

SHORT COMMUNICATIONS

**Substitution Reaction of Poly(chloromethylstyrene) with Some Nucleophilic Reagents Using Triphase Transfer Catalysis**

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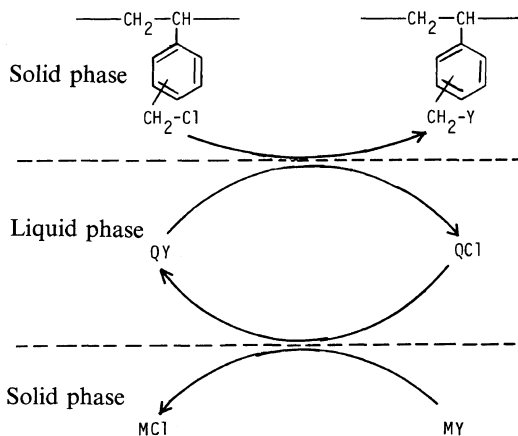
(Received August 29, 1983)

KEY WORDS Triphase Transfer Catalysis / Solid-Liquid-Solid / Poly(chloromethylstyrene) / Nucleophilic Reagents / Crown Ethers / Quaternary Salts / Mild Reaction Conditions /

Phase transfer catalysis is a useful method for organic syntheses, polymer syntheses, and their chemical modifications. Takeishi *et al.*<sup>1,2</sup> investigated the reaction of poly(vinyl chloride) with sodium azide in liquid-solid or solid-liquid two-phase transfer systems using quaternary ammonium salts. N<sup>o</sup>Guyen *et al.*<sup>3</sup> also reported the reaction of poly(1-chloro-2-epoxypropane-co-oxyethylene) dissolved in benzene with an aqueous solution of the nucleophilic reagent in a liquid-liquid two-phase transfer system in the presence of a quaternary ammonium salt. Fréchet and his coworkers<sup>4</sup> studied the reaction of crosslinking poly(chloromethylstyrene) with certain nucleophilic reagents in a liquid-liquid-solid triphase transfer system consisting of an aqueous solution of reagents, an organic solvent and a polymer gel at elevated temperature, using various quaternary ammonium salts as phase transfer catalysts (PTC). We have also reported the reaction of poly(chloromethylstyrene) (PCMS),<sup>5</sup> poly(1-chloro-2-epoxypropane),<sup>6</sup> poly(2-chloroethyl vinyl ether)<sup>7</sup> and poly[2-(2-chloro-5-nitrobenzoyloxy)ethyl methacrylate]<sup>8</sup> dissolved in toluene or anisole with solid nucleophilic reagents in a solid-liquid two-phase transfer system under mild reaction conditions using crown ethers or quaternary ammonium salts as a PTC, and found<sup>9</sup> an interesting relationship between the softness of PTC and the nu-

cleophilic reagent. However, the reaction of the polymer with the nucleophilic reagent in a solid-liquid-solid triphase transfer system consisting of a solid reagent, solvent and solid polymer, an important method for chemical modification of polymers and syntheses of functional polymers, has not been reported so far.

In this communication, we report on the substitution reactions of solid PCMS, dispersed in poor solvents such as *n*-hexane, cyclohexane and diisopropyl ether (DIPE), with solid reagents under mild reaction conditions using tetra-*n*-butylammonium bromide (TBAB), tetra-*n*-butylphosphonium bromide (TBPB), dicyclohexyl-18-crown-6 (DCHC) or 18-crown-6 (CR) as a PTC.



PCMS was prepared by the radical polymerization of chloromethylated styrene (mixture of 40% of *meta* and 60% of *para*) according to the reported method.<sup>5</sup> PCMS (4 mmol) was dispersed in 10 ml of poor solvent, followed by the addition of 4 mmol of the nucleophilic reagent and 0.4 mmol of PTC. The reaction mixture was stirred at *ca.* 300 rpm at 30°C for 48 h and then poured into methanol. The polymer product was purified by twice reprecipitating it from THF into water and from THF into methanol and was finally dried *in vacuo* at 50°C. The degree of substitution was calculated from chlorine analysis. The obtained polymer was confirmed by IR and <sup>1</sup>H NMR spectra.<sup>5</sup>

As shown in Table I, although the reaction of PCMS with potassium acetate did not occur in *n*-hexane without PTC, the reaction proceeded with 19.8, 42.4, 25.6, and 24.8 mol% in *n*-hexane when TBAB, TBPB, CR, and DCHC were used as a PTC, respectively. The reaction also proceeded with 12.5 mol% using TBAB in cyclohexane. TBPB apparently has a greater catalytic effect than TBAB, CR, and DCHC in a solid-liquid-solid triphase reaction of PCMS with potassium acetate.

The reactions of PCMS with potassium salts of S-anions such as potassium thiobenzoate, potassium ethylxanthate and potassium thiocyanate did not take place without PTC, but the addition of the PTC caused the reactions to proceed. The reaction of PCMS with potassium thiophenolate was observed in the absence of any PTC in *n*-hexane and the degree of thioetherification of the polymer increased on adding PTCs such as TBAB and DCHC. These results suggest that quaternary salts have more catalytic effect than crown ethers in the solid-liquid-solid triphase reactions of PCMS with S-anions salts.

The reactions of PCMS with the potassium salts of N-anions such as potassium azide, potassium phthalimide, and potassium carbazole also proceeded in a poor solvent using the PTC, although they did not take place without PTC. PCMS and potassium azide reacted to reach a high degree of substitution using PTCs. Potassium azide seems to have more reactivity than potassium phthalimide and potassium carbazole in a solid-liquid-solid triphase transfer system.

