ergetic differences between stabilization of monomers and radicals more so than differences on steric strain, but more experimental data would be necessary to give definitive conclusions.

Registry No. Methyl α-benzylacrylate, 3070-71-1; dimethyl malonate, 108-59-8; dimethyl benzylmalonate, 49769-78-0; benzyl chloride, 100-44-7; monomethyl benzylmalonate, 54561-75-0; formaldehyde, 50-00-0.

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Substitution Reaction of Poly((chloromethyl)styrene) with Salts of Various Nucleophilic Reagents Using Phase-Transfer Catalysts

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ABSTRACT: The substitution reactions of poly((chloromethyl)styrene) (polymer 1) with various nucleophilic reagents were studied by using phase-transfer catalysts (PTCs) such as tetrabutylammonium bromide (TBAB), tetrabutylphosphonium bromide (TBPB), dicyclohexyl-18-crown-6 (DCHC), 18-crown-6 (CR6), and 15-crown-5 (CR5) in solid–liquid and liquid–liquid two-phase reaction systems. From these studies, the following was found. The quaternary salts TBAB and TBPB were more effective than the crown ethers DCHC, CR6, and CR5 in the reaction of the chloromethyl group in polymer 1 with the salts of O-anions such as carboxylate and phenolate. On the other hand, the lipophilic crown ether DCHC showed higher catalytic activity than the quaternary salts in the reaction of the chloromethyl group in the polymer with the salts of S-anions. Also, the catalytic activity of the PTCs in the reaction of polymer 1 with salts of N-anions lies between those in the reactions of polymer 1 with salts of S-anions and O-anions. Generally, the solid–liquid two-phase system gives a polymer with a higher degree of substitution than does the liquid–liquid two-phase system. However, when lipophilic PTCs such as DCHC and lipophilic reagents such as S-anions are used, polymers with high degrees of substitution can be obtained by employing the liquid–liquid two-phase system.

Introduction

The substitution reactions of the pendant chloromethyl groups in the polymers with some nucleophilic reagents have been investigated[1] in aprotic polar solvents such as hexamethylphosphorus triamide, *N,N*-dimethylformamide (DMF), dimethyl sulfoxide and *N*-methyl-2-pyrrolidone, and the effect of the polymer skeletons on the reactivity of the pendant chloromethyl groups and the solvent effect in the reactions have been determined. Also, it was elucidated that the addition of the quaternary salts or crown ethers to these reaction systems accelerated[1c,e] the reaction of the pendant chloromethyl group in the polymer with the nucleophilic reagents. Recently, the substitution reactions of the pendant chloromethyl groups in the polymers with nucleophilic reagents have been studied[2] by using phase-transfer catalysts (PTCs) in nonpolar solvents such as toluene, chlorobenzene, diglyme, and others. This simple and economical method is very important for the modifications of the commercial polymers and the syntheses of the functional polymers such as polymer supports, polymeric reagents, polymeric catalysts, and polymeric carriers. Also the reactions of the active alkyl halide and alkyl sulfonates with nucleophilic reagents were carried out[3] with a great number of quaternary salts and crown ethers as PTCs in organic chemistry. The catalytic effect in each reaction, the reactivity of alkyl halides with nucleophilic reagents, and the solvent effect were studied from those results. However, the relationship between the catalytic activity of PTCs and the reactivity of haloalkyl groups with nucleophilic reagents has not been reported on the reactions of pendant chloromethyl groups contained in the polymers and the alkyl halides with nucleophilic reagents using PTC so far.

In an earlier article,[4] we have established the relationship between the catalytic activity of PTCs and the reactivity of chloromethyl group with the nucleophilic reagents in the solid–liquid two-phase reactions of poly((chloromethyl)styrene) (polymer 1) with potassium acetate and potassium thioacetate using quaternary salts and crown ethers as a PTC under mild conditions.

In this article, we wish to describe the catalytic effect of PTCs in the substitution reaction of polymer 1 with

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various nucleophilic reagents in solid–liquid and liquid–liquid two-phase systems using PTCs under mild conditions.

Experimental Section

Materials. Solvents, Reagents, Catalysts, and Polymer. The solvents were purified by distillation prior to use. Reagent grade (Wako Pure Chemical Ind.) of potassium acetate (KOAc), sodium acetate (NaOAc), lead acetate trihydrate [$Pb(OAc)_2 \cdot 3H_2O$], sodium benzoate, (NaBz), potassium thiocyanate (KSCN), sodium thiocyanate (NaSCN), sodium azide (NaN_3), potassium phthalimide (KNPht), 15-crown-5 (CR5), and 18-crown-6 (CR6), reagent grade (Tokyo Chemical Industry Co.) of tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI), tetrabutylammonium perchlorate (TBAP), and tetrabutylammonium hydrogen sulfate (TBAH), and reagent grade (Aldrich Chemical Co.) of tetrabutylphosphonium bromide (TBPB) and dicyclohexyl-18-crown-6 (DCHC) were used without further purification. Potassium benzoate (KOBz), potassium phenolate (KOPh), potassium thioacetate (KSAc), and potassium thiophenolate (KSPh) were prepared from the reaction of potassium hydroxide with the corresponding acids or phenol (Wako Pure Chemical Ind.) in methanol, and then they were recrystallized from methanol. Potassium azide (KN_3) was prepared according to the reported method.[5] Polymer 1 (the reduced viscosity of the polymer in benzene was 0.16 dL/g, measured at a concentration of 0.5 g/dL at 30 °C) was prepared in 90% yield by radical polymerization of chloromethylated styrene (mixture of 40% meta and 60% para) using AIBN in benzene at 60 °C for 8 h.

