Fixation of Carbon Dioxide into Polysilsesquioxane Containing Glycidyl Groups

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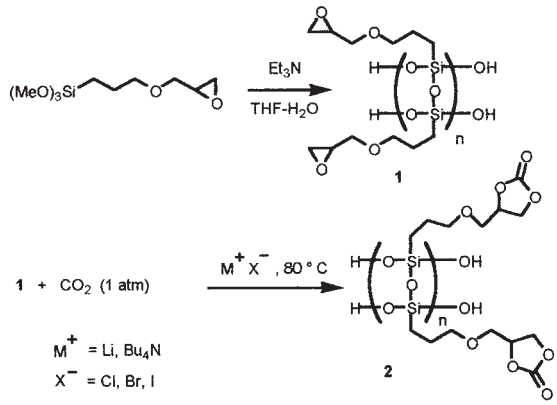
Fixation of carbon dioxide into the polysilsesquioxane containing glycidyl groups proceeded in the presence of a catalytic amount of tetrabutylammonium salts under atmospheric pressure, in which the solid phase reaction was notably effective for the transformation of oxirane groups into cyclic carbonate groups on the polysilsesquioxane.

The use of oxiranes for the reaction with carbon dioxide (CO_2) to construct carbonate structure has been investigated as an effective procedure with economical and environmental advantages.[1] Several groups including us proposed a practical and convenient reaction to fix CO_2 through the transformation of oxiranes into cyclic carbonates, in which common metal and ammonium salts were available as the catalyst and CO_2 was supplied under atmospheric pressure.[2,3] On the other hand, the polysilsesquioxane having oxirane groups (**1**) is a useful component for the synthesis of organic-inorganic hybrid materials.[4] The application of the procedure to fix CO_2 into oxirane groups on the polysilsesquioxane promises the extension of synthetic usages of **1**.[5] Because the polysilsesquioxane derivative having cyclic carbonate groups should be utilized as an intermediary compound or a cross-linking agent leading for various organic-inorganic hybrid materials. In addition, the investigations on the reactivity of **1** by considering the effects of polysiloxane ladder structure have not been developed so far. On the basis of such interests in the organofunctionalization and reactivity of polysilsesquioxane, the fixation of CO_2 into **1** by the use of a catalytic amount of lithium halide or tetrabutylammonium halide was studied in this work.

As shown in Scheme 1, the polysilsesquioxane **1** was prepared from the (3-glycidylpropyl) trimethoxysilane with a catalytic amount of triethylamine in the mixed solvents of THF and water under reflux for 18 h. **1** was obtained as viscous solid insoluble in diethyl ether and solidified after drying under reduced pressure (ca. 5 mmHg) at room temperature for 24 h. The yield of **1** was 92% yield based on Si.[6] The fixation of CO_2 into **1** was carried out under the modified conditions reported before.[3] A typical reaction procedure was as follows: A mixture of **1** [0.25 g, 1.00 mmol (oxirane unit)] and tetrabutylammonium bromide (0.04 g, 0.10 mmol) in DMF (1 ml) was heated at 80 °C for 24 h with CO_2 (1 atm). The resulting solution was poured into a large amount of acetone or diethyl ether to precipitate the product having cyclic carbonate groups (**2**). The conversion of oxirane groups to cyclic carbonate groups was estimated by the proton ratios of representative signals observed in the ^{1}H NMR spectra.[7]



Scheme 1.

The results of the reactions conducted under several different conditions were listed in Table 1. In these reactions, a slight increase of the weights of isolated polymers **2** according to the incorporation of CO_2 was observed. The conversions over 90% were recorded in the reactions using terabutylammonium halides (Run 4, 5, and 6). Interestingly, the efficient incorporation of CO_2 into oxirane group was observed in the reactions conducted in dioxane and without solvent (Run 7 and 8). For these reactions, **1** was ground to a powder and used. In the later reaction conducted without solvent, the catalyst and **1** were mixed in acetone, which can dissolve the catalyst but hardly dissolve **1** and, then, the solvent was removed by the evaporation under reduced pressure before a supply of CO_2. Under such conditions, **1** remained as a precipitate during the reaction and no gelation was observed, although the gel product was obtained in the reaction using methacrylate polymer having oxirane groups (**3**) under the analogous solid conditions.[3] This was supported by the IR spectra of the **1**, in which the absorption due to cyclic carbonate unit was observed at 1795 cm^{-1}, but no other one around this area assigned to non-cyclic carbonate group.[8] Consequently, in the reaction of **1**, the fixation of CO_2 seemed to proceed in each oxirane group with a high efficiency and selectivity, but not between plural oxirane groups.

