]				Polymer	
Polymer	Wt. of MVFA, g	Wt. of styrene, g	Wt. of DVB, mg	Wt. of AIBN, mg	Yield, g	N, %
1	5.01			47	3.65	7.36
2	3.45	2.05		64	4.48	4.76
3	5.50		0.085	58	3.35	7.22
4	4.78	0.87	0.094	59	3.72	6.37
5	3.45	2.04	0.106	66	3.83	4.83
6	2.53	2.38	0.099	72	3.10	4.07
7	1.26	4.16	0.131	79	3.62	2.31
8	3.45	1.92	0.265	66	3.48	4.78
9	3.46	1.75	0.530	66	5.49	4.47

[a] Temperature: 60°C; time: 40 hours; solvent: DMF (12 mL).

[b] MVFA: *N*-methyl-*N*-(*p*-vinylbenzyl)formamide; DVB: divinylbenzene containing 45% ethylstyrene and diethylbenzene; AIBN: 2,2′-azobisisobutyronitrile.

The catalytic activity was tested for the reaction of 1-bromooctane in toluene with powdered alkali metal thiocyanates. The results are summarized in Table 2.

$$n\text{-}C_8H_{17}Br + MSCN \xrightarrow[\text{Toluene}]{\text{Catalyst}} n\text{-}C_8H_{17}SCN + MBr \qquad (1)$$

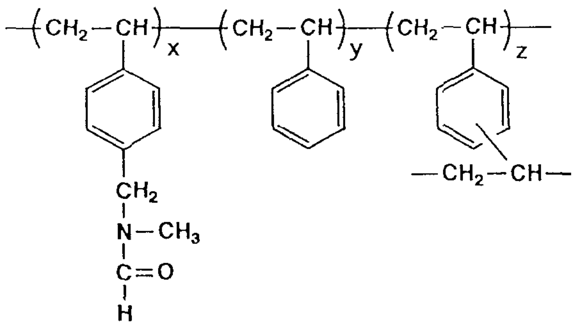
where M = Li, Na, K.

The reaction with potassium thiocyanate proceeded without detectable side reactions in the presence of an insoluble polymer **5** at 100°C, while the monomeric analogues such as DMF and *N*-benzyl-*N*-methylformamide were practically inactive. The polymer catalyst could be recovered by filtration and further used without significant loss in activity.

These observations can be understood by the assumption that a potassium cation interacts with several active sites to form a complex similar to the polymeric ureas [1], and the resulting anion attacks the substrate. This cooperative coordination of active sites would function effectively in polymers, and that would be the main essence of the appearance of catalytic activity.

In order to obtain information about the mechanism of solid-solid-liquid phase-transfer reactions, investigation on the experimental parameters which govern the reaction was carried out. Reaction rates were determined by using a large excess of the inorganic reagents, and they were monitored by following the disappearance of 1-bromooctane. Under these conditions, the reaction followed pseudofirst-order kinetics up to 60% conversion.

We first examined the effects of stirring and of the particle size of catalysts and reagents (Table 3). When the reaction was carried out in the presence of **5** without stirring, the reaction rate dropped remarkably compared to the case of vigorous stirring. Further, the rate decreased with increasing particle size of the catalyst. These facts imply the importance of mass transfer by collisional contact of



Polymer	x	y	z
1	100	0	0
2	49	51	0
3	98	0	2
4	74	24	2
5	50	48	2
6	40	58	2
7	20	78	2
8	50	45	5
9	47	43	10

SCHEME 1.

TABLE 2. Reaction of 1-Bromooctane with Potassium Thiocyanate under Solid-Liquid Phase-Transfer Conditions in the Presence of Monomeric and Polymeric Formamides[a]

Catalyst[b]	Yield of product, %
None	0
N,N-Dimethylformamide	Trace
N-Benzyl-*N*-methylformamide	Trace
5	98
5[c]	95

[a] Temperature: 100°C; time: 20 hours; [n-$C_8H_{17}Br$] = 1.65 mol/L in toluene, 2 mL; KSCN: 10 mmol; catalyst: 0.66 mmol based on amide unit.

