



# Carbon dioxide and carbon disulfide as resources for functional polymers

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## Abstract

This review describes polymer synthesis utilizing carbon dioxide and carbon disulfide as useful C1 resources. Chain and step copolymerizations are recounted with polymerizations of cyclic carbonates, especially five-membered ones, as monomers derived or potentially obtainable from carbon dioxide. Homopolymerization, copolymerizations, and application as a precursor for reversible chain transfer agents for RAFT polymerization are described for carbon disulfide based polymer synthesis. As polymerizations of monomers from carbon disulfide, ring-opening polymerizations of dithiocarbonates and thiourethanes are described.

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*Keywords:* Carbon dioxide; Carbon disulfide; Carbonate; Dithiocarbonate; Ring-opening polymerization; Copolymerization

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*Abbreviations:* BPO, Benzoyl peroxide; CHO, Cyclohexene oxide; CL,  $\epsilon$ -Caprolactone; Cp\*, Pentamethylcyclopentadienyl; CP MAS, Cross polarization magic angle scanning; DBU, 1,8-Diazabicyclo[5.4.0]undec-7-ene; DMAc, *N,N*-Dimethyl acetamide; DOA, (1,3-Dioxoran-2-one)ylmethyl acrylate; DOMA, (1,3-Dioxoran-2-one)ylmethyl methacrylate; DSC, Differential scanning calorimetry; DTBP, Di(*t*-butyl)peroxide; DTC, Dimethyltrimethylene carbonate; EC, Ethylene carbonate; Fmoc, *N*-Fluorenylmethoxycarbonyl; FT-IR, Fourier transfer infrared; GA, Glycidyl acrylate; GMA, Glycidyl methacrylate; LCST, Lower critical solution temperature; MMA, Methyl methacrylate;  $M_n$ , Number-average molecular weight;  $M_w$ , Weight-average molecular weight; Ni(COD)<sub>2</sub>, Bis(cyclooctadiene) nickel (0); NMP, *N*-Methyl pyrrolidone; NMR, Nuclear magnetic resonance; PC, Propylene carbonate; PHA, Poly(hydroxy alkanoate); PO, Propylene oxide; RAFT, Reversible addition-fragmentation chain-transfer; salen, Salicyl aldimine;  $S_L$ , 4(*S*)-(Methoxycarbonyl)-1,3-oxazolidine-2-thione;  $T_{d5}$ , 5%Weight loss temperature; TfOEt, Ethyl trifluoromethanesulfonate; TfOH, Trifluoromethanesulfonic acid; TMU, Tetramethylene urea;  $T_g$ , Glass transition temperature; THF, Tetrahydrofuran.

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## 1. Introduction

Many researchers have explored the chemistry of C1 heterocumulenes exhibiting unique reactivities based on their structures, which inherently comprise both electron-donor and electron-accepter moieties. Carbon dioxide and carbon disulfides are the most widely used heterocumulenes owing to their abundance and low cost. Carbon dioxide is a major emission product resulting from much biological and industrial activity, and its concentration in the atmosphere has been kept in rough through consumption via efficient natural carbon dioxide fixation system of photosynthesis. However, that balance appears to be tilting in favor of accumulation of carbon dioxide, leading to the greenhouse effect, and the present interest in on preventing its accumulation by reduction of carbon dioxide emission, e.g. as

suggested in the Kyoto Protocol adopted in 1997. This abundance makes carbon dioxide one of the most inexpensive raw materials, whose importance is accentuated by its low toxicity. Meanwhile, carbon disulfide, which also exists in the troposphere, has long been used as a sulfur source in organic chemistry and a solvent for various polymers, such as cellulose in industrial processes. Carbon disulfide finds use as a starting material for a variety of useful chemicals for agricultural, medicinal, and pharmaceutical applications.

Carbon dioxide and carbon disulfide have been utilized for polymer synthesis, both by their direct (co)polymerizations and polymerizations of monomers synthesized from them. Because polymerizations utilizing carbon dioxide have been described in several excellent reviews [1–8], this article deals with recent advances and highlight of past research in this

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