Table 1. Fixation of CO_2 into **1**

Run	Conditions		Conversion
	Solvent	Catalyst	%
1	DMF	LiCl	77
2	DMF	LiBr	75
3	DMF	LiI	73
4	DMF	$Bu_4N^+Cl^-$	90
5	DMF	$Bu_4N^+Br^-$	95
6	DMF	$Bu_4N^+I^-$	90
7	Dioxane[a]	$Bu_4N^+Br^-$	95
8	—[b]	$Bu_4N^+Br^-$	99

[a]**1** was insoluble in dioxane. [b]Solid phase reaction.

Further information on the reactivity of **1** and the catalytic activities of tetrabutylammonium halides were obtained in the

time-conversion curves of the reactions using **1**, glycidyl methyl ether (**4**), and **3**, in which DMF-d_7 was used as the solvent and the concentration of oxirane groups was adjusted to 0.1 M. As shown in Figure 1, the fixation of CO_2 into **1** proceeded more effectively compared to that into **4**. A remarkable enhancement of the fixation was observed in the solid phase reaction of **1** without solvent. In comparison with the solid phase reaction using **3**, the fixation of CO_2 into **1** proceeded more rapidly. Furthermore, interestingly, in the cases using **4**, tetrabutylammonium chloride exhibited the highest catalytic activity among the catalysts used here, while the use of the ammonium bromide showed the highest efficiency in the cases of **1**.

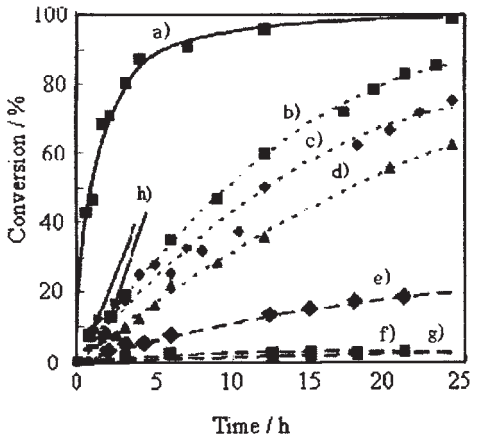


Figure 1. Fixation of CO_2 at 80 °C with 0.1 equivalent of the catalyst to oxirane groups: a) **1** with $Bu_4N^+Br^-$ without solvent, b) **1** with $Bu_4N^+Br^-$, c) **1** with $Bu_4N^+Br^-$, d) **1** with $Bu_4N^+Br^-$, e) **4** with $Bu_4N^+Br^-$, f) **4** with $Bu_4N^+Br^-$, g) **4** with $Bu_4N^+Br^-$, h) **3** with $Bu_4N^+Br^-$ without solvent.

The results mentioned above may allow providing the speculation that the high efficiency of the fixation of CO_2 into **1** owes to the polysiloxane ladder-like structure. Silica derivatives such as silica gel, natural clay minerals, and zeolites have been attracted much attention as the useful additives in various organic reactions.[9] As a reason of the acceleration of reactions by these additives, the provision of the reaction environment with Lewis acidity and/or hydrogen bonding is pointed out. In the reactions of **1** mentioned here, the polysiloxanes ladder-like structure seemed to provide the analogous environment, which acts advantageously to hold the catalyst and oxirane groups in a reaction area. The effects might be appeared typically in the solid phase reaction. The difference of the catalytic activities of ammonium chloride and bromide observed in the reactions using **4** and **1** may support such speculation. Because chloride anion should be kept more tightly to the Lewis acidic polysiloxane structure than bromide, and, in consequence, the catalytic activity of ammonium chloride may be depressed.

Thus, the successful fixation of CO_2 was shown by the use of **1**, which consisted of polysiloxane ladder-like backbone and oxirane reaction site. Further investigation concerning the effects of polysiloxanes such as polysilsesquioxanes, silsesquioxanes, and silica gel on the reaction is in progress.[10]

References and Notes

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6 **1** was soluble in DMF and DMSO, but hardly soluble in acetone, diethyl ether, methanol, and chloroform. The number-average molecular weight and M_w/M_n of **1** were 2200 and 1.20, respectively. The signals assigned to silicon-oxygen T^2 and T^3 units were observed at -59.0 ppm and -67.7 ppm and the ratio of integrations of these signals was $T^2/T^3 = 1/6$ in the solid-state ^{29}Si NMR spectra. Almost the same signals and the values were observed after the fixation of CO_2 in the spectra of **2**.

7 In the estimation of conversion, the signal at 3.16 ppm for **1** assigned to one of the methylene proton of epoxy ring and 5.32 ppm for **2** assigned to the methine one of the carbonate ring were employed.

8 The absorption assigned to carbonyl group of non-cyclic carbonate moiety was usually appeared around 1750 cm^{-1}.

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10 In the presence of poly(phenylsilsesquioxane) or silica gel, the fixation of CO_2 into glycidyl phenyl ether was accelerated.