

Copolymerization of carbon dioxide and butadiene via a lactone intermediate

Ryo Nakano, Shingo Ito and Kyoko Nozaki
Nature Chemistry. DOI:10.1038/nchem.1882

1. Introduction

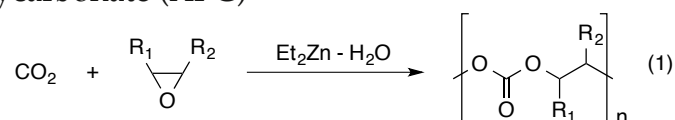
1.1 The utilization of carbondioxide

- The attractive C1 resources
- One of the greenhouse gas
- The reduction of CO₂ amount is required

Problem: The fixation of carbon dioxide is difficult due to its stability

1.2 Previous work – fixation of CO₂ into polymer by reaction with epoxides

- Aliphatic Polycarbonate (APC)^{1,2}



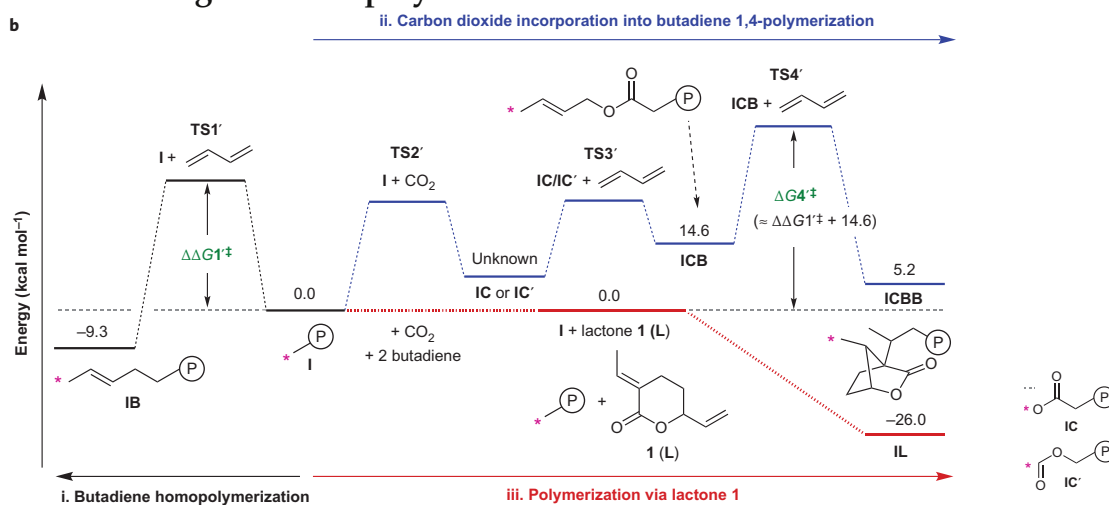
- S. Inoue developed the synthesis of polymer with CO₂ (eq 1)
- CO₂ cannot be fixed directly because of its stability. Therefore it is necessary to use a highly reactive reagent such as epoxide with CO₂

1.3 This work – copolymer of butadiene with CO₂

- Butadiene is relatively reactive and it is widely used as a raw material of synthetic rubber.
- Can the polymer be synthesized with CO₂ and butadiene?

2. Results and Discussion

2.1 The design of the copolymerization reaction



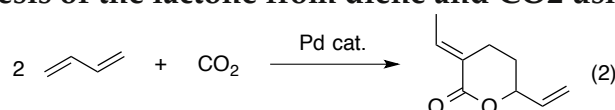
- The copolymer of CO₂ and butadiene cannot be obtained because the activation energy of polybutadiene is lower than that of the copolymer.
- It solved the problem to combine two reactions to afford the copolymer via the lactone intermediate.

Reaction 1) Pd cat. Reaction: it suppresses the polymerization of butadiene and promotes the reaction with CO₂ and butadiene

Reaction 2) Radical polymerization: its activation is low and it suppresses the inverse reaction with CO₂ and butadiene

2.2 The Optimization of the reaction condition

2.2.1 The synthesis of the lactone from diene and CO₂ using Pd catalyst



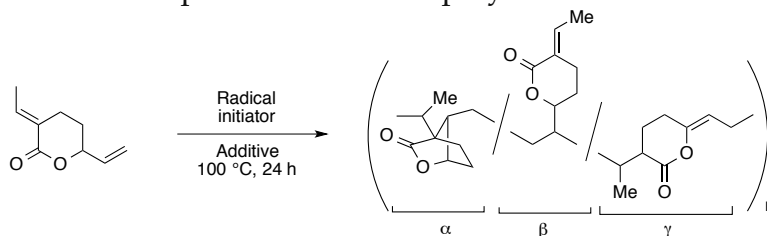
- Behr et al. optimized the reaction to accomplish 95% selectivity over butadiene conversion, and the conditions were applied on a mini-plant scale.