Apparatus. Infrared (IR) spectra were measured on the JASCO model A-202 spectrophotometer. The ^1H NMR spectra were performed on the JEOL Model JNM PS-100 spectrometer.

Substitution Reactions of Polymer 1 with Various Nucleophilic Reagents. Typical examples of the reactions of polymer 1 with nucleophilic reagents are as follows.

Substitution Reaction of Polymer 1 with Potassium Acetate in the Solid–Liquid Two-Phase System. Polymer 1 (0.61 g, 4 mmol) was dissolved in toluene (10 mL), and then potassium acetate (0.39 g, 4 mmol) and TBAB (0.13 g, 0.4 mmol) were added to the polymer solution. The reaction mixture was stirred at about 300 rpm at 30 °C for 24 h and then poured into methanol. The reaction product was purified by reprecipitating twice from tetrahydrofuran (THF) into water and from THF into methanol and then dried in vacuo at 50 °C. The yield of the polymer was 0.59 g. The degree of esterification of the polymer was 70.4 mol % (calculated from chlorine analysis[2a]). The reduced viscosity of the polymer in benzene was 0.17 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorptions at 1740 (C=O) and 1240 cm^{-1} (C—O—C). The ^1H NMR spectrum ($CDCl_3$) showed δ 2.0 (CO—CH_3) and 4.3 (CH_2—O).

Substitution Reaction of Polymer 1 with Potassium Acetate in the Liquid–Liquid Two-Phase System. To polymer 1 (0.61 g, 4 mmol) in toluene (10 mL) was added a saturated aqueous solution of potassium acetate (5 mL) and TBPB (0.16 g, 0.4 mmol). The mixture was stirred at about 300 rpm at 30 °C for 24 h and then poured into methanol. The reaction product was purified by reprecipitating twice from THF into water and from THF into methanol and then dried in vacuo at 50 °C. The yield of the polymer was 0.60 g. The degree of esterification of the polymer was 82.7 mol % (calculated from chlorine analysis). The reduced viscosity of the polymer in benzene was 0.16 dL/g, measured at a concentration of 0.5 g/dL at 30 °C.

Substitution Reaction of Polymer 1 with Potassium Phenolate in the Solid–Liquid Two-Phase System. The reaction of polymer 1 (0.61 g, 4 mmol) with potassium phenolate (0.53 g, 4 mmol) was carried out in the presence of TBAC (0.11 g, 0.4 mmol) in toluene (10 mL) at 30 °C for 24 h and the product was purified by the same procedure described above. The yield of the final polymer was 0.53 g. The degree of substitution of the polymer was 49.4 mol % (calculated from chlorine analysis). The reduced viscosity of the polymer in DMF was 0.18 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. The IR spectrum (film) showed absorption at 1240 cm^{-1} (C–O–C). The ^1H NMR spectrum ($CDCl_3$) showed δ 4.5 (CH_2–O).

Substitution Reaction of Polymer 1 with Potassium Thioacetate in the Solid–Liquid Two-Phase System. Polymer 1 (0.61 g, 4 mmol) was allowed to react with potassium thioacetate (0.46 g, 4 mmol) in the presence of TBAB (0.13 g, 0.4 mmol) in toluene (10 mL) at 30 °C for 24 h. The yield of the final polymer was 0.68 g. The degree of substitution was 99.0 mol % from chlorine analysis). The reduced viscosity of the polymer in DMF was 0.17 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (film) 1690 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.3 (CO–CH_3) and 4.0 (CH_2–S).

Substitution Reaction of Polymer 1 with Potassium Thiophenolate in the Solid–Liquid Two-Phase System. The reaction of polymer 1 (0.61 g, 4 mmol) with potassium thiophenolate (0.53 g, 4 mmol) was carried out in the presence of TBAB (0.13 g, 0.4 mmol) in toluene (10 mL) at 30 °C for 24 h. The yield of the final polymer was 0.78 g. The degree of substitution was 99.0 mol % (from chlorine analysis). The reduced viscosity of the polymer in DMF was 0.15 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (film) 1590 cm^{-1} (aromatic C=C); ^1H NMR ($CDCl_3$) δ 3.9 (CH_2–S).

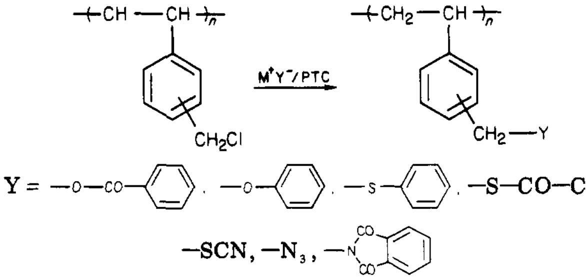
Substitution Reaction of Polymer 1 with Potassium Thiocyanate in the Solid–Liquid Two-Phase System. Polymer 1 (0.61 g, 4 mmol) was made to react with potassium thiocyanate (0.39 g, 4 mmol) in the presence of TBAB (0.13 g, 0.4 mmol) in toluene (10 mL) at 30 °C for 24 h. The yield of the final polymer was 0.51 g. The degree of substitution was 62.5 mol % (from chlorine analysis). The reduced viscosity of the polymer in DMF was 0.21 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (film) 2150 cm^{-1} (SCN); ^1H NMR ($CDCl_3$) δ 3.9 (CH_2–S).

