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Review article

Input of supercritical carbon dioxide to polymer synthesis: An overview

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The ongoing search for environmentally friendlier alternative to the organic solvents used in chemical processes has led to the development of technologies based on supercritical carbon dioxide (scCO_2), which is non-flammable, non-toxic and relatively inert fluid. Polymer chemistry does not escape this trend and last achievements in the field of polymer synthesis in scCO_2 are reviewed here. Without claiming to be exhaustive, we go through and discuss the benefits of the main polymerization processes in scCO_2 including homogeneous, precipitation, dispersion, suspension and emulsion systems. A particular attention is drawn to water/carbon dioxide emulsion polymerization and to the suited surface active agents. This review also underlines that heterogeneous polymerization based on CO_2 is more than a strategy for reducing the ecological footprint of the polymer production but it allows structuring the polymer materials into particles or highly interconnected macroporous networks.

Contents

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1. Properties and interest of $scCO_2$

Currently, organic solvents are involved in many chemical processes, notably as reaction medium in organic synthesis and polymer production. These are also often used for extraction/fractionation, purification and impregnation, etc. All these processes contribute to the large amount of emitted volatile organic solvent (VOC) such as dichloromethane, chloroform, toluene and hexane. Supercritical carbon dioxide ($scCO_2$) offers an attractive alternative to conventional solvents. Indeed, $scCO_2$ is inexpensive, non-toxic, non-flammable, relatively inert, odorless, its removal after the chemical transformation is not energy consuming and its recycling is environment friendly. It is thus promoted as a sustainable solvent (green-solvent). Furthermore, as shown by Table 1, CO_2 exhibits easily achievable critical parameters (P_c = 73.8 bar; T_c = 31.1 °C) compared to other substances. Above this critical pressure P_c and temperature T_c, CO_2 reaches the supercritical state exhibiting both gas-like and liquid-like properties as illustrated in Fig. 1. It is then characterized by a viscosity close to a gas, a density similar to a liquid ensuring a rather high mass transport capacity and a very high diffusion coefficient compared to the liquid (Table 2).

$ScCO_2$ is not only a green solvent but its properties, as a supercritical fluid, can advantageously easily be tuned by adjusting the pressure and/or temperature. As an example, the density of the supercritical fluid can vary from the density of gas to the density of liquid by modulation of pressure or temperature applied onto the fluid as illustrated by Fig. 2. This variation can affect the solvation capacity of CO_2 which can be exploited in extraction processes to dissolve selectively a compound.

Table 1
Critical parameters of some selected substances (P_c is critical pressure; T_c is critical temperature; ρ_c is density at critical parameters).

Solvent	T_c (°C)	P_c (bar)	ρ_c (g/mL)
Ethane	32.4	48.8	0.20
Ethene	10.0	51.2	0.20
Methanol	240.6	79.9	0.27
Water	374.2	220.5	0.32
Ammoniac	132.5	112.8	0.24
Carbon dioxide	31.1	73.8	0.47

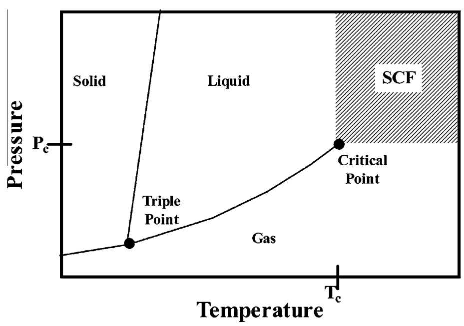

Fig. 1. Schematic pressure–temperature phase diagram for pure component delimited by triple (T) and critical (C) points. Reproduced from Ref. [1].

Table 2
Physical properties of CO_2 in various states. These data indicate an order of range.

State of matter	Density (g/cm^3)	Diffusivity (cm^3/s)	Dynamic viscosity (g/cm.sec)
Gas	$\approx 1 \times 10^{-3}$	$\approx 1 \times 10^{-1}$	$\approx 1 \times 10^{-4}$
Liquid	≈ 1	$\approx 5 \times 10^{-6}$	$\approx 1 \times 10^{-3}$
Supercritical state (at critical point)	≈ 0.47	$\approx 1 \times 10^{-3}$	$\approx 1 \times 10^{-4}$

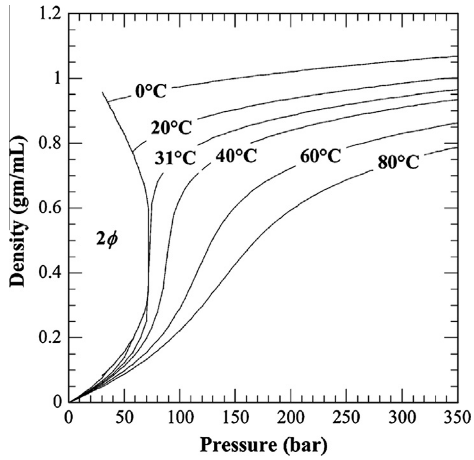

Fig. 2. Evolution of density of carbon dioxide as a function of pressure at various temperatures. Reproduced from [1].

Supercritical carbon dioxide being characterized by a low dielectric constant $\varepsilon \sim 2$, is thus a good solvent for nonpolar molecules with low molecular weight. In contrast, water and ionic compounds are insoluble. However, many small molecules including polar compounds like methanol, acetone, tetrahydrofuran and vinyl monomers are soluble. Indeed, although CO_2 have no dipole moment due to its symmetrical molecular structure, it exhibits a strong quadrupole moment which operates at shorter distance than dipolar interactions which contributes to its solubility parameter [2].

As a consequence, CO_2 is largely used in ***extraction processes***, especially in the agro-food sector [3,4], and allows the trapping of the substances of interest without contamination with organic solvents. The most common example is the caffeine dissolved and extracted from coffee berries using $scCO_2$. In order to recover products, a simple depressurization of CO_2 is performed leading to their precipitation. Currently, some methods are available to extract biomolecules as alkaloids, lipids (triglycerides, fatty acids, phospholipids…) from raw resources [5]. However, due to the low polarity of CO_2, its use as extraction solvent is mainly restricted to non-polar components.

In spite of the limited solubility of many reactants in $scCO_2$, numerous ***organic synthetic procedures*** were conducted in this medium including Diels–Alder, Suzuki coupling reaction, Michael addition, Friedel–Crafts alkylation reaction, Heck reaction, etc. [6–8]. Besides the absence of