2.2.2 The homo-polymerization of the lactone

- The polymerization of this lactone was investigated previously³⁾ but the reaction did not proceed in the presence of radical, cationic or anionic initiators.

→ The lactone is less reactive under common polymerization condition because it has a tiglic acid ester and an α-substituted allyl ester moiety

Table 1. The optimization of the polymerization condition



| Entry | Initiator | Additive | Solvent | Yield (%) | M _n (10 ³) | M _w /M _n | α:β:γ |
|-------|-----------|-------------------|---------|-----------|-----------------------------------|--------------------------------|--------|
| 1 | AIBN | - | - | 18 | 2.2 | 1.4 | 10:0:0 |
| 2 | AIBN | Galvinoxyl | - | - | - | - | - |
| 3 | AIBN | TEMPO | - | - | - | - | - |
| 4 | KPS | Aqueous SDS | - | 32 | 2.0 | 1.4 | 10:0:0 |
| 5 | MBrP | CuBr/bpy | - | - | - | - | - |
| 6 | V-40 | - | - | 22 | 5.7 | 1.3 | 10:0:0 |
| 7 | V-40 | AcOH | - | 17 | 19 | 1.1 | 10:0:0 |
| 8 | V-40 | MgCl ₂ | - | 2.3 | - | - | - |
| 9 | V-40 | ScCl ₃ | - | 18 | Insoluble | - | 6:1:3 |
| 10 | V-40 | YCl ₃ | - | Trace | - | - | - |
| 11 | V-40 | ZrCl ₄ | - | 15 | Insoluble | - | - |
| 12 | V-40 | FeCl ₃ | - | - | - | - | - |
| 13 | V-40 | CuCl ₂ | - | - | - | - | - |
| 14 | V-40 | ZnCl ₂ | - | 26 | 19 | 1.2 | 5:2:3 |
| 15 | V-40 | AlCl ₃ | - | - | - | - | - |
| 16 | V-40 | ZnCl ₂ | EC | 48 | 85 | 1.5 | 3:5:2 |
| 17 | V-40 | ZnCl ₂ | EC | 59 | 62 | 1.1 | 3:4:3 |

- The yield and molecular weight increased slightly with the use of 1,1'-azobis(cyclohexane-1-carbonitrile) (V-40), which has a higher 10 hour life-time temperature in toluene (88 °C) than that of AIBN (65 °C) (Table 1, entry 6).
- *Problem*: low molecular weight
- Most of the Lewis acids were ineffective (Table 1, entries 8, 10, 12, 13 and 15) or gave insoluble products (Table 1, entries 9 and 11).
 - The addition of zinc chloride improved the molecular weight. The reaction mixture, however, solidified within an hour without any other additive (Table 1, entry 14). The concurrent use of an equimolar amount of zinc chloride and ethylene carbonate as a solvent led to a significant increase in the polymer yield (48%) and M_n (85,000 g mol; Table 1, entry 16).
 - The coordination of zinc chloride to the carbonyl oxygen is expected to enhance the electrophilicity of an α -carbonyl radical formed by radical attack on the tiglate moiety. Subsequent intramolecular hydrogen abstraction to form an allyl radical species is thus expected to be accelerated
 - The glass-transition temperature was as high as 192 °C (Table 1, entry 17) . Moreover, it is hard to decompose (~340 °C). In addition the lactone moiety can be functionalized
- They suggest its potential application as a new engineering plastic.