Substitution Reaction of Polymer 1 with Sodium Azide in the Solid–Liquid Two-Phase System. The reaction of polymer 1 (0.61 g, 4 mmol) with sodium azide (0.26 g, 4 mmol) was carried out in the presence of TBAB (0.13 g, 0.4 mmol) in toluene (10 mL) at 30 °C for 24 h. The yield of the final polymer was 0.52 g. The degree of substitution was 99.0 mol % (from chlorine analysis). The reduced viscosity of the polymer in DMF was 0.17 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (film) 2100 cm^{-1} (N_3); ^1H NMR ($CDCl_3$) δ 4.1 (CH_2–N_3).

Substitution Reaction of Polymer 1 with Potassium Phthalimide in the Solid–Liquid Two-Phase System. The reaction was carried out as above on polymer 1 (0.61 g, 4 mmol) in the presence of TBPB (0.16 g, 0.4 mmol). The yield of the final polymer was 0.66 g. The degree of substitution was 65.8 mol % (from chlorine analysis). The reduced viscosity of the polymer in benzene was 0.12 dL/g, measured at a concentration of 0.5 g/dL at 30 °C. IR (film) 1770 and 1720 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 3.6 (CH_2–N).

Results and Discussion

Substitution Reaction of Polymer 1 with O-Anion of Nucleophilic Reagents. The substitution reactions of polymer 1 with various nucleophilic reagents were carried out using the typical PTCs such as TBAB, TBPB, CR5, CR6, and DCHC under mild conditions (eq 1). The reaction conditions and results of polymer 1 with O-anions of the reagents are summarized in Table I. The solid–liquid two-phase reactions between polymer 1 dissolved in toluene and solid potassium acetate or potassium benzoate did not occur in the absence of PTC (no. 1). How-



(1)

$M^+ = Na^+, K^+, Pb^{2+}$

Table I
Substitution Reaction of Polymer 1 with Salts of O-Anion Using PTC

no.	nucleophilic reagent	solvent	PTC	degree of substitution, mol %
1	KOAc (2.88)[a]	toluene	none	0
2	KOAc	toluene	CR5	trace
3	KOAc	toluene	CR6	24.3
4	KOAc	toluene	DCHC	4.2
5	KOAc	toluene	TBAB	73.9
6	KOAc	toluene	TBPB	78.9
7	KOAc	toluene/water[b]	CR5	trace
8	KOAc	toluene/water[b]	CR6	trace
9	KOAc	toluene/water[b]	DCHC	5.9
10	KOAc	toluene/water[b]	TBAB	66.4
11	KOAc	toluene/water[b]	TBPB	82.7
12	NaOAc (0.67)[a]	toluene	CR5	14.1
13	NaOAc	toluene	CR6	trace
14	NaOAc	toluene	DCHC	0
15	NaOAc	toluene	TBAB	37.9
16	NaOAc	toluene	TBPB	45.5
17	NaOAc	toluene/water[b]	CR5	0
18	NaOAc	toluene/water[b]	CR6	0
19	NaOAc	toluene/water[b]	DCHC	trace
20	NaOAc	toluene/water[b]	TBAB	11.0
21	NaOAc	toluene/water[b]	TBPB	18.9
22	$Pb(OAc)_2 \cdot 3H_2O$[c]	toluene	CR5	10.0
23	$Pb(OAc)_2 \cdot 3H_2O$	toluene	CR6	21.2
24	$Pb(OAc)_2 \cdot 3H_2O$	toluene	DCHC	5.3
25	$Pb(OAc)_2 \cdot 3H_2O$	toluene	TBAB	20.6
26	$Pb(OAc)_2 \cdot 3H_2O$	toluene	TBPB	34.0
27	KOBz (0.48)[a]	toluene	CR5	trace
28	KOBz	toluene	CR6	10.9
29	KOBz	toluene	DCHC	7.1
30	KOBz	toluene	TBAB	63.7
31	KOBz	toluene	TBPB	55.3
32	NaOBz (0.31)[a]	toluene	CR5	3.2
33	NaOBz	toluene	CR6	5.2
34	NaOBz	toluene	DCHC	trace
35	NaOBz	toluene	TBAB	42.8
36	NaOBz	toluene	TBPB	44.7
37	KOPh	toluene	none	0
38	KOPh	toluene	CR6	51.8
39	KOPh	toluene	DCHC	55.0
40	KOPh	toluene	TBAC	49.0
41	KOPh	diglyme	none	57.8
42	KOPh	diglyme	CR6	70.5
43	KOPh	diglyme	TBAC	60.9

[a] Solubility[14] is expressed as the number of mols of the reagent which can be dissolved in 100 g of water at 30 °C. [b] 5 mL of saturated aqueous solution of the reagent was added. [c] Solubility of $Pb(AcO)_2$[14] in water at 30 °C is 0.21 mol/100 g of water.

ever, the addition of PTC caused the reaction to proceed. In these reaction systems, CR6 showed higher catalytic activity than the other crown ethers such as CR5 and DCHC (no. 2–4, 27–29). Furthermore, the quaternary salts such as TBAB and TBPB showed higher catalytic activity than the crown ethers such as CR5, CR6, and DCHC in the reactions of polymer 1 with potassium salts of carboxylic acids (no. 5, 6, 30, 31). The same result has been reported by Vander Zwan et al.[6] in the reaction of benzyl chloride and hexyl bromide with some nucleophilic reagents. These results suggested that the quaternary salts are good PTCs in the reactions of polymer 1 with potassium salts of carboxylic acids in the solid–liquid two-phase system as well as in the liquid–liquid two-phase system (no. 7–10).

