Solid-state Catalytic Incorporation of Carbon Dioxide into Oxirane–Polymer. Conversion of Poly(glycidyl methacrylate) to Carbonate-Polymer under Atmospheric Pressure

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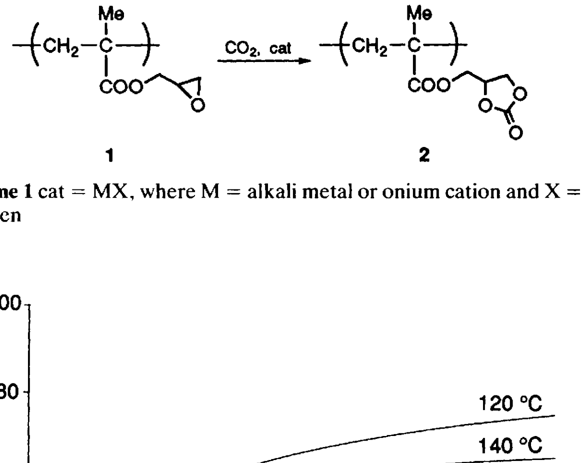
Carbon dioxide has been incorporated into a film of poly(glycidyl methacrylate) containing alkali metal or quaternary ammonium halide under an atmospheric pressure.

Catalytic incorporation of carbon dioxide into organic or polymeric compounds in the solid state is not conventional although it may be one of the most simple, economical, and effective methods to incorporate carbon dioxide into organic molecules. Here, we report the first example of the catalytic incorporation reaction of carbon dioxide into a solid-state polymer under atmospheric pressure.

We have reported quantitative incorporation of carbon dioxide into poly(glycidyl methacrylate) **1** in DMF under an atmospheric pressure.[1] Facile incorporation of carbon dioxide has been also accomplished using diglyme as a solvent in which the produced polymer **2** is insoluble. Therefore, these results suggested to us that the solvents may be unnecessary in the reaction of **1** and carbon dioxide.

When a film of **1** containing 6 mol% of catalyst was exposed to carbon dioxide under an atmospheric pressure, introduction of carbon dioxide was observed.† Fig. 1 shows the reactions of **1** and carbon dioxide using benzyltrimethylammonium bromide as a catalyst at various temperatures. IR spectra of the polymers obtained were very similar to those of **2**,[2] and the formation of the five-membered cyclic carbonate moiety was clearly confirmed by the characteristic IR absorption at 1800 cm^{-1}. Although the initial incorporation rate of carbon dioxide increased at higher temperature, the total amount of carbon dioxide incorporated decreased over 120 °C since decomposition of the polymer occurred at the higher temperature. When the reaction was carried out at 120 °C, 75% of the oxirane group was converted to the five-membered cyclic carbonate moiety after 500 min, and the degree of incorporation increased to 86 mol% after the 2500 min reaction.



Scheme 1 cat = MX, where M = alkali metal or onium cation and X = halogen

The resulting polymers were insoluble in any solvent, indicating the polymerization of the oxirane moieties occurred simultaneously, although such a side reaction was not observed in the corresponding solution-state reaction.[1] In fact, the intensities of IR absorption of the remaining oxirane group (ν_{C-O-C}, 910 cm^{-1}) were weaker than those calculated from the incorporation ratio.‡ Since the T_g of **1** is 44 °C,[3] the mobility of the catalyst may be secured in the polymer film. It should be noted that carbon dioxide can be incorporated into the polymer film at 100 °C even though the T_g of **2** is 120 °C.[4]

As reported previously,[5] a salt which consists of a more nucleophilic anion[6] and a Lewis acidic cation[7] is more active in the reaction of monomeric oxirane and carbon dioxide under an atmospheric pressure, *i.e.* the orders of activity of the salts are $Li^+ > Na^+ > R_4N^+$ and $Cl^- > Br^- > I^-$. Thus, the effect of the catalyst on the polymer reaction at the solid-state was investigated. Fig. 2 shows the results of incorporation of carbon dioxide into **1** catalysed by benzyltrimethylammonium halides at 130 °C. Although the chloride is the most active catalyst, it also catalysed the decomposition and side-reactions described above so that the CO_2 incorporation was reduced at the early stage of the reaction. The effect of the cation part of the catalyst is more complex as shown in Fig. 3. In the early stages of the reaction the incorporation rate of carbon dioxide depended on the activity of the catalyst[5] although the more active catalysts had a tendency to accelerate the side-reactions which inhibited the incorporation reaction. Thus, use of a catalyst, with average activity, afforded the highest degree of the incorporation. Further, the catalytic activity seemed to be

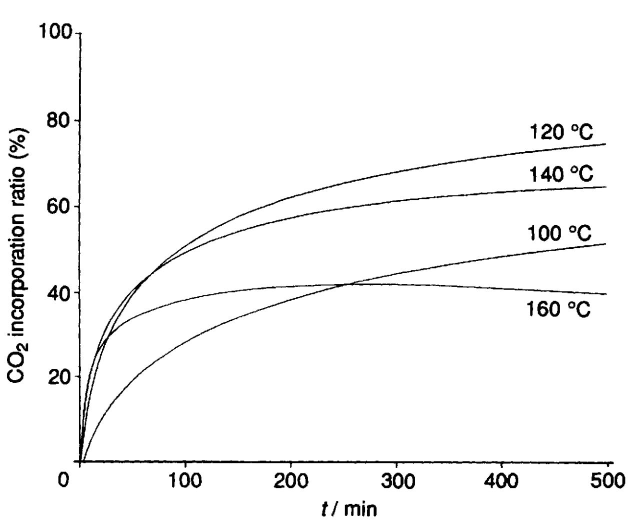


Fig. 1 Incorporation of CO_2 in the film of **1** under an atmospheric pressure catalysed by 6 mol% of benzyltrimethylammonium bromide at different temperatures

