Synthesis of sustainable polyol by simultaneous utilization of CO_2 and waste PET

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Significance and Relevance

This study proposes a novel approach for two key environmental issues: waste PET upcycling and CO_2 utilization. By glycolyzing waste PET bottles, high-purity bis(2-hydroxyethyl) terephthalate (BHET) was synthesized and used as an initiator in the copolymerization of CO_2 and propylene oxide (PO) to produce sustainable polyols. The PET-CO_2 polyols were successfully produced using a double metal cyanide (DMC) catalyst under various reaction condition including CO_2 pressures and PO/BHET feed ratios. These PET-CO_2 polyols were utilized to synthesize flexible polyurethane foams with comparable properties of commercial polyurethane.

Preferred and 2nd choice for the topic

1. CO_2 utilization and recycling
2. Green chemistry and biomass transformation, Renewable resources conversion

Preferred presentation: Poster

Introduction and Motivations

Effective carbon capture and recycling methods are essential, as the climate changes induced by CO_2 emissions and plastic waste are increasingly recognized as significant global challenges. In this study, waste PET was converted into BHET, which initiates the copolymerization of CO_2 and PO to yield PET-CO_2 polyol. This innovative approach not only recycles PET but also utilizes CO_2 to produce valuable polyols, offering a sustainable solution that mitigates pollutants and supports various industrial applications.

Results and Discussion

Production of BHET via glycolysis of waste PET

The glycolysis of waste PET (5 g) was carried out using ethylene glycol (50 g) and MgO catalyst (200 mg) at 190°C for 3 hours, resulting in a PET conversion of 92.6% and a BHET yield of 64.7%. The structural properties of the synthesized BHET were characterized by FTIR and ^{1}H NMR spectroscopy (**Figure 1**) and compared to those of commercial BHET (Sigma-Aldrich). In the FTIR spectra (**Figure 1a**), both synthesized and commercial BHET showed characteristic bands. A broad peak at 3436 cm^{-1} corresponds to O-H stretching, while peaks at 2964 cm^{-1} and 2880 cm^{-1} indicate asymmetric and symmetric C-H stretching of methylene groups[1]. The strong peak at 1713 cm^{-1} reflects C=O stretching, with additional peaks at 1503 cm^{-1}, 1686 cm^{-1}, and 724 cm^{-1} corresponding to aromatic C-H and benzene ring vibrations. The ^{1}H NMR spectra (**Figure 1b**) showed 8.12 ppm for aromatic protons, and 4.95 ppm for terminal -OH protons. 4.32 and 3.72 ppm indicate protons in methylene groups. Additionally, a peak at 4.68 ppm reveals BHET oligomers[2], which were present in commercial BHET but absent in the synthesized BHET, suggesting higher purity in the latter.

These results demonstrate the effective synthesis of high-purity BHET from waste PET via glycolysis. The absence of oligomeric impurities in the synthesized product highlights the potential of this method for producing high-quality monomers, contributing to the development of sustainable recycling strategies.

Synthesis of PET-CO_2 polyol

The Zn-Co double metal cyanide (DMC) catalyst with poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (P123) as a complexing agent was employed since this catalyst showed effective for CO_2 insertion in polypropylene carbonate (PPC) synthesis in our research[3]. Copolymerization was conducted under various CO_2 pressures (5, 10, 15, and 20 bar) and PO/BHET molar ratios (33.33, 50, 66.67, and 100), allowing detailed analysis of CO_2 pressure and reactant ratios on PET-CO_2 polyol properties.

Figure 2 presents FTIR and ^{1}H NMR spectra of the polyols synthesized under these conditions. **Figure 2a** shows spectra of polyols prepared with different CO_2 contents, and **Figure 2b** shows the effects of varying PO/BHET feed ratios on the structures of polyols. In the FT-IR spectra (**Figure 2a**), key peaks at 1742 cm^{-1} and 1264 cm^{-1}, corresponding to C=O and C-O stretching of carbonate units, increased with higher CO_2 content, indicating more carbonate incorporation. The ^1H NMR spectra also showed increasing intensities of carbonate proton peaks (4.8–4.9 ppm for C-H, 1.2–1.3 ppm for CH_3, and 3.8–3.9 ppm for CH_2), confirming greater CO_2 incorporation. **Figure 2b** shows polyols synthesized at different PO/BHET ratios. As the PO/BHET ratio increased, the carbonate C=O stretching peak at 1742 cm^{-1} intensified, while the BHET C=O peak decreased. Additionally, the O=C-O group peak at 754 cm^{-1} increased, while the aromatic C-H peak of BHET at 730 cm^{-1} diminished. The ^1H NMR spectra mirrored these trends, with BHET-related peaks (aromatic proton at 8.1 ppm and methylene protons at 4.4–4.6 ppm) increasing with higher BHET content, while peaks for carbonate units (C-H at 4.8–5.0 ppm and CH_3 at 1.25 ppm) decreased as BHET content increased. These observations suggest that a higher BHET feed reduces the incorporation of CO_2 into the polyol structure, thereby decreasing the proportion of carbonate units. This can be attributed to the reduced availability of CO_2 for copolymerization as the initiator BHET content increases, limiting its integration into the polymer chain.

