(8) Kyker, G. S.; Antkowiak, T. A. *Rubber Chem. Technol.* **1974**, *47*, 32.

(9) Tate, D. P. *J. Polym. Sci., Polym. Symp.* **1974**, *No. 48*, 33.

(10) Singler, R. E.; Schneider, N. S.; Hagnauer, G. L. *Polym. Eng. Sci.* **1975**, *15*, 321.

(11) Allcock, H. R. *Makromol. Chem.* **1981**, *Suppl. 4*, 3.

(12) For a general review of phase-transfer catalysts, see: Sjoberg, K. *Aldrichchimica Acta* **1980**, *13*, 55.

(13) Evans, T. L.; Allcock, H. R. *J. Macromol. Sci., Chem.* **1981**, *A16*, 409.

(14) The sodium salts of 4-nitrophenol, 4-hydroxybenzaldehyde, and 4-hydroxyacetophenone are insoluble in boiling dioxane. They become soluble in the presence of tetrabutylammonium bromide.

Esterification Reaction of Poly[(chloromethyl)styrene] with Salts of Carboxylic Acids Using Phase-Transfer Catalysts

Tadatomi Nishikubo,* Takashi Iizawa, Kazuo Kobayashi, and Yoshihiro Masuda

Laboratory of Polymer Chemistry, Faculty of Engineering, Kanagawa University, Kanagawa-ku, Yokohama-shi, 221 Japan

Makoto Okawara

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Midori-ku, Yokohama-shi, 227 Japan. Received June 1, 1982

ABSTRACT: The esterification reactions of poly[(chloromethyl)styrene] (polymer 1) with salts of carboxylic acids in solid–liquid or liquid–liquid two-phase systems were studied under mild conditions at room temperature using phase-transfer catalysts. In these reactions, the catalytic effects of a wide variety of crown ethers, quaternary ammonium salts, and a quaternary phosphonium salt were investigated. Tetrabutylammonium bromide (TBAB), tetrapentylammonium bromide (TPEAB), and tetrabutylphosphonium bromide (TBPB) showed excellent catalytic effects in the solid–liquid phase reaction between polymer 1 dissolved in an organic solvent and solid potassium acetate, and TBPB also showed an excellent catalytic effect in the liquid–liquid phase reaction between polymer 1 in an organic solvent and a saturated aqueous solution of potassium acetate. In contrast, crown ethers such as 18-crown-6 (CR6) and dicyclohexyl-18-crown-6 (DHCR) were better phase-transfer catalysts than the quaternary ammonium salts in the two-phase reaction of polymer 1 with potassium thioacetate.

Introduction

It is known that polymers with pendant chloromethyl groups are useful as polymeric supports[1] for the syntheses of polypeptides, polynucleotides, and polysaccharides and as starting polymers for the syntheses of other functional polymers[2] such as polymeric reagents, polymeric catalysts, polymeric carriers, polymeric photosensitizers, and photosensitive polymers[3]. Thus far, substitution reactions of the chloromethyl group in the polymer with a number of nucleophilic reagents have been widely carried out in aprotic polar solvents[4] such as *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide, and hexamethylphosphoramide. Acceleration by some quaternary ammonium salts and crown ethers had been found[5] in the reactions of a chloromethyl group in the polymer with nucleophilic reagents in aprotic polar solvents; however, these reactions even proceed without the quaternary ammonium salt and crown ether in aprotic polar solvents. On the other hand, over the pase several years phase-transfer catalysis has been found to be useful[6] in many organic reactions. Recently, phase-transfer catalysis was also applied to syntheses of polymers such as polycarbonate[7], polyether[8], poly(thioether)[9], and polyester[10] and to modifications of polymers such as poly(vinyl chloride)[11], cross-linked poly[(chloromethyl)sytrene][12], and poly(1-chloro-2,3-epoxypropane)[13]. However, almost all of these reactions were carried out at elevated temperatures.

In earlier articles[14], we reported the successful reaction of poly[(chloromethyl)styrene] (polymer 1) with a number of nucleophilic reagents in a two-phase-transfer system consisting of an aprotic nonpolar solvent and a solid reagent using phase-transfer catalysts (PTCs) such as crown ethers and quaternary ammonium salts under mild reaction conditions. This simple, mild and economical method is very interesting for syntheses of functional polyers. Especially, esterification reactions of the chloromethyl group in the polymer with salts of carboxylic acids are important from the point of view of polymeric supports. In this article, we report in detail the substitution reactions of polymer 1 with salts of carboxylic acids in the two-phase system using PTCs under mild conditions.

