

Copolymerization of CO₂ and 1,2-Cyclohexene Oxide Using a CO₂-Soluble Chromium Porphyrin Catalyst

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ABSTRACT: The copolymerization of 1,2-cyclohexene oxide (CHO) with carbon dioxide was performed, using supercritical carbon dioxide (scCO₂) as both solvent and reactant, to produce an aliphatic polycarbonate. A CO₂-soluble catalyst, tetra(pentafluorophenyl)porphyrin chromium(III) chloride (CrT-FPPCl), was synthesized and used to catalyze the polymerization in the presence of 4-(dimethylamino)pyridine (DMAP) as cocatalyst. The best yields for the copolymerization (up to ~75%) were obtained in the temperature range 95–110 °C over a period of 18 h, with a molar ratio of catalyst to monomer of 2.6×10^{-3} . High catalyst efficiencies (3.9 kg of polymer/g of Cr) were observed under these conditions. The copolymers consisted predominantly of carbonate linkages (90–97%), and the chain microstructure was analyzed by ¹H NMR and ¹³C NMR spectroscopy. Gel permeation chromatography revealed number-average molecular weights (*M_n*) of the order of 3500. In contrast to previous studies involving supercritical CO₂, narrow polymer molecular weight distributions were observed throughout (*M_w*/*M_n* < 1.4).

Introduction

In some respects, CO₂ is an ideal solvent choice for polymer synthesis since it is inexpensive, nontoxic, and nonflammable.^{1–5} At sufficiently high pressures and temperatures (*T_c* ≥ 31.1 °C, *P_c* ≥ 73.8 bar), CO₂ exists as a *supercritical fluid* (SCF).⁶ In the supercritical state, CO₂ exhibits hybrid properties of a liquid and a gas. Like a liquid, it can be relatively dense and dissolve solutes; however, like a gas, the fluid retains low viscosity, mixes with other gases, and is highly compressible. This gives rise to unique advantages. First, since supercritical CO₂ (scCO₂) is compressible, its density (and therefore its solvent properties) can be tuned by varying the pressure. In addition, scCO₂ reverts back to the gaseous state upon lowering the pressure, thus allowing simple separation of solvent from solute and recycling of the gaseous CO₂.

In general, CO₂ is a relatively unreactive molecule. However, in 1969 Inoue et al. reported the use of CO₂ as a comonomer in the alternating copolymerization of epoxides to form aliphatic polycarbonates using a ZnEt₂/H₂O catalyst system.⁷ More recently, Darensbourg et al. have shown that scCO₂ can be used as both solvent and reactant for the formation of polycarbonates, thus eliminating the use of toxic volatile organic solvents in the polymerization process. The copolymerization of propylene oxide and cyclohexene oxide (CHO) with CO₂ was conducted in scCO₂ using heterogeneous zinc catalysts.^{8,9} In common with most polymers,⁶ the resulting polycarbonates were insoluble in scCO₂ and precipitated from solution as they were formed. Catalyst efficiencies were low to average (i.e., 3–370 g of polymer/g of Zn), possibly because of the insoluble nature

of the catalysts. A substantial advance was made recently by Beckman, who demonstrated the formation of polycarbonates in scCO₂ using a CO₂-soluble catalyst.¹⁰ The copolymerization of CO₂ and cyclohexene oxide was carried out using a partially fluorinated zinc alkyl complex, giving rise to rather better catalyst efficiencies (~400 g of polymer/g of Zn).¹¹ Again, the polycarbonate precipitated from the supercritical solution as it was formed. Careful phase behavior studies were undertaken on the CO₂/cyclohexene oxide system in order to determine the best conditions for copolymerization.^{12,13} Despite these early successes, all of the systems described so far have involved precipitation polymerization in scCO₂ to yield polycarbonates with broad molecular weight distributions (*M_w*/*M_n* = 2.4–27), indicating no real control over product molecular weights.

Metalloporphyrin catalysts have been used for the copolymerization of CO₂ with certain monomers to form, for example, polyurethanes or polycarbonates.^{14–19} A particular feature of these catalysts is that polymers tend to be isolated with very narrow molecular weight distributions, even in the presence of protic species, and such systems have therefore been termed “immortal polymerizations”.²⁰ Catalyst turnover numbers of up to 10 000 per metal center have been reported, and in some cases, the catalysts have been shown to be recyclable. Typically, metalloporphyrin catalysts are tolerant toward water and air, so that extensive drying and purification of reagents are unnecessary.