[b] Particle size of polymer catalyst = 60–100 mesh.

[c] Recovered catalyst.

TABLE 3. Dependence of Reaction Rate on Particle Size of Catalysts and Reagent, Degree of Crosslinking, and Stirring for the Reaction of 1-Bromooctane with Potassium Thiocyanate[a]

Catalyst	Particle size of catalyst, mesh	Degree of crosslinking, mol%	Rate constant $10^6 k$, s^{-1}
5	60-100	2	38.7
5	60-100	2	2.8[b]
5	60-100	2	21.5[c]
5	100-200	2	44.1
1	Soluble	0	52.0
8	60-100	5	2.9
9	60-100	10	1.1

[a] Experimental conditions were the same as in Table 2.
[b] Without stirring.
[c] Reagent was not ground before use.

solid reagent and solid catalyst. This is further supported by the following observation: When the reagent used consisted of bigger particles, the rate was reduced in comparison with the reaction with a reagent consisting of fine particles.

Next, the dependence of the reaction rate on the degree of crosslinking was examined. If the degree of crosslinking is high, the activity is diminished because the cooperative effect of active sites is depressed and the diffusion of reagents in the polymer particle becomes difficult. As shown in Table 3, a remarkable effect was observed in the range from 0 to 10% crosslinking, and the highest activity was displayed by using the soluble polymeric amide **1**.

In previous reports on phase-transfer reactions in a liquid-solid-liquid system, we insisted upon the importance of a hydrophobic microenvironment around the active sites in catalytic activity [13, 15-17]. Although the solid-solid-liquid system does not contain water, it is of interest to examine the dependence of activity on copolymer composition. The activity was estimated by pseudofirst-order rate constants for the reaction of 1-bromooctane with alkali metal thiocyanates such as potassium, sodium, and lithium thiocyanates. The results are summarized in Fig. 1. Here, the degree of crosslinking of each polymer was 2%.

As can be seen from the figure, the rate constant increases significantly when the amide monomer unit increases from 0 to approximately 40% in all alkali metal thiocyanates. These results can be understood by the consideration that the increasing density of the active sites makes the cooperative coordination to alkali metal cations more effective. In fact, we have previously found that the potassium cation adsorption ability of these polymers increases with increasing active site density [15]. However, when the amide unit content exceeds 40%, the activity interestingly decreases with increasing density of the active site. This finding strongly suggests that catalytic activity is not only affected by cation binding ability, but also by the microenvironment of the active sites. We think that the introduction of styrene to polymeric formamide causes a reduction in polarity around the active sites. There-

