

Letter

Supercritical carbon dioxide as solvent for the copolymerization of carbon dioxide and propylene oxide using a heterogeneous zinc carboxylate catalyst

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Abstract

Supercritical carbon dioxide was found to be a suitable substitute for halogenated organic solvents in its copolymerization with propylene oxide. The system was studied utilizing a heterogeneous catalyst, zinc glutarate. The polymers were analyzed for selectivity in polycarbonate linkages by ^1H NMR spectroscopy and for molecular weight by gel permeation chromatography.

Keywords: Supercritical CO_2 ; Carbon dioxide; Propylene oxide; Zinc carboxylate catalyst

1. Introduction

Supercritical fluids (SCF's) exhibit unique physicochemical properties, such as density, diffusivity, dielectric constant, solvating strength, an viscosity that can be adjusted by varying temperature and pressure, and are, thus, potentially very useful solvents for chemical reactions [1]. Supercritical carbon dioxide is particularly advantageous because it has a relatively low critical temperature and pressure ($T_c = 304.2$ K and $P_c = 1056$ psi) and is non-flammable, inexpensive, and less of a health hazard than most organic solvents.

Since the region around the critical point is one of rapid changes of properties, a supercritical fluid provides greater flexibility as a reaction medium than more conventional organic solvents for

polymerization reactions, e.g. increasing pressure can result in an increase in polymerization rate and molar mass, and polymer processing [2]. In polymer processing SCF's allow for the extraction of low molecular weight contaminants and the fractionation of polymers by molecular weight and composition [3].

The interest in exploiting SCF's as a reaction medium for polymerization reactions has focused on using the tunability of their solvent power to control the precipitation threshold for polymer chains, swelling in the precipitate phase, molecular weight, and molecular weight distribution [2]. Most of the work reported in the literature concerns free radical polymerizations with the high-pressure, high-temperature polymerization of ethylene being the most well-known example [4]. However, polymers formed in inert SCF's have often been characterized by low yields and heterogeneous conditions at low conversions [2].

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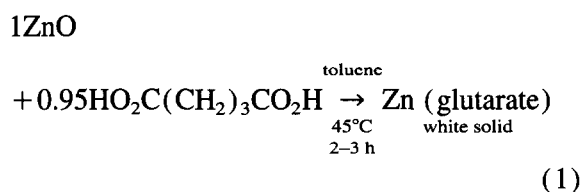
Inoue et al. first reported the alternating copolymerization of carbon dioxide and epoxides using $\text{Zn}(\text{CH}_2\text{CH}_3)_2$ and H_2O in 1969 [5]. Previously, Stevens had reported the co-polymerization of ethylene oxide and carbon dioxide in the presence of polyhydric phenols initially under supercritical conditions. However, the polymers formed were viscous liquids or waxes characterized by large sections of polyether linkages with three to ten carbonate units per molecule [6]. Since then various other catalysts [7] have been found for this polymerization with the most active being those prepared by the reaction of zinc oxide with dicarboxylic acids [8]. These reactions are very sensitive to proton donors due to a chain transfer mechanism [9]. The accepted mechanism for this reaction involves epoxide addition to a metal carbonate (or carboxylate for initiation) with subsequent CO_2 addition to a metal alkoxide.

This paper reports on the co-polymerization of propylene oxide and carbon dioxide to form pol-

ycarbonates in supercritical carbon dioxide utilizing zinc glutarate as a heterogeneous catalyst.

2. Results and discussion

The co-polymerization of CO_2 with propylene oxide was conducted under various conditions, using a heterogeneous zinc catalyst (Eq. 1) [10]¹.



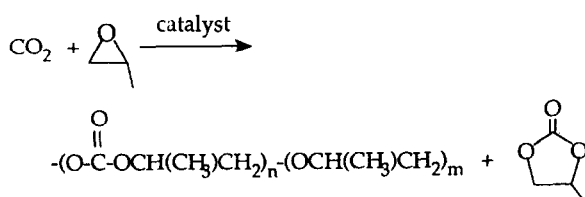
¹ In a typical preparation ZnO (8.5 g) and glutaric acid (13.1 g) were heated in toluene (200 ml) for three hours at 45°C. The white solid was collected by filtration and dried overnight in a vacuum oven at 90°C.