Experimental Section

Materials. Solvents, Reagents, Catalysts, and Polymer. The solvents were purified in the usual way prior to use. Potassium acetate (KOAc) and potassium benzoate (KOBz) were recrystallized from methanol. Potassium thioacetate (KSAc) and potassium thiobenzoate (KSBz) were synthesized from the reactions of potassium hydroxide with the corresponding thioacids in methanol, and then they were recrystallized from methanol and 2-propanol. Reagent grade sodium acetate (NaOAc), sodium benzoate (NaOBz), 15-crown-5 (CR5), 18-crown-6 (CR6), dibenzo-18-crown-6 (DBCR), dicyclohexyl-18-crown-6 (DHCR), tetramethylammonium bromide (TMAB), tetraethylammonium bromide (TEAB), tetrapropylammonium bromide (TPRAB), tetrabutylammonium bromide (TBAB), tetrabutylammonium chloride (TBAC), tetrabutylammonium iodide (TBAI), tetrabutylammonium hydrogen sulfate (TBAS), tetrabutylammonium perchlorate (TBAPC), tetrapentylammonium bromide (TPEAB), tetrahexylammonium bromide (THAB), tetraoctylammonium bromide (TOAB), benzyltrimethylammonium chloride (BTMAC), methyltrioctylammonium chloride (MTOAC), hexadecyltrimethylammonium chloride (HTMAC), tetrabutylphosphonium bromide (TBPB), and poly(ethylene oxide) (PEO) ($\bar{M}_w \cong 7500$) were used without further purification. Polymer 1 (the inherent 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. The chlorine content (measured by elemental analysis) in

0024-9297/83/2216-0722$01.50/0 © 1983 American Chemical Society

Table I
Esterification Reaction of Polymer 1 with Salts of Carboxylic Acids Using Crown Ethers as PTC

no.	nucleophilic reagent	solvent	PTC	degree of esterification, mol %
1	KOAc	toluene	none	0
2	KOAc	diglyme	none	0
3	KOAc	DMF	none	77.0
4	KOAc	1,4-dioxane	CR6	18.0
5	KOAc	toluene	CR6	24.3
6	KOAc	diglyme	CR6	32.9
7	KOAc	*o*-dichlorobenzene	CR6	36.9
8	KOAc	DMF	CR6	99.0
9	KOAc	*o*-dichlorobenzene[a]	CR6	57.3
10	KOAc	*o*-dichlorobenzene[b]	CR6	88.0
11	KOAc	toluene/water[c]	CR6	0
12	KOAc	toluene/water[d]	CR6	trace
13	KOAc	toluene	CR5	trace
14	KOAc	toluene	DBCR	trace
15	KOAc	diglyme	DBCR	3.5
16	KOAc	toluene	DHCR	4.3
17	KOAc	toluene/water[c]	DHCR	trace
18	KOAc	toluene/water[d]	DHCR	5.9
19	KOAc	toluene	PEO	0
20	NaOAc	toluene	CR6	trace
21	NaOAc	toluene	CR5	14.1
22	NaOAc	toluene	DHCR	0
23	KOBz	toluene	CR6	10.9
24	KOBz	toluene	DHCR	7.1

[a] The reaction was carried out at 50 °C. [b] The reaction was carried out at 80 °C. [c] 5 mL of water was added. [d] 5 mL of a saturated aqueous solution of KOAc was added.

the polymer was 23.20% (calcd 23.21%).

Apparatus. Infrared (IR) spectra were measured on a Hitachi Model EP-1-G3 spectrophotometer. ^{1}H NMR spectra were measured on a JEOL Model JNM PS-100 spectrometer.

Substitution Reaction of Polymer 1 with Salts of Carboxylic Acids. The following are typical examples of the reaction of polymer 1 with salts of carboxylic acids.

Substitution Reaction of Polymer 1 with Potassium Acetate. Polymer 1 (0.61 g, 4 mmol) was dissolved in toluene (10 mL), and 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 ca. 300 rpm at 30 °C for 24 h and then poured into methanol. The product was purified by twice reprecipitating from acetone into water and from acetone into methanol and then dried in vacuo at 50 °C. The degree of esterification of the polymer was 70.4% (calculated from chlorine analysis). The yield of the polymer was 0.59 g (87.3%). The inherent 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} (COC). The ^{1}H NMR spectrum ($CDCl_3$) showed absorptions at δ 2.0 ($COCH_3$) and 4.8 (CH_2OCO).

Substitution Reaction of Polymer 1 with Potassium Thioacetate. Polymer 1 (0.61 g, 4 mmol) was dissolved in toluene (10 mL), and potassium thioacetate (0.46 g, 4 mmol) and TBAC (0.11 g, 0.4 mmol) were added to the polymer solution. The reaction mixture was stirred at ca. 300 rpm at 30 °C for 24 h and then poured into methanol. The product was purified by twice reprecipitating from acetone into water and from acetone into methanol and then dried in vacuo at 50 °C. The degree of thioesterification of the polymer was 99.0% (calculated from chlorine analysis). The yield of the polymer was 0.68 g (88.5%). The inherent 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 an absorption at 1690 cm^{-1} (C=O). The ^{1}H NMR spectrum ($CDCl_3$) showed δ 2.3 ($COCH_3$) and 4.0 (CH_2SCO).

