Incorporation of Carbon Dioxide into Poly(glycidyl methacrylate)

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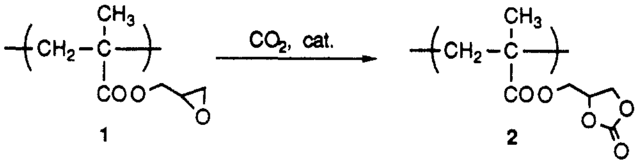
Active investigation of the incorporation of CO_2 into organic molecules has been carried out from an economical and environmental point of view.[1] Although application of CO_2 to polymer synthesis has been reported by a few researchers, CO_2 has been utilized as a comonomer,[1-3] and high CO_2 pressure (>20 atm) is necessary[1,2] to incorporate CO_2 quantitatively and to obtain a high molecular weight of polymer. No direct incorporation of CO_2 into a polymer has been reported so far. Meanwhile, the reaction of CO_2 and oxirane, which affords a five-membered cyclic carbonate, proceeds under an atmospheric pressure of CO_2 when an effective catalyst is used[4] or when an intramolecular reaction system is employed.[5] Thus, the incorporation of CO_2 into a polymer bearing epoxy groups by a polymer reaction (eq 1) using an atmospheric pressure of CO_2 would be superior to other methods because not only can both original and produced polymers be separated very easily from the reaction system but also severe conditions will not be necessary to obtain quantitative incorporation of CO_2. Further, the cyclic carbonate-containing polymer is interesting because a polymer bearing a five-membered cyclic carbonate group can be expected to be a useful reactive polymer.[6]



1 2 (1)

Herein, we report the first example of direct incorporation of CO_2 into a polymer by a polymer reaction under an atmospheric pressure of CO_2.

Poly(glycidyl methacrylate) (1) was selected as a candidate for the incorporation of CO_2. The reaction of 1 ($\bar{M}_n$ 41 000) with CO_2 was first carried out in *N,N*-dimethylformamide (DMF) (1 mol/L) in the presence of a mixture of NaI and Ph_3P as catalyst[4] (1.5 mol % each) at 100 °C under an atmospheric pressure of CO_2. The incorporation ratio of CO_2 was estimated from ^1H NMR, IR,[7] and titration[8] of the obtained polymer. As shown in Figure 1, CO_2 was gradually incorporated in the polymer, and after 24 h, the incorporation ratio of CO_2 reached 88–92%. Incorporation of CO_2 into 1 took place very easily in spite of polymer reaction. The other unit except for 1 and 2 could not be observed in the polymer from ^1H NMR and IR spectra.

The effect of solvent on the efficiency of the incorporation of CO_2 was notable as shown in Table I. A higher incorporation ratio of CO_2 was obtained in DMF, *N,N*-dimethylacetamide (DMAc), and 2-methylpyrrolidinone (NMP), while the incorporation ratio of CO_2 in dimethyl sulfoxide (DMSO) was only 59%, since DMSO oxidized the catalysts. Using a solvent in which NaI is insoluble (runs 5 and 6), the incorporation ratio of CO_2 was lower (30–34%), independent of the solubility of 2. These values were closely related to that obtained by using only Ph_3P as catalyst in DMF (45%). Further, the incorporation ratio of CO_2 in diglyme (run 7) was similar to that in DMF in spite of a heterogeneous reaction system. Thus, the solubility of NaI should be an important factor for the CO_2 fixation.

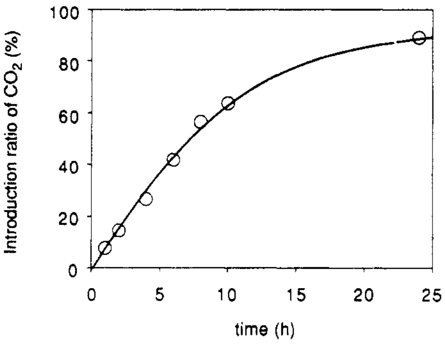


Figure 1. Incorporation of CO_2 (1 atm) into 1 in DMF (1 mol/L) at 100 °C in the presence of NaI-Ph_3P (1.5 mol %).