The degree of esterification of the polymer in the reaction of polymer 1 with solid sodium acetate was also lower than that in the reaction of polymer 1 with potassium acetate using the 18-crown-6 ethers as a PTC under the same conditions (no. 3, 4, 13, 14). On the other hand, the degree of esterification in the former reaction was greater than that in the latter reaction when CR5 was used as a PTC, because 18-crown-6 ethers easily form the complex with potassium ion and CR5 with sodium ion, respectively[7] (no. 2, 12).

Although the reaction using quaternary salts is assumed to be independent of metal ions of the reagents, the degree of esterification of the product in the reaction of polymer 1 with sodium acetate using the quaternary salts was lower than that in the reaction of polymer 1 with potassium acetate (no. 5, 6, 15, 16). Similar results were also observed in the reaction of polymer 1 with potassium benzoate or sodium benzoate in the solid–liquid two-phase system (no. 27–31, 32–36). The reaction of polymer 1 with lead acetate using the crown ethers proceeded in toluene with the same degree of esterification as the reaction of polymer 1 with potassium acetate (no. 22–24), while the degree of esterification in the former using the quaternary salts was lower than those in the reactions of polymer 1 with potassium acetate and sodium acetate (no. 25, 26).

These results suggested that the reactivity in the esterification of polymer 1 with salts of carboxylic acids strongly depended on the species of metal ions of the reagents when the quaternary salts were used as a PTC. This effect may be attributed to the extractivity of the anion from the solid phase to the organic phase. Although detailed mechanism for the extraction by the quaternary salts cannot be clarified in the solid–liquid two-phase system, the following two explanations are proposed: direct extraction of the anion from the crystal lattice of the reagent or the extraction of the anion from the saturated aqueous solution on the surface of the crystal lattice of the reagent arising from a trace amount of water in this system. Starks[8] has reported that when hexyltributylphosphonium bromide is used as a PTC, 1-chlorooctane reacts with sodium cyanate, although the reaction scarcely occurs under anhydrous conditions. This result also supported that the extraction proceeds through the latter mechanism. Consequently, it is proposed that the reactivity of polymer 1 with attacking anions depends on the solubility of the metal salts in water under the solid–liquid two-phase transfer conditions. The solubility of the reagents in water (mol/100 g of water) is also given in Table I. The order of the solubility is potassium acetate > sodium acetate > lead acetate (no. 1, 12, 22), and is essentially the same as that of the reactivity of polymer 1 with the salts of acetic acid.

Previously we have reported[4] that the degree of esterification becomes high upon increasing the concentration of potassium acetate in the aqueous phase. In the liquid–liquid two-phase reaction, the reactivity of polymer 1 with an excess amount of saturated aqueous solution of potassium acetate was higher than that with sodium acetate under the same conditions (no. 7–11, 17–21). This result suggested that the reactivity of polymer 1 with the saturated aqueous solutions also depends on the solubility of the salts in water.

When the liquid–liquid two-phase reaction between polymer 1 dissolved in toluene and an excess amount of saturated aqueous potassium acetate solution was carried out in the presence of the PTCs at 30 °C for 24 h, the degree of esterification was not high by using TBAB as a PTC and the reaction did not occur in the presence of CR5 and CR6 (no. 7, 8, 10). However, the same degree of esterification was attained for the corresponding reaction under the solid–liquid two-phase conditions using DCHC

Table II
Substitution Reaction of Polymer 1 with Salts of S-Anion in the Solid-Liquid Two-Phase System

no.	nucleophilic reagent	solvent	PTC	degree of substitution, mol %
44	KSPh	toluene	none	0
45	KSPh	toluene	CR6	99.0
46	KSPh	toluene	TBAB	99.0
47	KSPh	toluene	TBPB	99.0
48	KSAc	toluene	none	trace
49	KSAc	toluene	CR6	99.0
50	KSAc[a]	toluene	CR6	55.6
51	KSAc	toluene	DCHC	99.0
52	KSAc[a]	toluene	DCHC	88.1
53	KSAc	toluene	TBAB	99.0
54	KSAc[a]	toluene	TBAB	35.9
55	KSAc	toluene	TBPB	99.0
56	KSAc[a]	toluene	TBPB	64.2
57	KSAc	diglyme	none	99.0
58	KSCN (2.62)[b]	toluene	none	trace
59	KSCN	toluene	CR5	12.7
60	KSCN	toluene	CR6	trace
61	KSCN	toluene	DCHC	76.5
62	KSCN	toluene	TBAB	62.5
63	KSCN	toluene	TBPB	64.0
64	KSCN	diglyme	none	87.6
65	NaSCN (2.02)[b]	toluene	CR5	10.0
66	NaSCN	toluene	CR6	trace
67	NaSCN	toluene	DCHC	55.5
68	NaSCN	toluene	TBAB	29.0
69	NaSCN	toluene	TBPB	48.9

[a] The reaction was carried out for 60 min. [b] Solubility of the reagent[14] (mol/100 g of water).

and TBPB as a PTC (no. 9, 11). It seems that the catalytic activity depended on the lipophilicity of the PTCs in the liquid–liquid two-phase reaction. TBPB and DCHC are more lipophilic than TBAB, CR5, and CR6, respectively, because TBPB has higher extractivity of thiophenolate anion from water to benzene than TBAB.[9] Also, the solubility of DCHC in water is lower than that of CR5 and CR6.[10] On the other hand, when a hydrophilic PTC such as CR6 was used, the polymer with high degree of esterification was obtained in the solid–liquid two-phase reaction of polymer 1 with salts of carboxylic acids. These results suggest that the esterification reaction in the solid–liquid two-phase system is superior to the reaction in the liquid–liquid two-phase system.