Results and Discussion

Esterification Reaction. Substitution reactions of polymer 1 with salts of carboxylic acids were investigated with two-phase-transfer systems consisting of a solid–liquid and a liquid–liquid combination under mild reaction conditions. As shown in Table I, although the reaction of polymer 1 with potassium acetate in aprotic solvents such as DMF proceeded even in the absence of any PTC at 30 °C (no. 3), the reaction did not proceed in aprotic nonpolar solvents such as toluene and diglyme under the same conditions (nos. 1 and 2). However, the reaction between polymer 1 dissolved in an aprotic nonpolar solvent and solid potassium acetate proceeded at 30 °C when CR6 was added as a PTC. In addition, the degree of esterification of the polymer increased with increasing polarity of the applied solvents[15] (nos. 4–8). The degree of esterification of the polymer obtained from the reaction in toluene and *o*-dichlorobenzene was lower than that of the polymer obtained from the reaction in DMF; however, the

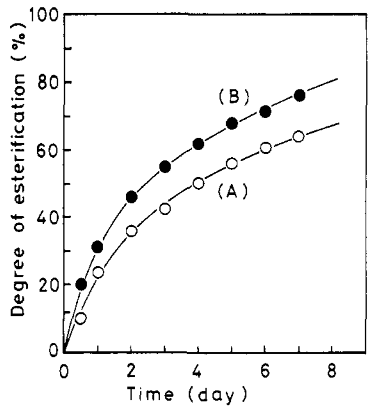


Figure 1. Esterification reaction of polymer 1 with KOAc in a solid–liquid two-phase system using CR6 as a PTC. The reaction of polymer 1 (4 mmol) in an organic solvent (10 mL) with KOAc (4 mmol) in the presence of CR6 (0.4 mmol) was carried out at 30 °C (A) in toluene and (B) in *o*-dichlorobenzene.

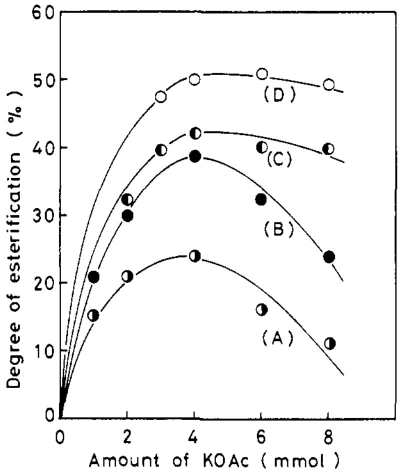
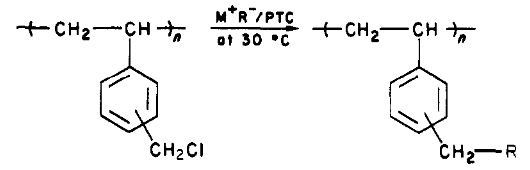


Figure 2. Relation between the degree of esterification and the amount of added KOAc using CR6 as a PTC in a solid–liquid two-phase system. The reaction of polymer 1 (4 mmol) in toluene (10 mL) with KOAc was carried out at 30 °C for 24 h: (A) 0.4 mmol of CR6 was used; (B) 1.2 mmol of CR6 was used; (C) 2 mmol of CR6 was used; (D) 4 mmol of CR6 was used.



(1)

1 2a-d

M = K, Na; R = CH_3COO, C_6H_5COO, CH_3COS, C_6H_5COS

Table II
Esterification Reaction of Polymer 1 with Salts of Carboxylic Acids Using Quaternary Salts as PTC

no.	nucleophilic reagent	solvent	PTC	degree of esterification, mol %
25	KOAc	toluene	TMAB	trace
26	KOAc	toluene	TEAB	2.7
27	KOAc	toluene	TPRAB	14.6
28	KOAc	toluene	TBAC	55.4
29	KOAc	toluene	TBAB	70.4 (71.4)[a]
30	KOAc	diglyme	TBAB	81.2
31	KOAc	toluene/water[b]	TBAB	trace
32	KOAc	toluene/water[c]	TBAB	29.8
33	KOAc	toluene/water[d]	TBAB	62.4
34	KOAc	toluene	TBAI	17.9
35	KOAc	toluene	TBAS	3.9
36	KOAc	toluene	TPEAB	79.0
37	KOAc	toluene	THAB	6.4
38	KOAc	toluene	TOAB	3.0
39	KOAc	toluene	BTMAC	trace
40	KOAc	toluene	HTMAC	trace
41	KOAc	toluene	MTOAC	46.7
42	KOAc	toluene/water[b]	MTOAC	trace
43	KOAc	toluene	TBPB	78.1
44	KOAc	toluene/water[d]	TBPB	82.4
45	NaOAc	toluene	TBAB	37.9
46	NaOAc	toluene	TBPB	29.4
47	KOBz	toluene	TBAB	63.9
48	KOBz	toluene	TBPB	55.3
49	NaOBz	toluene	TBAB	42.8
50	NaOBz	toluene	TBPB	44.7

[a] Dehydrated toluene was used as a solvent. [b] 5 mL of water was added. [c] 200 μL of water was added. [d] 5 mL of a saturated aqueous solution of KOAc was added.

degree of esterification increased when elevated temperatures (nos. 9 and 10) and long reaction times were used, as shown in Figure 1, and when greater amounts of PTC were added, as shown in Figure 2.