Table 1
Copolymerization of propylene oxide (P.O.) and carbon dioxide^a

Weight catalyst (g)	P.O. (ml)	Co-solvent (ml)	$P(\text{CO}_2)$ (psi) ^b	Temp. (°C)	Yield (g/g Zn)	Cyclic carbonate (%) ^c	$F_c^{\text{c,d}}$ (%)	M_n^e	M_w^e	PDI ^f
3.0	25	25(CH_2Cl_2)	300	60	15.9	0	91	26 783	108 412	4.04
3.0	25	25(CH_3CN)	1200	60	3	7	97	4 780	40 527	8.48
3.0	25	25 (hexane)	1440	60	4.8	5	97	5 020	36 278	7.23
3.0	25	–	300	60	18.9	4	73	15 339	70 083	4.57
3.0	25	–	300	60	21	9	70	8 863	63 219	7.13
3.0	25	–	500	60	21.6	10	74	12 805	77 174	6.02
3.0	25	–	760	60	17.7	9	94	16 516	65 464	3.96
3.0	25	–	830	60	24	13	90	26 955	153 409	5.69
3.0	25	–	850	60	14.4	8	96	29 394	98 965	3.37
3.0	25	–	860	60	12.6	2	93	14 114	109 484	7.76
3.0	25	–	1120	60	9.6	10	98	13 077	114 023	8.72
2.0	25	–	1200	60	10.2	14	89	14 875	140 446	9.44
3.0	25	–	1200	60	13.2	10	86	6 563	89 441	13.6
3.0	50	–	1200	60	8.7	12	95	4 206	36 235	8.61
3.0	60	–	1200	60	18	13	93	11 699	39 565	3.38
3.0	25	–	1190	85	13.5	11	84	5 103	24 906	4.88
3.0	25	–	1200	85	15.6	8	85	7 783	31 632	4.06
3.0	50	–	1200	85	34.8	11	85	12 141	36 072	2.97
3.0	60	–	1200	85	7.5	11	87	4 014	76 516	19.1
3.0	75	–	1150	85	8.4	11	89	12 478	53 494	4.29
1.0	30	–	1200	40	trace	–	–	–	–	–

^a Reaction time 4 h. ^b 14.6959 psi = 1 atm = 101.3 kPa. ^c Propylene carbonate and polymer linkages calculated from NMR spectra. ^d $F_c = (\text{polycarbonate linkage}/\text{polycarbonate} + \text{polypropylene oxide linkages}) = n/m + n$ (Eq. 2). ^e M_n = number average molecular weight and M_w = weight average molecular weight. ^f PDI = polydispersity = M_w/M_n .

In a typical run, zinc glutarate (3 g) is heated in a Parr reactor under vacuum overnight. The reactor is charged with the appropriate amount of distilled propylene oxide and co-solvent, heated to 40, 60, or 85°C, and raised to the appropriate pressure with bone dry carbon dioxide (Eq. 2)². The results are shown in Table 1. The presence of propylene carbonate, a cyclic monomer, was detected by the presence of a peak at 1800 cm⁻¹ in the infrared spectrum and by NMR spectroscopy. Increasing the temperature increases the production of this byproduct, as well as the relative percentage of polyether linkages.



Supercritical CO₂ is a suitable substitute for organic solvents in polymerization reactions in which CO₂ is also a reactant. The presence of an organic solvent under supercritical carbon dioxide, such as hexane or acetonitrile, significantly decreases the yield of polymer isolated but increases the fraction of carbonate linkages relative to ether linkages while the use of methylene chloride as co-solvent increases the selectivity for forming polycarbonates without this adverse impact on the yield. The use of CO₂ (at pressures greater than 700 psi) as solvent also resulted in high selectivity for polycarbonate versus polyether formation. Furthermore, the advantage of using supercritical carbon dioxide is that it is as effective a solvent as methylene chloride for the copolymerization process, yet it is environmentally benign.

² The supercritical pressures were reached utilizing bone dry carbon dioxide equipped with a full length diptube and helium headspace and a Milton Roy Simplex miniPump Solvent Delivery System from LDC Analytical. The head of the pump was equipped with a cooling jacket which was cooled to -15°C.

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