The solid–liquid two-phase reaction of polymer 1 with solid potassium phenolate did not occur without PTC in toluene (no. 37), while about 50 mol % of substitution was obtained by the addition of the PTCs such as CR6, DCHC, and TBAC (no. 38–40). On the other hand, the reaction yielded 58 mol % of substitution without PTCs in diglyme and 70 and 61 mol % of substitution by the addition of CR6 and TBAC, respectively (no. 41–43). Therefore, it suggests that potassium phenolate is soluble in diglyme which has the same skeletons as the crown ethers.

From these results, the catalytic activity of the quaternary salts turned out to be superior to that of the crown ethers in the reaction of polymer 1 with O-anions of the nucleophilic reagents.

Substitution Reaction of Polymer 1 with S-Anions of Nucleophilic Reagents. The substitution reactions between polymer 1 dissolved in organic solvents and solid salts of S-anions were carried out under the mild conditions, and the results are summarized in Table II. The reaction of polymer 1 with the salts of S-anions hardly occurred in the absence of PTCs in toluene (no. 44, 48, 58). The reactions of polymer 1 with potassium thioacetate and potassium thiophenolate proceeded quantitatively in the presence of the PTCs (no. 45–47, 49, 51, 53, 55). However, when the reaction of polymer 1 with potassium thioacetate was carried out at 30 °C for 60 min using the PTCs, the PTCs showed different catalytic activity, which decreased in the following order: DCHC > TBPB > CR6 > TBAB (no. 50, 52, 54, 56). This tendency suggests that the crown ethers, especially DCHC, have higher catalytic activity than the quaternary salts, compared with the reaction of polymer 1 with O-anions.

The catalytic effects observed in these reactions can be interpreted as follows. Chemical reaction in the organic phase is as shown in eq 2. Q^+ represents a quaternary salt

$$\text{R–X (org)} + [\text{Q}^+\text{Y}^-]\ \text{(org)} \rightleftarrows \text{R–Y (org)} + [\text{Q}^+\text{X}^-]\ \text{(org)} \qquad (2)$$

or a crown alkali metal complex. Extraction equilibrium between the organic phase and the solid phase or the aqueous phase is as shown in eq 3.

$$[\text{Q}^+\text{Y}^-]\ \text{(org)} + [\text{M}^+\text{X}^-]\ \text{(solid or aq)} \rightleftarrows [\text{Q}^+\text{X}^-]\ \text{(org)} + \text{M}^+\text{Y}^-\ \text{(solid or aq)} \qquad (3)$$

In eq 2, the higher the concentration of $[Q^+Y^-]$ is, the further the equilibrium lies to right. Although the effective PTCs are regarded as relatively soft species in HSAB concept,[11] they can be classified into two categories: the softer PTCs, the crown ethers without electric charge, and the harder PTCs, the quaternary salts with an electric charge, respectively. The softness of crown ethers increases in the order of their bulkiness, DCHC > CR6 > CR5. Furthermore, the softer PTCs easily form the complex ($[Q^+Y^-]$) with a soft anion and the harder PTCs with a hard anion, respectively. When these combinations of PTCs and anions were used, the concentration of the complex in the organic phase increases; however, the relationship between the extractivity and the lipophilicity of the phase-transfer catalysis has been established.[3b,c] Accordingly, the softer PTCs are effective in the reaction with a soft anion such as S-anions and the harder PTCs in the reaction with a hard anion such as O-anions, respectively.

The solid–liquid two-phase reaction of polymer 1 with potassium thiocyanate did not proceed with high degree of substitution even when the PTCs were added, since thiocyanate anion has lower nucleophilicity than thiophenolate anion.[12] The reaction took place with about 60 mol % when TBAB and TBPB were used as PTCs (no. 62, 63), and the degree of substitution was 76.5 mol % by using DCHC (no. 61). However, we could not explain why CR6 showed no catalytic activity in the reaction of polymer 1 with potassium or sodium thiocyanate (no. 60, 66). On the other hand, the reaction of polymer 1 with sodium thiocyanate proceeded with 10 mol % of substitution when CR5 was added as a PTC, which was similar to the result of the reaction of polymer 1 with potassium thiocyanate (no. 65, 59). Therefore, the softness of the PTC and the reagent has greater effect on the reactivity than the exact correspondence between the cavity size and the diameter of the metal ion. These results suggest that DCHC has the highest catalytic activity of the PTCs used in this reaction system.