Despite the potential advantages, the application of metalloporphyrin complexes in polymerization has been limited so far to traditional solvents. Most common metalated porphyrins exhibit negligible solubility in scCO₂. Nevertheless, by adding CO₂-solubilizing moieties (e.g., fluorinated groups), it is possible to generate CO₂-soluble metalloporphyrin complexes. It was demonstrated during the course of the present study that both octabromotetrakis(pentafluorophenyl)porphyrin-

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atoiron(III) chloride and tetrakis(pentafluorophenyl)porphyrinatoiron(III) chloride are both soluble in scCO_2 and are active catalysts for selective aerobic oxidations.^{21,22}

We have extended this approach to the synthesis of polycarbonates in scCO_2 , using CO_2 as both solvent and reactant. A novel CO_2 -soluble metalloporphyrin was synthesized for this purpose. The advantages associated with porphyrin catalysis were also apparent in scCO_2 (i.e., narrow molecular weight distributions and insensitivity to impurities). In addition, polycarbonates could be formed in fair to good yields without the use of any VOC (volatile organic chemical) solvents in the polymerization process. Catalyst efficiencies were found to be considerably higher than any reported so far for a SCF -based process of this type. Very recently, Coates has demonstrated the synthesis of polycarbonates with narrow molecular weight distributions via the copolymerization of cyclohexene oxide with CO_2 in the presence of a zinc imine complex [(BDI)ZnOAc (50 °C, 100 psi of CO_2)].^{23,24} Our method differs in that we have used a catalyst that is CO_2 -soluble: as such, we believe catalysts of this type will find use in other applications such as homogeneous catalysis in scCO_2 .

Experimental Section

Materials. (Dimethylamino)pyridine (DMAP) (Aldrich), cyclohexene oxide (CHO) (Aldrich), tetrakis(pentafluorophenyl)porphyrine-21*H*,23*H* (Aldrich), anhydrous chromium(II) chloride (Aldrich), anhydrous dimethylformamide (Aldrich), and carbon dioxide (Messer Griesheim, grade 5*5) were all used as received.

Equipment. A 10 mL Hastelloy steel reactor, equipped with a sapphire view window, was used for all reactions.⁴ Liquid carbon dioxide was delivered to the reactor using a Pickel PM 101 nitrogen driven pump. The pressure in the reactor was measured with a pressure transducer (A105, RDP Electronics) and displayed on a digital display (E308, RDP Electronics). The internal temperature was measured with an Industrial Mineral Isolated thermocouple (type K, RS Electronics) and displayed on a temperature indicator (T 200, RS Electronics). A PTFE-coated magnetic stir bar was used to mix the contents of the reactor.

Synthesis of CrTFPPCl (2). The procedure reported for the metalation of tetraphenylporphyrin was followed.²⁵ Tetrakis(pentafluorophenyl)porphyrin (TFPPH₂) **1** (100 mg) was dissolved in anhydrous DMF (20 mL), and an excess of anhydrous chromium(II) chloride was added under an inert atmosphere. The mixture was stirred under reflux for 1 h and allowed to cool, and the solvent was evaporated. The crude product was purified by flash column chromatography with acetone as the eluent over neutral alumina (Brockmann grade II-III) to give the corresponding chromium porphyrin complex (80 mg, 75.5%) **2** as a dark green solid: $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ 332 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 43 889), 404 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 70 898), 438 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 148 548), 560 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 10 128), 618 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 30 385); FTIR (KBr) 1567, 1520, 1492, 1299, 1057, 1011, 986, 949, 764 cm^{-1} ; ¹⁹F NMR (235 MHz, acetone-*d*₆): δ -140.8 (q, 2 F, *o*-Ar-F), -156.8 (t, 1 F, *p*-Ar-F), -163.2 (multiplet, 2 F, *m*-Ar-F). Anal. Calcd for C₄₄H₈F₂₀N₄CrCl: C, 49.9; H, 0.8; N, 5.3. Found: C, 49.5; H, 1.0; N, 5.4. MS (FAB) *m/z* 1059 [(M⁺), 13%], 1025 (38); [Found: (M⁺) 1059.9847 C₄₄H₈F₂₀N₄CrCl requires *M* 1059.9982].

Solubility Test of Metalloporphyrin Complex 2 in scCO_2 . The metalloporphyrin complex **2** (3 mg) was added to the 10 mL Hastelloy steel reactor. The vessel was then filled with liquid CO_2 at ambient temperature and heated to 80 °C (70–215 bar). The phase behavior was observed through a sapphire window fitted in the end of the reactor. Dissolution of the porphyrin complex resulted in an intensely green colored homogeneous solution.

