Catalysis of Polymers Containing Quaternized Linear Poly(*N*-alkylethyleneimine) Chain in Aqueous–Organic Hetero-Phase Reactions

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ABSTRACT: This paper describes the catalyst activity of quaternized poly(styrene-*g*-ethyleneimine) (cross-linked with 3-% divinylbenzene) having linear (nonbranched) polyethylenimine blocks. The reactions employed were substitution reaction ($\text{RBr} + \text{Y}^- \rightarrow \text{RY} + \text{Br}^-$; $\text{Y}^- = \text{CN}^-$, CH_3CO_2^-) and dichlorocyclopropanation of cyclohexene with CHCl_3 – NaOH system. The above catalyst which was quaternized with butyl bromide, **1**, showed a higher catalyst activity in comparison with similar cross-linked resins having dimethylbutylbenzylammonium **2** and trimethylbenzylammonium groups **3**, respectively. In addition, the catalyst activity of quaternized polyethyleneimine having linear structure, **4**, was also examined and compared with that of other quaternary ammonium salts **5**–**8**.

KEY WORDS Polymer Catalyst / Quaternized Poly(styrene-*g*-ethyleneimine) / Linear Polyethyleneimine / Phase-Transfer Catalysis / Substitution Reaction / Dichlorocyclopropanation /

Recently, a considerable number of papers have dealt with studies on the polymer catalysts and polymer reagents, in which the usefulness as well as the convenience of polymers have been pointed out.^{1,2}

Recently, we reported on the preparation of cross-linked poly(styrene-*g*-ethyleneimine) (PSt-*g*-EI) having linear polyethyleneimine blocks. It was prepared by the graft polymerization of 2-methyl-2-oxazoline onto chloromethylated polystyrene (cross-linked with 3-% divinylbenzene) and the subsequent hydrolysis of the graft copolymer.³ The product PSt-*g*-EI could be quaternized by the reaction with alkyl bromide. This paper reports the application of the quaternized PSt-*g*-EI as a catalyst for the nucleophilic substitutions of butyl and octyl bromides by cyanide and acetate anions in aqueous–organic hetero-phase and

for dichlorocyclopropanation of cyclohexene in a CHCl_3 – NaOH (aq) system. Tetralkylammonium salts are known to catalyze many aqueous–organic hetero-phase reactions involving various anions, as first reported by Starks (phase-transfer catalysis).⁴ Moreover, many organic reactions can be achieved by such catalysis even without organic solvents. Phase-transfer catalysts, however, sometimes emulsify the reaction system to cause inconvenience to the work-up and separation procedures. In order to eliminate such inconvenience, an anion exchange resin was once used which had similar functions of a phase-transfer catalyst and at the same time was readily separated from the reaction mixture.² In this study, it has been found that quaternized PSt-*g*-EI is more effective than a similar type of anion exchange resin. The catalysis of water soluble quaternized linear polyethyl-

eneimines is also described.

RESULTS AND DISCUSSION

Nucleophilic Substitutions

The substitutions shown in eq 1 were carried out in an aqueous-organic system using quaternary ammonium salts, 1—8. Quaternized PSt-*g*-EI (1) and *N*-butylated (2) and *N*-methylated (3) poly- (*N,N*-dimethylaminomethylstyrene)s are in the form of macroporous beads (40—100 mesh) whose polystyrene backbone is cross-linked with 3-% divinylbenzene. Catalysts 4 and 5 are quaternized linear polyethyleneimines, and are water soluble polymers. Quaternary ammonium bromides, 6, 7, and 8 are employed here for the purpose of comparison with the polymeric catalysts. Tetrabutylammonium bromide 8 is known as one of

R = butyl, octyl

Y⁻ = CN⁻, CH₃CO₂⁻

Catalysts :

phase.^{4,5}

The addition of 0.3 mmol of catalyst 1 was very effective for these reactions. The catalyst amount employed was five times as much as all the other systems. However, the reaction was accelerated by only 1.2 times (No. 2 and No. 3 in Table I).

Catalyst 1 has an -NH- group not quaternized. This group was not very important in accelerating

the most effective phase-transfer catalyst.^{4,5} Among the eight catalysts above 7, 8⁴ and a similar type of 2² have so far been employed as catalysts.