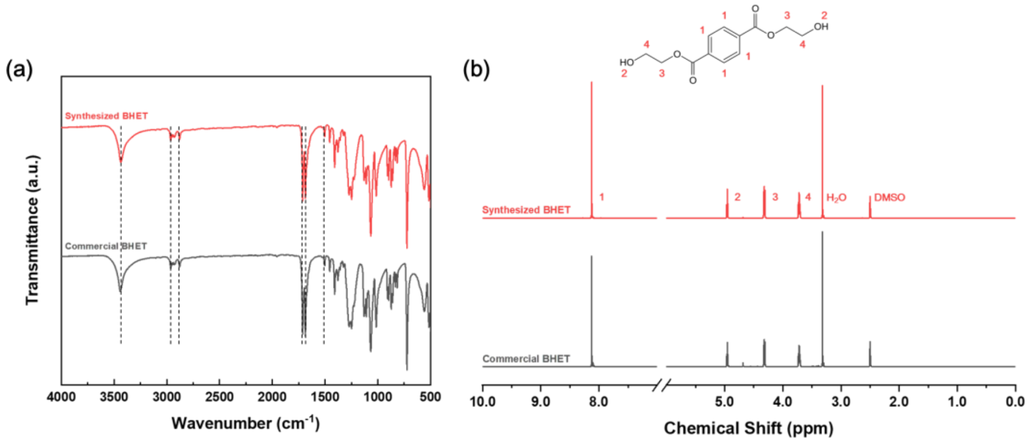

Figure 1 Structural properties of synthesized and commercial BHET monomer. (a) FTIR and (b) ^1H NMR spectra.

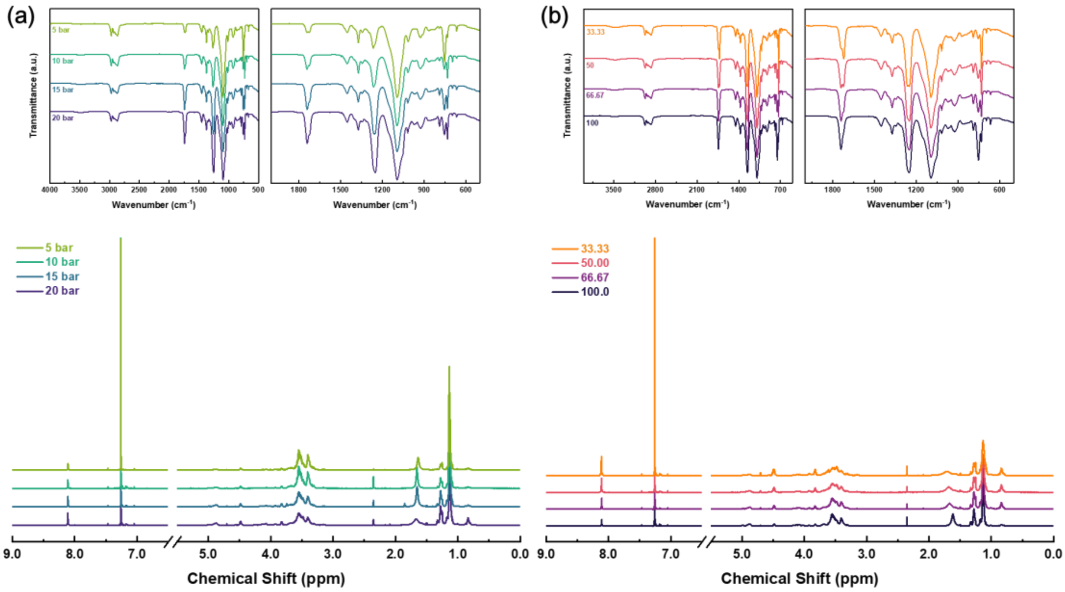

Figure 2 Structural properties of PET-CO_2 polyols. FTIR and ^1H NMR spectra of (a) various CO_2 content and (b) PO/BHET molar ratio.

References

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3. H. Kim, *ACS Omega* **2023**, *42*, 39279-39287.