An interesting result was obtained, as shown in Figure 2, for the effect of polymer 1/potassium acetate molar ratio. The ratio strongly influenced the degree of esterification of the polymer, which passed through a maximum with increasing amounts of KOAc in the solid–liquid two-phase-transfer system when CR6 was used as a PTC. That is, polymers with a relatively high degree of esterification were obtained from the equimolar reaction, but the degree of esterification of the polymers decreased with the addition of excess amounts of potassium acetate in the presence of catalytic quantities of CR6. One of the reasons for this seemed that excess solid potassium acetate adsorbed CR6 and interfered with the diffusion of the catalyst into the organic layer.

On the other hand, the reaction of polymer 1 with potassium acetate did not proceed in the liquid–liquid two-phase system containing an aqueous solution of potassium acetate when CR6 was used as a PTC (nos. 11 and 12). Furthermore, the reaction did not proceed in the solid–liquid two-phase system when toluene was used as a solvent and CR5, DBCR, or PEO was used as a PTC (nos. 13, 14, and 19) although the reaction did proceed slightly in diglyme when DBCR was used as a PTC (no. 15) and in toluene when DHCR was used as a PTC (no. 16).

Even though the reaction between polymer 1 dissolved in toluene and a dilute aqueous solution of potassium acetate did not proceed, the reaction between polymer 1 dissolved in toluene and a saturated aqueous solution of potassium acetate proceeded slightly when DHCR was used as a PTC (nos. 17 and 18).

The reaction of polymer 1 with sodium acetate did not proceed in the solid–liquid two-phase system with CR6 and DHCR as a PTC (nos. 20 and 22); however, the reaction proceeded under the same reaction conditions when CR5 was used as a PTC (no. 21). Furthermore, the catalytic effect of DHCR in the reaction between polymer 1 and potassium benzoate was nearly equal to that of DHCR in the reaction between polymer 1 and potassium acetate in the system (nos. 24 and 16); however, the catalytic effect of CR6 in the former reaction was lower than that of CR6 in the latter reaction (nos. 23 and 5).

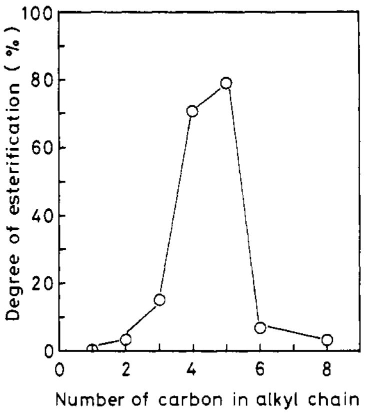


Figure 3. Relation between the degree of esterification and chain length in a symmetric tetraalkylammonium salt in a solid–liquid two-phase system. The reaction of polymer 1 (4 mmol) in toluene (10 mL) with KOAc (4 mmol) in the presence of a catalyst (0.4 mmol) was carried out at 30 °C for 24 h.

These results suggested the following: (1) CR6 has a higher catalytic effect than the crown ethers CR5, DBCR, and DHCR in solid–liquid two-phase-transfer systems of polymer 1 with potassium salts of carboxylic acids. (2) The catalytic effect of DHCR is slightly higher than that of CR6 in liquid–liquid two-phase-transfer systems of polymers 1 with potassium salts of carboxylic acids. Similar results have been reported[16] in liquid–liquid two-phase-transfer systems of benzyl chloride with potassium acetate. (3) CR5 has a higher catalytic effect[17] than CR6 and DHCR in the solid–liquid two-phase-transfer system between polymer 1 and sodium acetate.

The reaction of polymer 1 with potassium acetate did not proceed in a solid–liquid two-phase system when TMAB, BTMAC, and HTMAC were used as PTCs (nos. 25, 39, and 40), and the reaction proceeded only slightly in the same reaction system when TEAB, TPRAB, TBAI, TBAS, THAB, and TOAB were used as PTCs (nos. 26, 27, 34, 35, 37, and 38). On the other hand, the reaction proceeded with a high degree of esterification when TBAC, TBAB, MTOAC, and TBPB were used as PTCs (nos. 28, 29, 36, 41, and 43), and diglyme was better a reaction solvent than toluene in this reaction (no. 30). As shown in Figure 3, the degree of esterification of the polymer was influenced by the length of the alkyl group when symmetric ammonium salts were used as PTCs, and TPEAB showed the highest catalytic effect in the system.

On the other hand, the catalytic effect of MTOAC, which has one methyl group and three octyl groups, was higher than that of TOAB, which has four octyl groups (nos. 41 and 38). These results suggested that although a hydrophobic interaction of the organic layer with the catalyst was important in obtaining polymer with a high degree of esterification, bulky alkyl groups such as octyl or hexyl cause steric hindrance in the two-phase-transfer reaction of polymer 1 with the anion carried by the PTC. Furthermore, as shown in Figure 4, the degree of esterification of the polymer was influenced by the paired ion of the ammonium salt, and Br^- and Cl^- were more effective than ClO_4^-, I^-, and HSO_4^- as a counterion of the ammo-

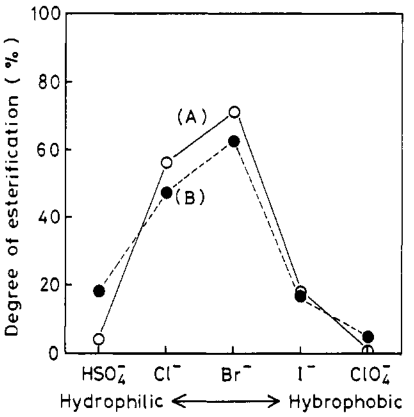


Figure 4. Relation between the degree of esterification and paired ion of tetrabutylammonium in solid–liquid and liquid–liquid two-phase systems. The reaction of polymer 1 (4 mmol) in toluene (10 mL) with KOAc (4 mmol) or a saturated aqueous solution of KOAc (5 mL) in the presence of a catalyst (0.4 mmol) was carried out at 30 °C for 24 h: (A) solid–liquid; (B) liquid–liquid.