The reaction of polymer 1 with solid sodium thiocyanate proceeded with lower degree of substitution than the reaction of polymer 1 with potassium thiocyanate under the same conditions when the PTCs other than CR5 were used (no. 66–69), because the solubility of potassium thiocyanate in water is higher than that of sodium thiocyanate (no. 58, 65). This result suggested that the reactivity of polymer

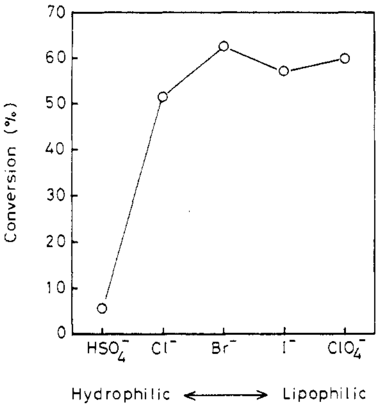


Figure 1. Relation between the degree of substitution and the paired ion of tetrabutylammonium in the solid–liquid two-phase system. The reaction of polymer 1 (4 mmol) in toluene (10 mL) with KSCN (4 mmol) in the presence of a catalyst (0.4 mmol) was carried out at 30 °C for 24 h.

1 with salts of thiocyanate anion also depends on their solubilities in water. Furthermore, in the reaction of polymer 1 with sodium thiocyanate, DCHC showed the highest catalytic activity of the PTCs, because the complex of 18-crown-6 ethers such as DCHC with sodium ion seemed to be softer than that of CR5, which may be formed more easily than the former complex.

As shown in Figure 1, the degree of substitution of polymer 1 was influenced by the species of counterions of tetrabutylammonium salts in the reaction of polymer 1 with potassium thiocyanate, and even ClO_4^- and I^-, which were less effective in the reaction of polymer 1 with potassium acetate than Br^- and Cl^- as a counterion of tetrabutylammonium salts,[4] were as effective as the latter ions in this reaction, while HSO_4^- was not effective. Herriott et al.[9] have reported that TBAI showed slightly higher than TBAB in the liquid–liquid two-phase reaction of 1-bromooctane with sodium thiophenolate. The lipophilicity of these anions increases in the following order: $NCS^- > ClO_4^- > I^- > Br^- > Cl^- > HSO_4^-$.[3b,c] This result suggests that tetrabutylammonium salts paired with lipophilic counterions such as ClO_4^- and I^- show excellent catalytic activity when the more lipophilic S-anion such as thiocyanate anion was used as an attacking anion, although it is better to use the more hydrophilic anion as a counteranion of quaternary salts. On the other hand, the lowest catalytic activity of TBAH, which has the most hydrophilic counterion, may be attributed to the other reason. However, we could not explain why the catalytic activity of TBAH was so low.

These results suggested that the softer PTC is effective in the reaction of polymer 1 with a soft anion such as S-anion, although other factors such as solvation and lipophilicity of the anion would affect in the solid–liquid two-phase reaction system. Consequently, the order of the catalytic activity is shown as follows in this reaction system: DCHC > CR6 > CR5, and DCHC > TBPB ≥ TBAB.

The reaction of polymer 1 with salts of the S-anions was carried out in the liquid–liquid two-phase system, and the results are summarized in Table III. When TBAB was used as a PTC, the equimolar reaction between polymer 1 dissolved in toluene and the aqueous solution of potassium thiophenolate proceeded quantitatively (no. 70), while the reaction of polymer 1 with potassium thioacetate proceeded with only 65 mol % of substitution under the same conditions (no. 71).

In the equimolar reaction of polymer 1 with potassium thiocyanate, the reaction proceeded with the same degree of substitution as the reaction in the solid–liquid two-phase system when lipophilic PTCs such as DCHC and TBPB were used (no. 74, 76). However, the reaciton did not occur when hydrophilic PTCs such as CR6 and CR5 were used (no. 78–80). When TBAB which was less lipophilic than TBPB[9] was used as a PTC, the equimolar reaction in the liquid–liquid two-phase system showed lower degree of substitution than the reaction in the solid–liquid two-phase system (no. 75). However, the reaction of polymer 1 with an excess amount of saturated aqueous solution of potassium thiocyanate proceeded with the same degree of substitution as the result of the solid–liquid reaction (no. 76). It seemed that the concentration of TBAB in the organic phase was increased by the salting out effect of the saturated reagent. The same result was observed in the reaction of polymer 1 with potassium acetate using TBAB.

Table III
Substitution Reaction of Polymer 1 with Salts of S-Anion in the Liquid–Liquid Two-Phase System

no.	nucleophilic reagent	solvent	PTC	degree of substitution, mol %
70	KSPh	toluene/water[a]	TBAB	99.0
71	KSAc	toluene/water[a]	TBAB	65.1
72	KSCN	toluene/water[a]	CR5	0
73	KSCN	toluene/water[a]	CR6	0
74	KSCN	toluene/water[a]	DCHC	75.8
75	KSCN	toluene/water[a]	TBAB	21.8
76	KSCN	toluene/water[b]	TBAB	60.0
77	KSCN	toluene/water[a]	TBPB	52.9
78	NaSCN	toluene/water[a]	CR5	0
79	NaSCN	toluene/water[a]	CR6	0
80	NaSCN	toluene/water[b]	CR6	0
81	NaSCN	toluene/water[a]	DCHC	6.1
82	NaSCN	toluene/water[b]	DCHC	72.9
83	NaSCN	toluene/water[a]	TBAB	17.2
84	NaSCN	toluene/water[b]	TBAB	18.5
85	NaSCN	toluene/water[a]	TBPB	52.9
86	NaSCN	toluene/water[b]	TBPB	56.9

[a] 5 mL of water was added. [b] 5 mL of saturated aqueous solution of reagent was added.