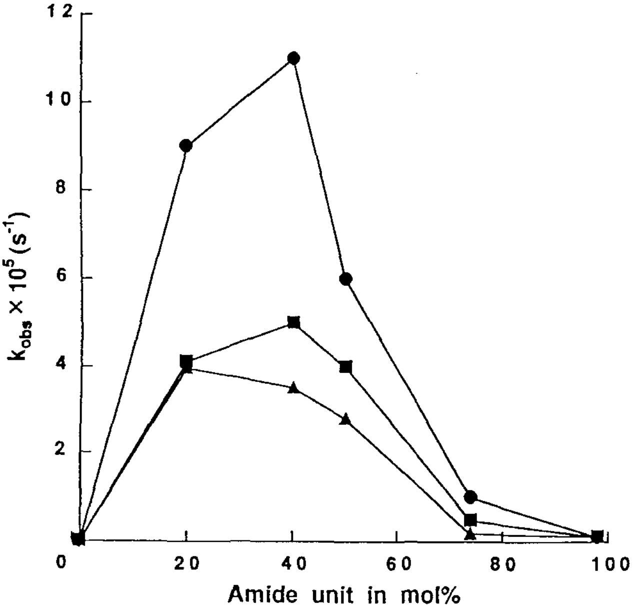


FIG. 1. Dependence of the reaction rate on copolymer composition for the reaction of 1-bromooctane with alkali metal thiocyanates under solid–solid–liquid triphase conditions. Temperature = 100°C; [n-$C_8H_{17}Br$] = 8.0 mol/L in toluene, 2 mL; LiSCN, NaSCN, KSCN: 10 mmol. Catalyst: 0.66 mmol based on the amide unit. Particle size of catalyst = 60–100 mesh. (▲) LiSCN, (●) NaSCN, (■) KSCN.

fore, nucleophiles in these polymeric catalysts become more active compared to those in polymer **1**.

From the above discussions it is clear that complex formation, transfer of reagent into polymer particles, and the microenvironment around active sites are important factors for these catalytic reactions. The transfer of solid reagent into a solid polymer particle might also be affected by the lattice energy of the reagents. It is known that the lattice energy decreases in the order LiSCN > NaSCN > KSCN [18]. Therefore, potassium thiocyanate is expected to react most readily with 1-bromooctane. However, the order of reaction rate was NaSCN > KSCN > LiSCN. This result suggests that the diffusion of alkali metal ions into polymer particles is also an important factor for catalytic activity because the potassium ion is the biggest of the alkali metal ions employed here.

The importance of lattice energy was further implied for the reaction of benzyl bromide with alkali metal acetates. The results are summarized in Table 4.

$$C_6H_5CH_2Br + Ch_3COOM \xrightarrow[100°C]{\text{Catalyst}} C_6H_5CH_2OCOCH_3 + MBr \qquad (2)$$

where M = Li, Na, K.

Polymer catalyst **5** showed low activity for the reaction with sodium acetate and high activity for the reaction with potassium acetate, although the reaction with lithium acetate did not proceed in the presence of **5**. That is, the activity decreased

TABLE 4. Reaction of Benzyl Bromide with Alkali Metal Acetates in the Presence of **5** under Solid–Liquid Phase-Transfer Conditions[a]

Reagent	Lattice energy, kJ/mol[c]	Product yield, %
CH_3COOLi	881	Trace
CH_3COONa	763	5
CH_3COOK	682	92
CH_3COOLi[b]		27

[a] Temperature: 100°C; time: 20 hours; $[C_6H_5CH_2Br] = 1.65$ mol/L in toluene, 2 mL; CH_3COOM: 10 mmol; **5**: 0.33 mmol based on amide unit.

[b] 3 mL water was added.

[c] Reference 18.

with increasing lattice energy, indicating the importance of the transfer of molecular reagent into polymer particles from the solid reagent. In addition, it is interesting that the lattice energy of sodium acetate is comparable to that of lithium thiocyanate, with which the reaction of 1-bromooctane proceeded smoothly. If the importance of lattice energy for catalytic reaction is reasonable, the substitution reaction of alkyl bromides would occur by elimination of the effect on lattice energy. In fact, the reaction of benzyl bromide with lithium acetate in the presence of **5** proceeded when a small amount of water was added (Table 4). On the other hand, Liotta et al. explained a similar phenomenon on the basis of the formation of a sigma phase [19].

CONCLUSION

Polystyrene-supported dimethylformamides worked as phase-transfer catalysts for the reaction of alkyl bromides with alkali metal thiocyanates and potassium acetate in a solid–solid–liquid triphase system, although the corresponding monomeric species were inactive. The activity depended remarkably on the composition of polymer catalysts. From an investigation of the experimental parameters, the catalytic reaction was thought to proceed as follows. First, a powdered reagent makes contact with a solid polymer particle and then a complex is formed by cooperative coordination of active sites in the polymer to an alkali metal ion in the reagent. The resulting nucleophile attacks a substrate in the polymer particle to afford the product.

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