The experiments were carried out in a glass tube equipped with a reflux condenser. Three kinds of reagents (butyl or octyl bromide, sodium cyanide or potassium acetate, and a catalyst) were added in a mixture of water and ethylbenzene (an internal standard for GLPC analysis). The mixture was stirred at 100°C for 2 hr, and then the organic phase was analyzed by means of GLPC. The rate of stirring of the system was the same throughout. It was checked by GLPC that butyl or octyl bromide no longer reacted with the catalysts. These results are shown in Table I.

The catalysis of 1 is noteworthy. Among cross-linked type catalysts 1—3, the best result was obtained with 1. The catalyst activity of 1 was clearly demonstrated especially in the reaction with longer alkyl substrates, *e.g.*, octyl bromide. The higher efficiency of 2 than that of 3 is probably due to the increased affinity toward organic

the reactions. For example, the use of cross-linked PSt-*g*-EI hydrogen bromide ([NH], 1 mmol) gave only *ca.* 3% of BuCN under the same conditions in Table I. In experiment No. 2, all the nitrogen was added (No. 2 and No. 5 in Table I). Catalyst 1 contains a small amount of an acetamide group which is not hydrolyzed in the preparation of PSt-*g*-EI. This group is shown to be less effective

Table I. Catalysis on substitutions^a and dichlorocyclopropanation^b

Run no.	Catalyst	Product yield, % ^c
		BuCN	OctCN	BuOAc	OctOAc		
1	none	0	0	~0	~0		~0
2	1	64 (84) ^f	54	39	34		53
3 ^d	1	72 (95) ^f	—	—	—		—
4	2	37	7	21	3.2		21
5 ^e	2	—	14	—	8		—
6	3	7.3	0.3	13	0.5		3
7	4	~100	95	72	63		36 ^g
8	5	—	16	—	17		—
9	6	~0	~0	~0	~0		—
10	7	6	1.8	7	1.9		—
11	8	~100	~100	~100	~100		47 ^g

^a Reactions: $\text{RBr} + \text{Y}^- \rightarrow \text{RY} + \text{Br}^-$, R = butyl or octyl, $\text{Y}^- = \text{CN}^-$ or AcO^- . Conditions: catalyst, 0.3 mmol (as ammonium group); RBr, 10 mmol; salt (NaCN or KOAc), 30 mmol; PhEt (internal standard), 1 ml; H_2O , 2 ml; 100°C; 2 h.

^b Reaction: . Conditions: catalyst, 1 mmol (as ammonium group); cyclohexene, 10 mmol; CHCl_3 , 4 ml; decalin (internal standard), 1 ml; 50-% NaOH aq, 2 ml; 50°C; 22 h.

^c Yields are based on RBr or cyclohexene.

^d Catalyst, 1.5 mmol (as ammonium group).

^e Catalyst: ammonium group, 0.67 mmol; total nitrogen, 0.8 mmol.

^f 3 h.

^g 2 h.

Table II. Catalysis of acetamide unit^a

Catalyst	none	Poly(<i>N</i> -acetyl ethylenimine)	<i>N,N</i> -Dimethyl acetamide
Yield of BuCN, %	8.2	8.6	36

^a Reaction conditions: BuBr 2 mmol; NaCN, 2.4 mmol; acetone, 2 ml; catalyst, 10 mmol; 60°C; 8 h.

tive especially as a polymeric form in the catalysis of these reactions as shown in Table II.

A water-soluble polymer **4** was found to be even more effective than **1**–**3**. However, the activity of **4** was lower than that of **8** (Table I), probably due to the decreased solubility of the former in an organic phase. The function of **4**, therefore, is different from that of the phase-transfer catalyst **8**. The substitution using **4** as catalyst probably proceeds at the interface between organic and aqueous phases. It is shown that quaternary ammonium salts soluble in organic phase are more suitable

than less soluble ones for phase-transfer catalysts.^{4,5} For example, soluble compound **8** is effective, whereas tetraethylammonium bromide **6** having the decreased solubility is not effective (see Table I and ref 5). **4**, a polymeric analogue of tetraethylammonium bromide, is quite effective although it is insoluble in organic phase. Similarly, **5** was more effective than **7**. This is due to the longer linear quaternary ammonium structure of **5**. In addition, the presence of an *N*-benzyl group generally reduces the catalyst activity.⁴ The greater activity of **4** compared with that of **5** may be due to this reason.