Whereas the equimolar reaction of polymer 1 with sodium thiocyanate hardly occurred using the crown ethers (no. 78, 79, 81), the reaction of polymer 1 with an excess amount of the saturated aqueous solution of sodium thiocyanate proceeded with 73 mol % of substitution using DCHC and showed higher degree of substitution than the reaction in the solid–liquid two-phase system (no. 82, 67). On the other hand, the equimolar reaction between polymer 1 dissolved in toluene and an aqueous solution of sodium thiocyanate proceeded with the same degree of substitution as the reaction of polymer 1 with an excess amount of the saturated aqueous solution using the quaternary salts (no. 83–86). However, the degree of substitution was lower than that of the corresponding reaction in the solid–liquid two-phase system using TBAB (no. 83, 68). The equimolar reaction of polymer 1 with sodium thiocyanate also showed the same reactivity as the reaction with potassium thiocyanate using the quaternary salts under the same conditions (no. 83, 85, 75, 77).

In addition, the reaction of polymer 1 with salts of the S-anions proceeded with high degree of substitution in the absence of PTCs in diglyme (no. 57, 64). It seemed that diglyme consisting of ethylene oxide units acts as a PTC similar to crown ethers.

These results suggest that the reaction of polymer 1 with the S-anions proceeds with high degree of substitution in the solid–liquid and liquid–liquid two-phase systems under the mild phase-transfer catalysis, since the S-anions have higher lipophilicity and nucleophilicity than the O-anions.

Table IV
Substitution Reaction of Polymer 1 with Salts of N-Anion Using PTC

no.	nucleophilic reagent	solvent	PTC	degree of substitution, mol %
87	NaN_3 (0.64)[a]	toluene	none	0
88	NaN_3	toluene	CR5	8.9
89	NaN_3	toluene	CR6	27.7
90	NaN_3	toluene	DCHC	16.1
91	NaN_3	toluene	TBAB	94.5
92	NaN_3	toluene	TBPB	97.6
93	NaN_3	diglyme	none	41.5
94	KN_3 (0.63)[a]	toluene	CR5	70.4
95	KN_3	toluene	CR6	85.0
96	KN_3	toluene	DCHC	88.7
97	KN_3	toluene	TBAB	54.1
98	KN_3	toluene	TBPB	51.2
99	KNPht	toluene	none	0
100	KNPht	toluene	CR6	65.9
101	KNPht	toluene	DCHC	12.0
102	KNPht	toluene	TBAB	53.6
103	KNPht	toluene	TBPB	65.8
104	KNPht	diglyme	none	3.7

[a] Solubility of the reagent[14] (mol/100 g of water at 20 °C).

Also, the equimolar reaction in the liquid–liquid two-phase system proceeded with high degree of substitution when lipophilic PTCs such as TBPB were used.

Substitution Reaction of Polymer 1 with N-Anions of Nucleophilic Reagents. The substitution reaction between polymer 1 dissolved in the organic solvents and solid salts of N-anions was carried out using the PTCs, and the results are summarized in Table IV. The reaction of polymer 1 with sodium azide did not occur in toluene without PTCs (no. 87); however, the reaction proceeded with 42 mol % of substitution in diglyme in the absence of PTCs (no. 93). The reaction proceeded quantitatively in toluene when the quaternary salts were added as the PTC (no. 91, 92). Similar results[2g] have been reported in the reactions of poly(vinyl chloride) and isopropyl chloride with solid sodium azide in the solid–liquid two-phase system using some quaternary salts. The reaction took place with low degree of substitution when the crown ethers were used as a PTC (no. 88–90). The 18-crown-6 ethers showed higher catalytic activity than CR5 in this reaction. This result means that the softness of the crown ethers becomes more important than the exact correspondence between the cavity size in the crown ethers and the diameter of the metal ion in the reaction of polymer 1 with sodium azide, which is similar to the result of the reaction of polymer 1 with sodium thiocyanate.

The reaction of polymer 1 with potassium azide proceeded with only 50 mol % of substitution by using the quaternary salts (no. 97, 98), while the reaction yielded 85–89 mol % and 70 mol % of substitution by the addition of the 18-crown-6 ethers and CR5, respectively (no. 94–96). The higher catalytic activity of the crown ethers in the reaction suggested that azide anion, which is classified as a borderline anion for softness,[13] was a relatively soft anion. Furthermore, the reaction with sodium azide showed higher reactivity than that with potassium azide when the quaternary salts were used, because the solubility of azide in water is higher than that of potassium azide (no. 87, 94). Recently, we observed[25] the same catalytic effects in the reaction of pendant chloronitrobenzoic ester in the polymers with salts of azide ion.

The reaction of polymer 1 with solid potassium phthalimide did not occur without PTC (no. 99). However, 54–66 mol % of substitutions were obtained when CR6, TBAB, and TBPB were added (no. 100, 102, 103). The reaction proceeded with only 12 mol % of substitution using DCHC (no. 101). Also, the reaction hardly occurred without PTC in diglyme at 30 °C (no. 104). The catalytic activity increased in the order CR6 > DCHC and TBPB > TBAB. This result was similar to that of the reaction of polymer 1 with solid potassium acetate in toluene and also suggested that phthalimide anion would be a hard one.

From these results, it is supported that the reactivity of N-anions lies between those of the S-anions and O-anions.

Conclusions

From all these results, the following conclusions can be obtained.

(1) The quaternary salts such as TBAB and TBPB are better phase-transfer catalysts than the crown ethers in the reaction of chloromethyl group in the polymer with O-anions of the reagents in the solid–liquid and liquid–liquid two-phase systems.