Polymerizations. In a typical reaction, tetrakis(pentafluorophenyl)chromium(III) porphyrin (CrTFPPCl) **2** (5 mg, 4.7×10^{-3} mmol), DMAP (5 mg, 0.04 mmol), and CHO (1.3 g, 13 mmol) were added to the reactor. The reaction vessel was then purged with CO_2 and filled with liquid carbon dioxide to approximately three-quarter capacity. Stirring was commenced, and the solution was heated to the reaction temperature. If necessary, more CO_2 was added at a temperature close to the reaction temperature in order to reach the desired pressure. Phase behavior in the vessel was observed carefully over the first few hours. In all cases, the copolymer was observed to precipitate from solution as it was formed. After the allotted reaction time, the carbon dioxide was vented through excess acetone to trap any residual monomer. Remaining products in the reactor were rinsed with acetone into the same solution. The solvent was then partially evaporated, and the concentrated polymer solution was precipitated into an excess of hexane to give the polycarbonate as a fine powder. The polymer was dried under vacuum to constant weight, and the yield was determined gravimetrically.

Analysis of Copolymers 4. NMR spectra were recorded in deuteriochloroform at room temperature using a Bruker WM-250 NMR spectrometer. IR spectra were recorded on a Nicolet 510 FT-IR spectrometer. Molecular weights were determined by gel permeation chromatography (GPC) using $2 \times \text{PL}$ gel columns (30 cm, 5 μm , mixed C) at 30 °C, running in chloroform at 1 mL/min with polystyrene ($M_n = 600$ – 10^6 g/mol) standards. Static light scattering analysis was carried out using a DAWN DSP instrument by Wyatt Technology Corp. Differential scanning calorimetry (DSC) thermograms were recorded on a Perkin-Elmer DSC 7. In all cases, the temperature range scanned was from 0 to 250 °C at a scanning rate of 10 °C/min, and indium metal was used as a standard. Glass transition temperatures (T_g) were taken at the midpoint of the change in heat capacity, and melting temperatures (T_m) were measured during the second scan. Thermal stability was determined with a Perkin-Elmer TGA 7 in a nitrogen atmosphere. The temperature range scanned was from 30 to 800 °C at a scanning rate of 10 °C/min.

Typical Data for Copolymer 4. FTIR (KBr): 2987, 2939, 2861, 1748, 1459, 1439, 1357, 1260, 1188, 1088, 967, 891, 837 cm^{-1} . ¹H NMR (250 MHz, CDCl₃): δ 4.6 (br s, 2H, CHOC(O)O-), 3.6 (br s, 2H, -CH-O-), 2.3–2.1, 1.9–1.7 (br s, 4H, -CH₂-), 1.4–1.2 (br m, 4H, -CH₂-). ¹³C NMR (62.5 MHz, CDCl₃): δ 153.9, 153.2 (-C(O)), 82.2, 72.5 (-O-CH-), 29.3, 28.6 (-CH₂), 23.8, 22.8 (-CH₂). Anal. Calcd for C₇H₁₀O₃: C, 59.1; H, 7.2. Found: C, 59.1; H, 7.2. Thermal analysis: $T_{\text{max}} = 310$ °C; $T_g = 117$ °C; dn/dc (CHCl₃, 25 °C, 633 nm) = 0.68.

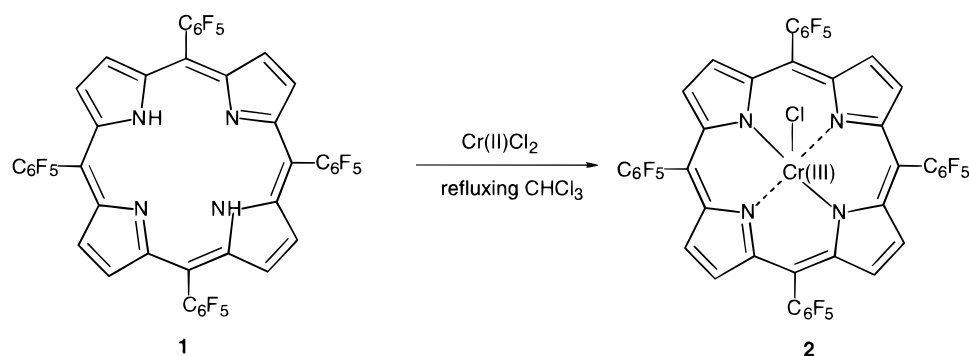
Results and Discussion

The chromium porphyrin complex **2** containing pentafluorophenyl substituents in the *meso*-position (Scheme 1) was found to be soluble in both liquid and supercritical CO_2 at moderate pressures (70–215 bar) and temperatures (20–80 °C) to give a deeply colored, homogeneous, green solution.