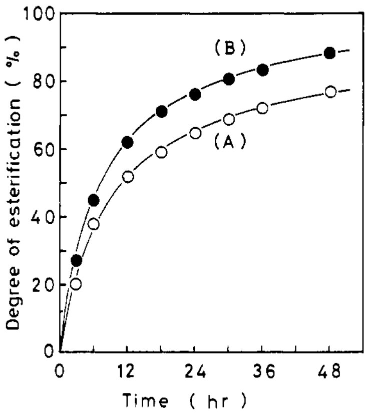


Figure 5. Esterification reaction of polymer 1 with KOAc in a solid–liquid two-phase system using quaternary salts as a PTC. The reaction of polymer 1 (4 mmol) in toluene (10 mL) with KOAc (4 mmol) in the presence of a catalyst (0.4 mmol) was carried out at 30 °C: (A) TBAB; (B) TBPB.

nium salt in the solid–liquid and liquid–liquid two-phase reaction.

One of the reasons for this behavior seemed to be the differences of the catalytic effect based on the concentration of soluble acetate anion of the ammonium salt and the anion participating in the equilibrium, but we could not completely understand the effect of the pair ion of the ammonium salt. Herriat et al.[18] have reported that TBAI has a slightly higher catalytic effect than TBAB in the liquid–liquid two-phase reaction between 1-bromooctane in benzene and sodium thiophenoxide in water. These results suggested that the effect of the paired ion of the quaternary ammonium salts changed the type of reaction[19].

As shown in Figure 5, the rate of reaction of polymer 1 with potassium acetate when TBAB or TBPB was used as a PTC was higher than that of the reaction when CR6 was used as a PTC (Figure 1) in a solid–liquid two-phase system. This result suggested that the quaternary ammonium and phosphonium salts with a proper hydrophobic alkyl chain and counterion are better phase-transfer catalysts than the crown ethers in the system. The same results have been also reported[20] in the reaction of benzyl chloride with potassium acetate. As shown in Figure 6, the degree of esterification of the polymer was not influenced by the amount of added potassium acetate in the solid–liquid two-phase system when TBAB was used as a PTC, and the degree of esterification did not decrease with the addition of excess amounts of the solid nucleophilic reagent at low catalyst concentrations.

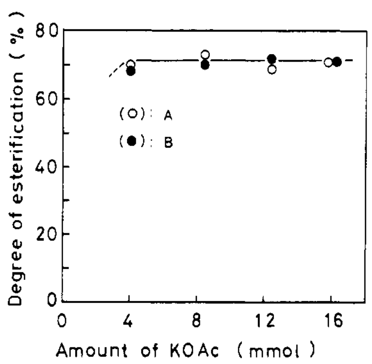


Figure 6. Relation between the degree of esterification and amount of added KOAc using TBAB as a PTC. The reaction of polymer 1 (4 mmol) in toluene (10 mL) with KOAc (4 mmol) was carried out at 30 °C for 24 h: (A) 0.4 mmol of TBAB was used; (B) 2 mmol of TBAB was used.

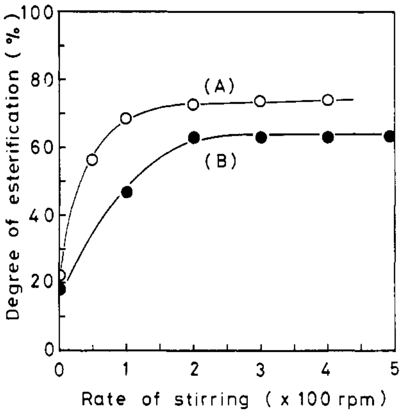


Figure 7. Relation between the degree of esterification and rate of stirring in solid–liquid and liquid–liquid two-phase systems using TBAB as a PTC. The reaction of polymer 1 (4 mmol) in toluene (10 mL) with KOAc (4 mmol) or a saturated aqueous solution of KOAc (5 mL) in the presence of TBAB (0.4 mmol) was carried out at 30 °C for 24 h: (A) solid–liquid; (B) liquid–liquid.

As shown in Figure 7, the degree of esterification of the polymer obtained from the solid–liquid two-phase-transfer reaction of polymer 1 with potassium acetate with TBAB as a PTC was influenced by the rate of stirring, and the degree of esterification of the polymer reached a limit at 200-rpm stirring. Also, the same result was obtained from the liquid–liquid two-phase system, as well as the result of the reaction of 1-chlorooctane with sodium cyanide[21]. Although the solid–liquid two-phase-transfer reaction proceeded even under unstirred conditions when TBAB was used as a PTC, stirring was effective in obtaining a polymer with a high degree of esterification.

