

Opportunities for the utilization of CO₂ as C1 building block in chemical synthesis

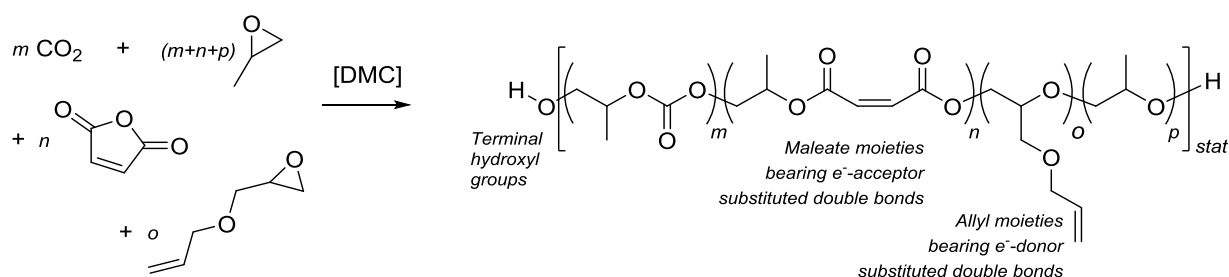
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The utilization of carbon dioxide (CO₂) as an inexpensive and renewable C1 feedstock is of strategic importance for decreasing our dependence on petroleum-derived raw materials. In this context, the direct build-up of polymers, at least partially, from CO₂ is a particularly interesting approach. As an auspicious technology, the catalytic copolymerisation of CO₂ and epoxides to polycarbonates has emerged. Non-alternating polyethercarbonate polyols, which are characterized by a relatively low T_g of -40 to -60°C, are promising intermediates for the production of polyurethanes due to the high reactivity of the terminal hydroxyl groups.¹ Motivated by the goal of expanding the technology to further application fields, the focus of this study is the synthesis and application of tailored polyunsaturated polyethercarbonates.



Scheme 1. Multi-component polymerisation provides polyunsaturated polyethercarbonates with divergent functional groups allowing for versatile polymer chemistry.

Tailored polyunsaturated polyethercarbonates were obtained by multi-component copolymerisation of CO₂ and propylene oxide with suitable comonomers (Scheme 1). Maleic anhydride and allyl glycidyl ether were used as comonomers to incorporate double bonds with electron-acceptor and electron-donor properties, respectively. As polymerisation catalyst, a double metal cyanide (DMC) based on zinc hexacyanocobaltate was used. The low viscosity and the low glass transition temperature of the resulting polyunsaturated polyethercarbonates make them ideally suited pre-polymers for further processing.

Transparent films were obtained by ultraviolet light (UV) initiated curing of neat polyunsaturated polyethercarbonates. Much faster hardening of polyunsaturated polyethercarbonates with ABXBA multi-block structure in comparison to polyunsaturated polyethercarbonates with AXA multi-block structure is attributed to the better local dispersion of the electron-acceptor and electron-donor double bonds, which assists an efficient crosslinking of the polymer chains. Noteworthy, the combination of electron-acceptor and electron-donor substituted double bonds allows for particularly facile UV-initiated free-radical curing.²

Due to their high transparency the resulting materials are highly interesting for coating applications. The value of the storage modulus of the cured films renders them ideal for application as soft coatings, which feel warm to the touch by a person.

¹ Langanke, J. ; Wolf, A. ; Hofmann, J. ; Böhm, K. ; Subhani, M. A. ; Müller, T. E. ; Leitner, W. ; Gürtler, C. *Green Chem.* **2014**, *16*, 1865-1870.

² Subhani, M. A. ; Köhler, B. ; Gürtler, C. ; Leitner, W. ; Müller, T. E. *ACIE* **2016**, *accepted*.