Dichlorocyclopropanation

Using **1**–**4** or **8** as catalyst, the dichlorocyclopropanation of cyclohexene with chloroform and aqueous sodium hydroxide was carried out in a similar manner (last column in Table I). The resin catalysts **1**–**3** were less effective than **4** and **8** because of the disadvantage of their cross-linked

structure. The cyclohexene gave dichloronorcarane in 3–50% yields after 22 h of reaction with **1**–**3**. On the other hand, with **4** or **8**, 40–50% dichloronorcarane was obtained after 2-h reaction. The order of catalytic effectiveness was in agreement with that of the substitutions. In the generation of dichlorocarbene at an interface between chloroform and aqueous sodium hydroxide, the polymeric quaternary ammonium salt **1** was also more effective than **2** and **3**.

Repeated Use of **1**

1 was easily recovered from the reaction system simply by filtration and washing with methanol and water. The repeated use of the catalyst was attempted in a substitution. As shown in Table III, the repeated use of catalyst **1** even slightly increased the catalytic activity. It may be due to the increase in surface area of the resin since resin catalyst **1** was crushed during the reaction with vigorous stirring.

Table III. Repeating use of **1**^a

	Reaction time, h	Yield of BuCN, %
1st	3	95
2nd	3	98
3rd	2.5	100

^a Reaction: $\text{BuBr} + \text{CN}^- \longrightarrow \text{BuCN} + \text{Br}^-$.

Conditions: **1**, 0.5 g; BuBr, 10 mmol; NaCN, 30 mmol; PhEr, 1 ml; H₂O, 2 ml; 100°C.

Catalytic Functions

The above findings have shown that polymeric quaternary ammonium salts **1** and **4** accelerate the substitution at an interface. With the so-called phase-transfer catalyst, the substitution reaction is known to occur in organic phase.⁵ In the reaction catalyzed by **4** between alkyl bromide and aqueous sodium cyanide, the reaction path is probably shown as follows, *i.e.*, the displacement of anion of the polymeric ammonium salt (QBr) occurs in an aqueous phase (eq 2) and the substitution of alkyl bromide proceeds in an interface (eq 3). The difference with the phase-transfer

catalysis⁴ is step of eq 3.

Catalytic functions of **1** may be similar to tri-

phase catalysis.² The efficiency of **1**, however, was much higher than that of triphase catalyst **2**, indicating the importance of the linear polyethyleneimine chain. The holes of the macroporous resin such as **1**–**3** are filled with organic and aqueous phases. The combination of organic and aqueous phases present in a hole is important for the reaction. The bromide anion of the quaternary ammonium in the resin is replaced by cyanide (or acetate) in the aqueous phase, and then the substitution of alkyl bromide by cyanide (or acetate) takes place in the organic phase to produce alkyl cyanide (or acetate). In this process the availability of the quaternary ammonium group is much higher in **1** than **2** or **3** due to the higher mobility of the long polyethyleneimine chain of **1**. The organic and aqueous phases in the holes are freely interconvertible with the respective phases outside of the resin with diffusion of stirring.

EXPERIMENTAL

Materials

Commercial reagents of butyl and octyl bromides, cyclohexene and all solvents were distilled under nitrogen. Other reagents which are commercially available, were used without further purification. Linear polyethyleneimine was obtained by the polymerization of 2-methyl-2-oxazoline followed by alkaline hydrolysis of the polymer.³ The degree of hydrolysis was 92% (from N%), 100% (from NMR) and $[\eta]_{\text{MeOH}}^{30^\circ\text{C}}$ was 0.23 dl/g. *Anal.* Found: C, 53.27; H, 11.29; N, 30.14. Cross-linked PSt-*g*-EI was prepared from chloromethylated polystyrene (cross-linked with 3-% divinylbenzene) and 2-methyl-2-oxazoline as reported previously.³ The ethylenimine unit content was 9.92 mmol/g (degree of hydrolysis = 67.3%), and the $\overline{\text{DP}}$ of the graft chain was 15.9. *Anal.* Found: C, 58.51; H, 10.22; N, 20.64.