Although the degree of esterification of the polymer reached in dry toluene was nearly equal to that in toluene purified in the usual way under the solid–liquid system, the addition of a small amount of water to the system strongly decreased the degree of esterification of the polymer (nos. 29 and 32).

The liquid–liquid two-phase reaction between polymer 1 dissolved in toluene and a excess amount of saturated aqueous solution of potassium acetate using TBAB proceeded at 30 °C. However, the degree of esterification of the polymer obtained from this reaction system was lower than that of the polymer obtained from the solid–liquid two-phase reaction system (nos. 33 and 29).

On the other hand, the liquid–liquid two-phase reaction between polymer 1 dissolved in toluene and a dilute aqueous solution of potassium acetate using the quaternary

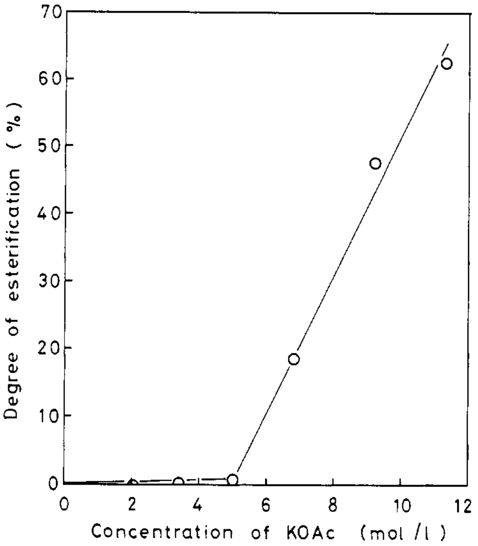


Figure 8. Relation between the degree of esterification and concentration of the aqueous layer in a liquid–liquid two-phase system. The reaction of polymer 1 (4 mmol) in toluene (10 mL) with an aqueous solution of KOAc (5 mL) in the presence of TBAB (0.4 mmol) was carried out at 30 °C for 24 h.

ammonium salts TBAB and TOMAC did not proceed (nos. 31 and 42), and as shown in Figure 8, the degree of esterification of the polymer strongly depended on the concentration of the aqueous solution of potassium acetate in the system.

The degree of esterification of the polymer obtained from the liquid–liquid two-phase reaction between polymer 1 dissolved in organic solvent and a saturated aqueous solution of potassium acetate was nearly equal to that of the polymer obtained from the solid–liquid two-phase system when TBPB was used as a PTC (nos. 43 and 44). This result suggested that TBPB was best as a PTC in the liquid–liquid two-phase-transfer reaction.

These effects concerning the amount of water have been suggested by Starks and Liotta[6c] in the field of organic reaction. It was suggested that the use of an excess amount of the saturated aqueous solution of the nucleophilic reagent was important in obtaining polymer with a high degree of esterification.

Furthermore, the reaction of polymer 1 with sodium acetate, potassium benzoate, and sodium benzoate also proceeded in the solid–liquid two-phase system when TBAB and TBPB were used as PTCs (nos. 29, 43, and 45–50). This result suggested that the catalytic effect of the quaternary salts differed according to species of the paired ion of the nucleophilic reagent and according to the type of substituent group of the carboxylate anion.

Thioesterification Reaction. Although substitution reactions of polymer 1 with potassium thioacetate and thiobenzoate in solid–liquid two-phase systems proceeded quantitatively in the absence of any PTC at 30 °C when diglyme was used as a reaction solvent (nos. 52 and 61), the reactions proceeded only slightly in the system in the absence of the PTC when toluene was used as a solvent (nos. 51 and 60) The reaction also proceeded quantitatively in the same system when CR6, DHCR, TBAB, TBAC, and TBPB were used as PTCs (nos. 53, 54, 56, 58, 59, 62, and 63). On the other hand, the catalytic effect of PEO could not be comfirmed in the system (no. 55), and diglyme, which has a structure similar to that of PEO, was a good solvent for the reaction.

The liquid–liquid two-phase reaction between polymer 1 dissolved in toluene and a dilute aqueous solution of potassium thioacetate also proceeded with a relatively high degree of thioesterification with TBAB as a PTC at room temperature.

Table III

Thioesterification Reaction of Polymer 1 with Salts of Thiocarboxylic Acids Using Crown Ethers and Quaternary Salts as PTC

no.	nucleophilic reagent	solvent	PTC	degree of esterification, mol %
51	KSAc	toluene	none	trace
52	KSAc	diglyme	none	99.0
53	KSAc	toluene	CR6	99.0
54	KSAc	toluene	DHCR	99.0
55	KSAc	toluene	PEO	trace
56	KSAc	toluene	TBAB	99.0
57	KSAc	toluene/water[a]	TBAB	65.1
58	KSAc	toluene	TBAC	99.0
59	KSAc	toluene	TBPB	99.0
60	KSBz	toluene	none	4.2
61	KSBz	diglyme	none	99.0
62	KSBz	toluene	CR6	99.0
63	KSBz	toluene	TBAB	99.0

[a] 5 mL of water was added.