(2) Generally, the lipophilic crown ether such as DCHC has higher catalytic activity than the quaternary salts in the reaction of a chloromethyl group in the polymer with the S-anions of the reagents in the solid–liquid and liquid–liquid two-phase systems.

(3) The catalytic activity of the PTCs in the reaction of polymer 1 with salts of N-anions lies between those in the reaction of polymer 1 with salts of S-anions and O-anions.

(4) The nucleophilic reactivity of the S-anions with a pendant chloromethyl group in the polymer is higher than that of the O-anions under the phase-transfer catalysis, and the reactivity of the N-anions lies between those of S-anions and O-anions.

(5) When quaternary salts are used as a PTC in the reaction of the same anion, the reactivities of the salts depend on their solubilities in water in the solid–liquid two-phase system.

(6) When crown ethers are used as a PTC, the reactivities of the nucleophilic reagents are determined by the balance of the exact correspondence between the cavity size of the crown ethers and the diameter of metal ions.

(7) We proposed that the effective phase-transfer catalysts are classified into two categories: soft phase-transfer catalysts, the crown ethers without electric charge, and hard phase-transfer catalysts, quaternary salts with an electric charge, respectively. Generally, a soft PTC is effective in the two-phase reaction of the pendant chloromethyl group in the polymer with a soft nucleophilic reagent such as the S-anion. On the other hand, a hard PTC is effective in the two-phase reaction of the chloromethyl group with a hard nucleophilic reagent such as O-anion.

(8) The softness of the PTCs, which is governed by their bulkiness as well as electric charge, was estimated as follows: DCHC > CR6 > CR5 and DCHC > TBPB ≥ TBAB.

(9) Generally, the polymers with higher degrees of substitution are obtained in the solid–liquid two-phase system rather than in the liquid–liquid two-phase system. However, when lipophilic PTCs such as DCHC and lipophilic reagents such as S-anions are used polymers with high degrees of substitution can be obtained in the liquid–liquid two-phase system.

Registry No. KOAc, 127-08-2; NaOAc, 127-09-3; $Pb(OAc)_2$, 301-04-2; NaBz, 532-32-1; KSCN, 333-20-0; NaSCN, 540-72-7; NaN_3, 26628-22-8; KNPht, 1074-82-4; CR5, 33100-27-5; CR6, 17455-13-9; TBAB, 1643-19-2; TBAC, 1112-67-0; TBAI, 311-28-4; TBAP, 1923-70-2; TBAH, 32503-27-8; TBPB, 3115-68-2; DCHC, 16069-36-6; KOBz, 582-25-2; KOPh, 100-67-4; KSAc, 10387-40-3;

KSPh, 3111-52-2; KN_3, 20762-60-1; poly[(chloromethyl)styrene] (homopolymer), 9080-67-5.

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Computer Simulation of Kinetics of Gelation by Addition Polymerization in a Solvent

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ABSTRACT: We have performed Monte Carlo simulations on the kinetics of free radical initiated addition copolymerization in a solution of vinyl and divinyl monomers, using the kinetic gelation model recently proposed by Herrmann et al. The simulation is done on 20 × 20 × 20 and 45 × 45 × 45 simple cubic lattices and allows for mobility of unreacted vinyl and divinyl monomers. The extent of reaction at the gel point, p_c, increases with decreasing fraction of divinyl monomer, with increasing solvent concentration, and with increasing initiator concentration. These predictions, and the observed trends for the dependence of the overall polymerization rate on the same concentrations, are in qualitative agreement with laboratory experiments. Trapping of radicals in this simulation gives an upper limit to the extent of reaction and can be used to construct a phase diagram of gel (infinite cluster) vs. no gel (only finite cluster).

Introduction

The copolymerization of vinyl and divinyl monomers in a suitable solvent is a commonly used procedure for preparing irreversible gels. In such systems the properties of the gel such as the extent of cross-linking at the gel point and various molecular weight averages are strongly dependent on the proportion of divinyl to vinyl monomer and total monomer concentration. The earlier theoretical investigations of this type of gelation process have been based on the Flory–Stockmayer theory[3-6] and on the cascade model developed by Gordon and co-workers,[5] and more recently modified by Miller and Macosko.[6] The kinetics of such reactions have usually been analyzed in the framework of mass-action kinetics.[4]

There exists an extensive literature dealing with the measurement of the kinetics of free radical initiated vinyl polymerization.[7] Recently, Hild and Rempp[8] reported a very detailed quantitative study of the kinetics of network formation in free radical initiated copolymerization of styrene with a variety of divinyl monomers. Also there have appeared a few studies[9] investigating the critical behavior in this type of gelation and the results are mixed—some of the critical behavior is in agreement with percolation models[10] while others are in agreement with the classical approach based on the Flory–Stockmayer theory.

The recognition that the Flory–Stockmayer theory is equivalent to percolation on a Bethe lattice has led to the notion that perhaps percolation on a lattice may be appropriate to gelation,[10] and this offers one way of incorporating loops (or cycles) that were neglected in the Flory–Stockmayer theory. However, as pointed out by Manneville and de Seze[11] standard percolation models may not be appropriate for free radical initiated addition polymerization reactions; and they developed a computer model that took into account some of the features of radical-initiated polymerization. More recently, Herrmann et al.[12] performed extensive simulations of a model very similar to that of Manneville and de Seze[11] and discussed how the critical behavior very close to the gel point of this model differs from the standard percolation models.

In contrast to earlier theories in the Flory–Stockmayer spirit,[4] this computer model[12] takes into account the excluded volume effects which prohibit different macro-

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