From the above results, it was found that the reactions of PCMS with nucleophilic reagents in a

**Table I.** Substitution reactions of PCMS with salts of nucleophilic reagents in a solid-liquid-solid triphase transfer system

No.	Nucleophilic reagent	Solvent	PTC	Degree of substitution
				mol%
1	CH <sub>3</sub> -COOK	<i>n</i> -Hexane	None	0
2	CH <sub>3</sub> -COOK	Cyclohexane	TBAB	12.5
3	CH <sub>3</sub> -COOK	<i>n</i> -Hexane	TBAB	19.8
4	CH <sub>3</sub> -COOK	<i>n</i> -Hexane	TBPB	42.4
5	CH <sub>3</sub> -COOK	<i>n</i> -Hexane	CR	25.6
6	CH <sub>3</sub> -COOK	<i>n</i> -Hexane	DCHC	24.8
7	Ph-COSK	<i>n</i> -Hexane	None	0
8	Ph-COSK	<i>n</i> -Hexane	TBPB	32.4
9	Ph-COSK	<i>n</i> -Hexane	DCHC	30.6
10	Ph-SK	<i>n</i> -Hexane	None	9.6
11	Ph-SK	<i>n</i> -Hexane	TBAB	79.8
12	Ph-SK	<i>n</i> -Hexane	DCHC	76.4
13	EtO-CS-SK	<i>n</i> -Hexane	None	0
14	EtO-CS-SK	DIPE	TBAB	47.1
15	EtO-CS-SK	Cyclohexane	TBAB	68.1
16	EtO-CS-SK	<i>n</i> -Hexane	TBAB	56.1
17	EtO-CS-SK	<i>n</i> -Hexane	CR	39.9
18	NCSK	<i>n</i> -Hexane	None	0
19	NCSK	DIPE	TBAB	22.9
20	NCSK	Cyclohexane	TBAB	35.7
21	NCSK	<i>n</i> -Hexane	TBAB	43.3
22	NCSK	<i>n</i> -Hexane	DCHC	39.8
23	N <sub>3</sub> K	<i>n</i> -Hexane	None	0
24	N <sub>3</sub> K	DIPE	TBAB	22.9
25	N <sub>3</sub> K	Cyclohexane	TBAB	68.1
26	N <sub>3</sub> K	<i>n</i> -Hexane	TBAB	70.6
27	N <sub>3</sub> K	<i>n</i> -Hexane	TBPB	73.9
28	N <sub>3</sub> K	<i>n</i> -Hexane	CR	25.2
29	N <sub>3</sub> K	<i>n</i> -Hexane	DCHC	59.9
30	N <sub>3</sub> K	<i>n</i> -Hexane	DCHC <sup>a</sup>	46.6
31	Pht. K <sup>b</sup>	<i>n</i> -Hexane	None	0
32	Pht. K <sup>b</sup>	<i>n</i> -Hexane	TBAB	13.9
33	Pht. K <sup>b</sup>	<i>n</i> -Hexane	TBPB	29.5
34	Pht. K <sup>b</sup>	<i>n</i> -Hexane	DCHC	20.3
35	Carb. K <sup>c</sup>	<i>n</i> -Hexane	None	0
36	Carb. K <sup>c</sup>	DIPE	TBAB	7.7
37	Carb. K <sup>c</sup>	Cyclohexane	TBAB	7.2
38	Carb. K <sup>c</sup>	<i>n</i> -Hexane	TBPB	7.8
39	Carb. K <sup>c</sup>	<i>n</i> -Hexane	CR	5.3
40	Carb. K <sup>c</sup>	<i>n</i> -Hexane	DCHC	10.1

The reaction was carried out with each of PCMS and the nucleophilic reagent and 0.4 mmol of the PTC at 30°C for 48 h.

<sup>a</sup> 0.08 mmol of DCHC was used.

<sup>b</sup> Potassium phthalimide.

<sup>c</sup> Potassium carbazole.

solid-liquid-solid triphase transfer system consisting of a solid reagent, poor solvent, and solid polymer proceeded with the PTC under mild conditions.

#### REFERENCES

1. M. Takeishi, R. Kawashima, and M. Okawara, *Makromol. Chem.*, **167**, 261 (1973).
2. M. Takeishi, Y. Naito, and M. Okawara, *Angew. Makromol. Chem.*, **28**, 111 (1973).
3. T. D. N'Gueyen, A. Deffieux, and S. Boileau, *Polymer*, **19**, 423 (1978).
4. J. M. J. Fréchet, M. D. de Smet, and M. J. Farrall, *J. Org. Chem.*, **44**, 1774 (1979).
5. T. Nishikubo, T. Iizawa, K. Kobayashi, and M. Okawara, *Makromol. Chem., Rapid Commun.*, **1**, 765 (1980).
6. T. Nishikubo, T. Iizawa, Y. Mizutani, and M. Okawara, *Makromol. Chem., Rapid Commun.*, **3**, 617 (1982).
7. T. Iizawa, T. Nishikubo, M. Ichikawa, and M. Okawara, *Makromol. Chem., Rapid Commun.*, **4**, 93 (1983).
8. T. Nishikubo, T. Iizawa, N. Numazaki, and M. Okawara, *Makromol. Chem., Rapid Commun.*, **4**, 187 (1983).
9. T. Nishikubo, T. Iizawa, K. Kobayashi, Y. Masuda, and M. Okawara, *Macromolecules*, **16**, 722 (1983).