Table I
Effect of Solvent on the Incorporation of CO_2 into 1[a]

run	solvent[b]	incorporation ratio of CO_2[c] (%)	solubility[d] NaI	solubility[d] 2
1	DMF	89	○	○
2	DMAc	84	○	○
3	NMP	84	○	○
4	DMSO	59	○	○
5	CH_3NO_2	30	×	○
6	PhCl	34	×	×
7	diglyme	85[e]	○	×

[a] In CO_2 atmosphere (1 atm), 100 °C, 24 h, catalyst = Ph_3P (1.5 mol %) and NaI (1.5 mol %). [b] 1 mol/L. For abbreviations, see text. [c] Estimated by ^1H NMR. [d] ○, soluble; ×, insoluble. [e] Cross-linked polymer was obtained. The incorporation ratio of CO_2 was estimated from the decrease of epoxide by titration.

Table II
Effect of Reaction Conditions on the Incorporation of CO_2 into 1[a]

run	temp (°C)	conc (mol/L)	catalyst (mol %)	incorporation ratio of CO_2[b] (%)
1	80	1.0	NaI (1.5) + Ph_3P (1.5)	68
2	100	1.0	NaI (1.5) + Ph_3P (1.5)	89
3	120	1.0	NaI (1.5) + Ph_3P (1.5)	99[c]
4	100	0.5	NaI (1.5) + Ph_3P (1.5)	78
5	100	2.0	NaI (1.5) + Ph_3P (1.5)	100
6	100	1.0	NaI (4.0) + Ph_3P (4.0)	100
7[d]	100	1.0	NaI (1.5) + Ph_3P (1.5)	93
8	100	1.0	$PhCH_2N^+Me_3I^-$ (1.5)	65
9	100	1.0	NaI (2.5)	94
10	100	1.0	Ph_3P (1.5)	45

[a] In DMF, under CO_2 atmosphere (1 atm), 24 h. [b] Estimated by ^1H NMR. [c] Cross-linked polymer was obtained. The incorporation ratio of CO_2 was estimated from the decrease of epoxide by titration. [d] Under 6 atm of CO_2.

The effects of reaction temperature, concentration of polymer, and catalyst on CO_2 fixation into 1 were studied in DMF, and the results are summarized in Table II. The incorporation ratio increased with rising reaction temperature, although cross-linking occurred at 120 °C. High concentration of the polymer (2.0 mol/L, run 5) resulted in quantitative incorporation of CO_2. ^1H NMR and IR spectra of the resulting polymer were identical to those of 2,[6] where no other unit was observed. Quantitative incorporation of CO_2 was also demonstrated by use of 4.0 mol % of the catalysts (run 6), whereas high CO_2 pressure

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(6 atm) was not as effective (run 7). Benzyltrimethylammonium iodide was not such an effective catalyst (run 8). When NaI (2.5 mol %) was used without Ph_3P, effective incorporation of CO_2 was also achieved, indicating Ph_3P was not an essential cocatalyst. Ph_3P has only weak catalytic activity (run 10).

Consequently, quantitative incorporation of CO_2 into a polymer bearing epoxy groups by a polymer reaction was accomplished under an atmospheric pressure of CO_2 in the presence of NaI and Ph_3P as catalysts.

References and Notes

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(3) Five-membered cyclic carbonates synthesized by fixation of carbon dioxide were used as monomers; see: Mikheev, V. V.; Svetlakov, N. V.; Sysoev, V. A.; Brus'ko, N. V. *Deposited Doc. SPSTL* **1982**, *41*, Khp-D82; *Chem. Abstr.* **1983**, *98*, 127745a. Rokicki, G. *Makromol. Chem.* **1985**, *186*, 331. Rokicki, G.; Pawlicki, J.; Kuran, W. *Polym. J.* **1985**, *17*, 509. Nomura, R.; Kori, M.; Matsuda, H. *Makromol. Chem., Rapid Commun.* **1988**, *9*, 739.

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(6) Kihara, N.; Endo, T. *Makromol. Chem.*, in press.

(7) The introduction ratio of CO_2 was estimated by the peak area ratio of the IR spectrum [$\nu_{C=O}$ (1800 cm^{-1}) of the cyclic carbonate group vs ν_{C-O} (910 cm^{-1}) of the oxirane group] calibrated by pure **1** and **2**.

(8) Iwakura's method (Iwakura, Y.; Kurosaki, T.; Nagakubo, K.; Takeda, K.; Miura, M. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 1349) was employed with some modification.

Registry No. DMF, 68-12-2; DMAc, 127-19-5; NMP, 872-50-4; DMSO, 67-68-5; CH_3NO_2, 75-52-5; PhCl, 108-90-7; NaI, 7681-82-5; Ph_3P, 603-35-0; $MesN^+CH_2Ph{\cdot}I^-$, 4525-46-6; diglyme, 111-96-6.