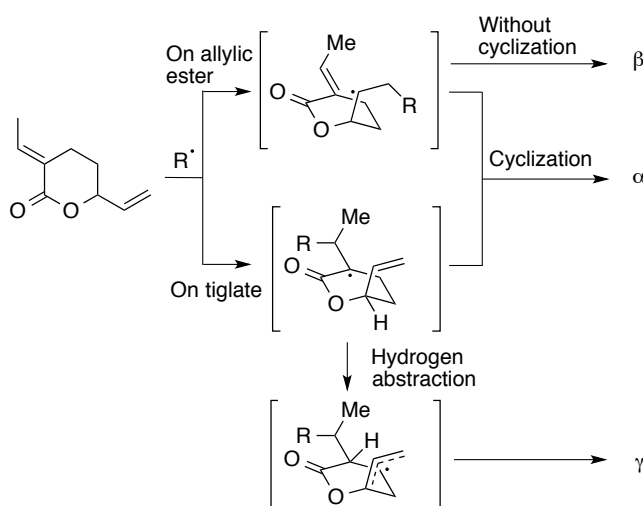
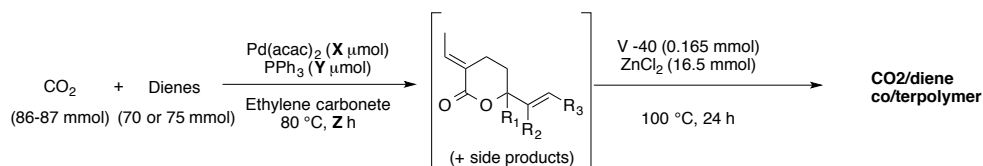


Figure 2. Proposed reaction pathways

2.3 One-pot synthesis of copolymer

- The discover of optimal solvent enabled the one-pot synthesis
- Zinc additive inactivated Pd catalyst, which suppressed the reverse reaction from lactone intermediate

Table 2 . One-pot/two-step co/terpolymerization



| Entry | Initial load of dienes (mmol) | First step: lactone synthesis | | | | Major lactone products | Yield/ selectivity of lactone (%) | Second step: polymerization | | | | |
|-------|--------------------------------------|-------------------------------|----------|----------|--|------------------------|-----------------------------------|-----------------------------|-----------------------------------|--------------------------------|---------------------|--|
| | | X (μmol) | Y (μmol) | Z (μmol) | Yield/ selectivity of polymer (%) | | | CO2 incorporation (wt%) | M _n (10 ³) | M _w /M _n | T _g (°C) | |
| 1 | Butadiene (70) | 50 | 150 | 3 | 1 (R ₁ = R ₂ = R ₃ = H) | 44/77 | 47/81 | 23 | 19 | 1.6 | 102 128 | |
| 2 | Butadiene (25) Isoprene (50) | 100 | 300 | 20 | 1 (R ₁ = R ₂ = R ₃ = H) 7a (R ₁ = Me, R ₂ = R ₃ = H) 7b (R ₁ = R ₃ = H, R ₂ = Me) | - | 46/- | 20 | 5.5 | 2.5 | 63 | |
| 3 | Butadiene (25) 1,3-pentadiene(50) | 100 | 300 | 20 | 8 (R ₁ = R ₂ = H, R ₃ = Me) | - | 35/- | 24 | 16 | 2.0 | 33 | |

- This method could be used for the polymerization of other 1,3-diene

3 Conclusion

- The intermediacy of a lactone provided a breakthrough for the kinetic and thermodynamic obstacles in the challenge of CO₂/olefin copolymerization.

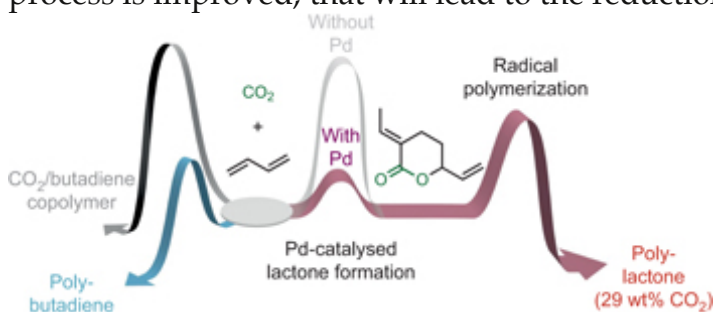
- Zn additive and carbonate solvent enabled the one-pot synthesis of copolymer. Moreover this method could be used for other 1,3-dienes

- CO₂/butadiene copolymers with a carbon-dioxide incorporation ratio of 33 mol%, which is comparable to a theoretical maximum value by typical direct copolymerization of carbon dioxide and 1,3-butadiene.

- In incineration it does not generate nitrogen oxide

- It is able to mold in melting because it has a high decomposition temperature

→ it is expected that it is used as a film. If it is widely used and the produce process is improved, that will lead to the reduction of CO₂



4 Reference

1) S. Inoue et al., *J. Polym. Sci., Polym. Lett. Ed.*, **7**, 287 (1969)

2) S. Inoue et al., *Makromol. Chem.*, **130**, 210 (1969).

3) Dinjus, E. et al. *Die Angew. Makromol. Chem.* **257**, 19–22 (1998).