Preparation of **1**

Cross-linked PSt-*g*-EI (1.50 g) was swollen in 10 ml of ethanol and then 6.4 ml of butyl bromide were added to the swollen PSt-*g*-EI. The mixture was stirred under nitrogen at 80°C for 30 h. The product was isolated by filtration and washed successively with ethanol, 2-*N* NaOH aqueous solution, water and ethanol. The reaction with butyl bromide was repeated twice. The product was

washed with ethanol, followed by vacuum drying at 70°C, and 1.58 g of **1** was obtained. *Anal.* Found: C, 53.32; H, 9.24; N, 10.15; Br, 24.35. The ammonium group content calculated from Br content was 3.05 mmol/g, which corresponds to 42% of nitrogen atoms are in a form of ammonium nitrogens.

Preparation of **2** and **3**

In order to prepare **2**, commercial anion-exchange resin (DIAION WA30) was treated with butyl bromide. The degree of quaternization and the quaternary ammonium group content were 84.5% and 2.73 mmol/g, respectively. A commercial anion-exchange resin (DIAION PA306) treated successively with NaOH aq and HBr aq was used for **3**. The quaternary ammonium group content was 3.68 mmol/g. The screen grading of the commercial resins was 297–1190 μ according to the specification. We used finer samples (about 150–400 μ) by grinding the resins.

Preparation of Quaternized Linear Polyethylimine **4**

To 2.70 g of linear polyethyleneimine dissolved in 20 ml of methanol was added 15.8 ml of ethyl bromide. The mixture was refluxed under nitrogen for 48 h. After the solvent and excess ethyl bromide were distilled off, the product was dissolved in water. The solution was allowed to flow down through a column packed with an anion-exchange resin (DIAION PA306, OH form) and the effluent solution was evaporated. To the residue, 20 ml of methanol and 15.8 ml of ethyl bromide were added. The mixture was refluxed for 48 h under nitrogen. The product was purified by reprecipitation using ether and dried in vacuo at 70°C to give 2.93 g of quaternized polyethylimine **4**. *Anal.* Found: C, 41.87; H, 9.09; N, 13.26; Br, 36.44. The ammonium group content calculated from Br content was 4.56 mmol/g, which corresponds to 48% of nitrogen atoms in the form of ammonium nitrogens.

Preparation of **5**

Poly(2-phenyl-2-oxazoline) was reduced by LiAlH_4 .⁶ To 0.33 g of the reduction product **9** dissolved in 4 ml of ethanol was added 1 ml of ethyl bromide. The mixture was refluxed under nitrogen for 48 h.

x , 59.3%; y , 25.9%; z , 14.8%; $\overline{M}_n$, 4,600.

The product was purified by reprecipitation using hexane and dried in vacuo at 70°C; yield 0.42 g. *Anal.* Found: C, 53.95; H, 7.51; N, 9.62; Br, 25.46. The ammonium group content calculated from elemental analysis (Br%) was 3.19 mmol/g. On the other hand, the NMR analysis of **5** (in D_2O) gave the integration ratio of peaks at δ 0.6–1.6 (CH_3), 2.1–4.5 (NCH_2) and 7.24 (C_6H_5) ppm of 42: 170: 95, corresponding to 3.15 mmol/g of the ammonium group content. These results were in close agreement with each other.

Substitution and Dichlorocyclopropanation

The experimental conditions are shown in the foot notes of the Tables I, II, and III. The yield of the main product was calculated from the gas chromatogram. A typical experiment was as follows. Butyl bromide (10 mmol), sodium cyanide (30 mmol), water (2 ml) and 1 ml of ethylbenzene (internal standard) were mixed. The mixture was stirred at 100°C without or with catalyst (0.3 mmol of ammonium group). The organic phase was analyzed by gas chromatography every 1 h.

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