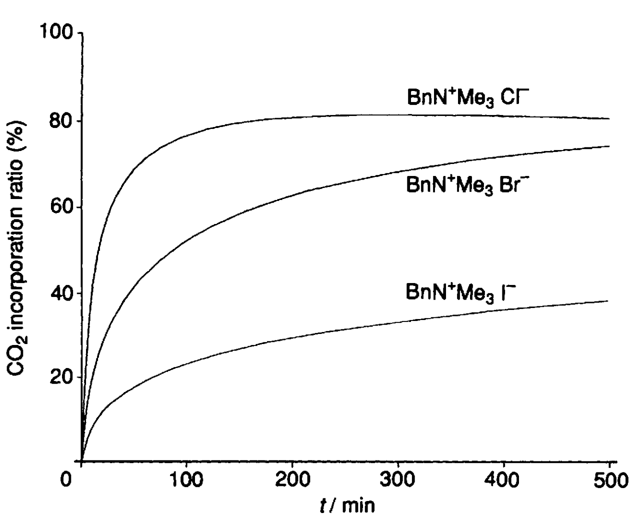


Fig. 2 Incorporation of CO_2 in the film of **1** under an atmospheric pressure catalysed by 6 mol% of benzyltrimethylammonium halides at 130 °C

affected by the lipophilicity of the cation. Thus, the onium salts showed considerable activity in the solid-state reaction whereas they showed far less activity than the alkali metal salts in the solution-state reaction.[5] The mobility of the salts in the solid-state polymer may affect the catalytic activity.

Consequently, the effective catalytic incorporation of carbon dioxide into the polymer (*ca.* 85%) in the solid-state was accomplished under atmospheric pressure as well as in the solution. The degree of side reactions, polymerisation of the oxirane group was estimated, can be controlled by the catalyst and the reaction conditions. Although the organic reaction in the solid-state has been thought to be unsuitable for the catalytic reaction[8] and only proton, which is the most mobile ion, has been used as catalyst for the solid-state catalytic reaction,[9] we can demonstrate that the catalytic organic reactions of the solid-state polymer is widely accessible.

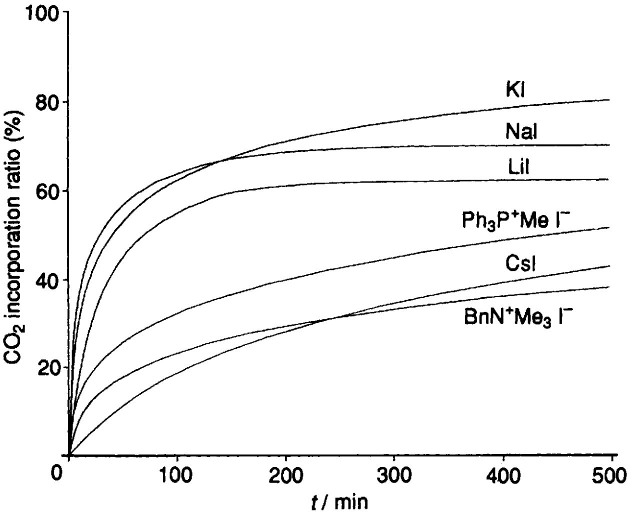


Fig. 3 Incorporation of CO_2 in the film of **1** under an atmospheric pressure catalysed by 6 mol% of various iodides at 130 °C

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Footnotes

† A solution of 49.7 mg (0.35 mmol unit) of **1** ($\bar{M}_n$; 47 000) and 4.8 mg (0.02 mmol) of benzyltrimethylammonium bromide in 1 ml of MeCN was cast on a glass plate (56.7 cm^2). The solvent was evaporated carefully and the film was dried *in vacuo* overnight to obtain a flat coat of the polymer (thickness 12 μm). Since no peak corresponding to the crystal of the catalyst was observed in XRD analysis of the film, homogeneous dispersion of the catalyst in the polymer film was confirmed. 5 mg of the film was scraped off the glass plate and was heated in a CO_2 stream; the mass of the film being monitored by TGA. The incorporation ratio of CO_2 was estimated from the mass increase of the film.

‡ When the side-reactions can be neglected, the incorporation ratio of carbon dioxide can be calculated from the IR absorption at 1800 cm^{-1} (carbonate, $\nu_{C=O}$) and 910 cm^{-1} (oxirane, ν_{C-O-C}) using eqn. (1),

$$\text{Incorporation ratio} = \frac{A}{A+E} \qquad (1)$$

where A denotes abs (1800 cm^{-1})/abs (910 cm^{-1}) and E denotes ε (1800 cm^{-1})/ε (910 cm^{-1}). The value of E calibrated by **1** and **2** was 21.7.

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