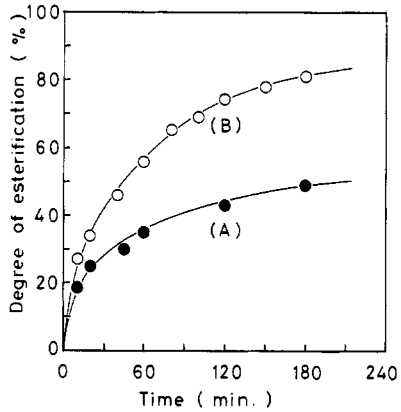


Figure 9. Thioesterification reaction of polymer 1 with KSAc in a solid–liquid two-phase system using PTC. The reaction of polymer 1 (4 mmol) in toluene (10 mL) with KSAc (4 mmol) in the presence of a catalyst (0.4 mmol) was carried out at 30 °C: (A) TBAB; (B) CR.

These results suggested that the salts of thiocarboxylic acids have a higher reactivity compared with that of the salts of carboxylic acids in the two-phase-transfer reaction system. Also, Figure 9 shows that the catalytic effect of CR6 is better than that of TBAB in the two-phase-transfer reaction between polymer 1 and potassium thioacetate. A similar catalytic effect has also been reported[18] in the reaction between 1-bromooctane and sodium thiophenoxide. It seemed that soft PTCs such as crown ethers were more effective than hard PTCs such as quaternary salts in the reaction of polymer 1 with soft reagents.

Conclusions

From the foregoing results, the following conclusions may be obtained: (1) TBAC, MTOAC, and especially TBAB, TPEAB, and TBPB were better phase-transfer catalysts in the reaction of polymer 1 with hard nucleophilic reagents[22] such as salts of carboxylic acids in the solid–liquid two-phase system.

(2) TBPB was a better phase-transfer catalyst than crown ethers, PEO, and quaternary ammonium salts in the reaction of polymer 1 with salts of carboxylic acids in the liquid–liquid two-phase system.

(3) Generally, a solid–liquid two-phase reaction system is better than a liquid–liquid two-phase reaction system

for obtaining polymer with a high degree of esterification.

(4) When the liquid–liquid two-phase reaction system is adapted for obtaining polymer with a high degree of esterification, an excess amount of saturated aqueous solution of the salt of carboxylic acids should be used as a water layer.

(5) Crown ethers such as CR6 and DHCR were better phase-transfer catalysts than quaternary ammonium salts and quaternary phosphonium salts for the reaction of polymer 1 with soft nucleophilic reagents such as the salt[22] of thiocarboxylic acid in the two-phase system.

(6) Although potassium salts used as a nucleophilic reagent have a higher reactivity than the corresponding sodium salts in the two-phase reaction of polymer 1 with salts of carboxylic acids, when CR6, DHCR, quaternary ammonium salts, and quaternary phosphonium salts are used as a PTC, sodium salts have a higher reactivity than potassium salts in the system when CR5 was used as a PTC.

(7) TBAB and TPEAB, which have a symmetric alkyl chain based on either *n*-butyl or *n*-pentyl, were better PTCs than other quaternary ammonium salts in the two-phase reaction of polymer 1 with the potassium salts of carboxylic acids, because hydrophobic interaction of the catalysts with an organic layer and steric hindrance increased with increasing number of carbon atoms in a quaternary ammonium salt, and both compounds have an excellent balance between the effects.

Registry No. 1, 9080-67-5; KOAc, 127-08-2; NaOAc, 127-09-3; KSAc, 10387-40-3; KOBz, 582-25-2; KSBz, 28170-13-0; NaOBz, 532-32-1; CR6, 17455-13-9; CR5, 33100-27-5; DBCR, 14187-32-7; DHCR, 16069-36-6; PEO, 25322-68-3; TMAB, 64-20-0; TEAB, 71-91-0; TPRAB, 1941-30-6; TBAC, 1112-67-0; TBAB, 1643-19-2; TBAI, 311-28-4; TBAS, 32503-27-8; TPEAB, 866-97-7; THAB, 4328-13-6; TOAB, 14866-33-2; BTMAC, 56-93-9; HTMAC, 112-02-7; MTOAC, 5137-55-3; TBPB, 3115-68-2.

References and Notes

(1) (a) Merrifield, R. W. *J. Am. Chem. Soc.* **1963**, *85*, 2149. (b) Lestinger, R. L.; Kornet, M. J. *Ibid.* **1963**, *85*, 3045. (c) Lestinger, R. L.; Mahadevan, V. *Ibid.* **1965**, *87*, 3526. (d) Frechet, J. M.; Schuerch, C. *Ibid.* **1971**, *93*, 492.

(2) For example: (a) Okawara, M. "Chemical Reaction of Polymers"; Kagakudojin: Kyoto, 1972. (b) Klaus, M. A.; Patchornik, A. *J. Polym. Sci., Macromol. Rev.* **1980**, *15*, 55. (c) Akelah, A.; Sherrington, D. C. *Chem. Rev.* **1981**, *81*, 557.

(3) (a) Nishikubo, T.; Tomiyama, Y.; Maki, K.; Takaoka, T. *Kobunshi Kagaku* **1972**, *29*, 295; *Chem. Abstr.* **1972**, *77*, 75870*g*. (b) Nishikubo, T.; Iizawa, T.; Hasegawa, M. *J. Polym Sci., Polym. Lett. Ed.* **1981**, *19*, 113.

(4) (a) Ayres, J. T.; Mann, C. K. *J. Polym. Sci., Polym. Lett. Ed.* **1965**, *3*, 505. (b) Minoura, Y.; Shiina, K.; Yoshikawa, K. *J. Polym. Sci., Part A-1* **1967**, *5*, 2843. (c) Okawara, M.; Ochiai, Y. *ACS Symp. Ser.* **1980**, *No. 121*, 41.

(5) (a) Nishikubo, T.; Ichijyo, T.; Takaoka, T. *Nippon Kagaku Kaishi* **1973**, 35; *Chem. Abstr.* **1973**, *78*, 160375*q*. (b) Roeske, R. W.; Gesellshen, P. D. *Tetrahedron Lett.* **1976**, 3369. (c) N'guyen, T. D.; Deffieux, A.; Boileau, S. *Polymer* **1978**, *19*, 423. (d) N'guyen, T. D.; Boileau, S. *Tetrahedron Lett.* **1979**, 2651.

(6) (a) Dehmlow, E. V. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 170. (b) Wever, W. P.; Gokel, C. W. "Phase Transfer Catalysis in Organic Synthesis"; Springer-Verlag: Heidelberg, 1977. (c) Starks, C. M.; Liotta, C. "Phase Transfer Catalysis"; Academic Press: New York, 1978.

(7) (a) Soga, K.; Hosoda, S.; Ikeda, S. *J. Polym. Sci., Polym. Lett. Ed.* **1977**, *15*, 611. (b) Soga, K.; Toshida, Y.; Hosoda, S.; Ikeda, S. *Makromol. Chem.* **1977**, *178*, 2749.

(8) (a) Imai, Y.; Ueda, M.; Ii, M. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 85. (b) Imai, Y. *J. Macromol. Sci., Chem.* **1981**, *A15*, 833. (c) Jin, J.-I.; Jung, Y.-W.; Lee, K.-S.; Chung, K.-W. *Taewan Hwahakhoe Chi* **1979**, *23*, 259; *Chem. Abstr.* **1980**, *92*, 129392*h*. (d) Banthia, A. K.; Lundsford, D.; Webster, D. C.; McGrath, J. E. *J. Macromol. Sci., Chem.* **1981**, *A15*, 943.

(9) Imai, Y.; Kato, A.; Ii, M.; Ueda, M. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 579.

(10) Cameron, G. G.; Buchan, G. M.; Law, K. S. *Polymer* **1981**, *22*, 558.

(11) (a) Takeishi, M.; Kawashima, R.; Okawara, M. *Makromol. Chem.* **1973**, *167*, 261. (b) Takeishi, M.; Naito, Y.; Okawara, M. *Angew. Makromol. Chem.* **1973**, *28*, 111. (c) Lewis, J. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 119.

(12) (a) Farrall, M. J.; Frĉhet, J. M. J. *J. Am. Chem. Soc.* **1978**, *100*, 7998. (b) Frĉhet, J. M. J.; de Smet, M. D.; Farrall, M. J. *Tetrahedron Lett.* **1979**, 137. (c) Frĉhet, J. M. J.; de Smet, M. D.; Farrall, M. J. *J. Org. Chem.* **1979**, *44*, 1774. (d) Roovers, J. E. L. *Polymer* **1979**, *17*, 1107. (e) Gozdž, A. S.; Rapak, A. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 359, 595.

(13) (a) Nishikubo, T.; Iizawa, T.; Nakagawa, A.; Okawara, M. *Polym. Prepr. Jpn.* **1980**, *29* (1), 192. (b) Nishikubo, T.; Iizawa, T.; Mizutani, M.; Okawara, M. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 617.

(14) (a) Nishikubo, T.; Iizawa, T.; Kobayashi, K.; Okawara, M. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 765. (b) Nishikubo, T.; Iizawa, T.; Kobayashi, K.; Okawara, M. *Ibid.* **1981**, *2*, 387.

(15) (a) Miller, J.; Paker, A. J. *J. Am. Chem. Soc.* **1981**, *83*, 1117. (b) Paker, A. J. *Chem. Rev.* **1969**, *69*, 1.

(16) Knochel, A.; Oehler, J.; Rudolph, G. *Tetrahedron Lett.* **1975**, 3167.

(17) Pederson, C. J. *J. Am. Chem. Soc.* **1967**, *89*, 7019.

(18) Herriot, A. W.; Picker, D. *J. Am. Chem. Soc.* **1975**, *97*, 2345.

(19) Dehmow, E. V.; Lissel, M. *Tetrahedron Lett.* **1976**, 1783.

(20) Zwan, M. C. V.; Hartner, F. W. *J. Org. Chem.* **1978**, *43*, 2655.

(21) Starks, C. M.; Owens, R. M. *J. Am. Chem. Soc.* **1973**, *95*, 3613.

(22) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827.