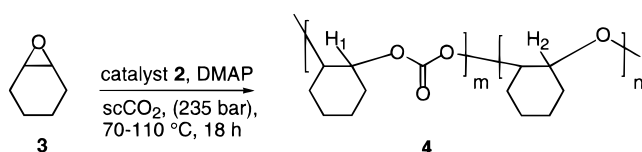
The CrTFPPCl/DMAP system showed catalytic activity for the ring-opening copolymerization of cyclohexene oxide and CO_2 to form the copolymer, poly(cyclohexene carbonate-co-cyclohexene ether) **4**, with a high carbonate content (Scheme 2, Table 1). The reactions generated CO_2 -insoluble polymers, and precipitation commenced during polymerization. The formation of low molecular weight byproducts (e.g., cyclohexene carbonate) was not observed. Control experiments indicated that the presence of both CrTFPPCl and DMAP was required for the formation of polymer (Table 1, entries 1 + 2).

The effect of varying reaction temperature was explored, as shown in Table 1. In all cases, the reaction was left for 18 h, although polymer precipitation commenced after just a few hours. All of these reactions were carried out under conditions where the reaction

Scheme 1



Scheme 2

Table 1. Effect of Temperature on the Copolymerization of Cyclohexene Oxide and CO₂ in scCO₂^a

entry	temp [°C]	yield [%]	<i>m</i> [%]	<i>M_n</i> [g/mol]	<i>M_w/M_n</i>	comment
1	95			<i>b</i>		no CrTFPPCl
2	95			<i>b</i>		no DMAP
3	70	24	0	800	1.04	
4	95	35	95	2960	1.12	
5	110	56	95	3450	1.15	
6	110	56	97	9370	1.08	
7	140	11	95	2460	1.16	

^a Conditions: [CHO] = 13% w/v, *p* = 3300 psi, *t* = 18 h, *N*_{CrTFPPCl}/*N*_{CHO} ≈ 2.6 × 10⁻³. ^b Monomer.

mixture was initially homogeneous (i.e., a single homogeneous phase was observed in the reactor prior to polymerization). The outcome of the reaction was strongly temperature-dependent. At lower temperatures, only oligomeric polyether formation was observed (entry 3). Higher reaction temperatures (95–110 °C) were found in general to lead to higher CO₂ incorporations and higher polymer yields (entries 4–7), although at much higher temperatures (140 °C, entry 7), a significant decrease in yield and molecular weight was observed. These observations are consistent with a polymerization process governed by equilibrium thermodynamics.¹³ Under such conditions, the decrease in polymer yield and molecular weight at higher temperatures may be explained by the onset of a ceiling temperature. Such observations had already been made by Beckman^{11,13} in studies involving a fluorinated zinc catalyst. This interpretation was further supported by long duration thermal gravimetric analysis (TGA) made on our polymers at temperatures above 110 °C. For example, it was found that depolymerization processes led to significant weight loss (12%) at 180 °C under a nitrogen atmosphere over a period of 15 h. It should be noted that while this series of experiments described in Table 1 was carried out at constant pressure, the density of the reaction mixture changed as the temperature was raised. In general, the density (and the mole fraction of CO₂ in the system) was considerably lower in the reactions carried out at higher temperatures. Calculation of the precise density for the multicomponent mixture is somewhat complicated (N.B., boiling point CHO at 1 bar = 129–130 °C).

Table 2. Effect of Time on the Copolymerization of Cyclohexene Oxide and CO₂ in scCO₂^a

entry	time [h]	yield [%]	<i>m</i> [%]	<i>M_n</i> [g/mol]	<i>M_w/M_n</i>
8	4	47	85	1900	1.19
9	8	63	93	3450	1.19
10	18	56	95	3450	1.15
11	24	50	91	3930	1.16
12	72	53	93	2810	1.23

^a Conditions: [CHO] = 13% w/v, *T* = 110 °C, *p* = 3300 psi, *N*_{CrTFPPCl}/*N*_{CHO} ≈ 2.6 × 10⁻³.

Table 3. Effect of Molar Ratio on the Copolymerization of Cyclohexene Oxide and CO₂ in scCO₂^a

entry	temp [°C]	I:M	yield [%]	<i>m</i> [%]	<i>M_n</i> [g/mol]	<i>M_w/M_n</i>
13	95	1:1317	56	90	3085	1.13
14	95	1:2638	35	95	2960	1.11
15	95	1:5429	34	78	1510	1.39
16	110	1:1360	41	95	3560	1.18
17	110	1:2580	56	95	3450	1.15
18	110	1:4275	73	97	3930	1.16

^a Conditions: [CHO] = 13% w/v, *p* = 3300 psi, *t* = 18 h.

Our catalyst was not overly sensitive to air and water impurities, although reactions carried out under rigorously anaerobic and anhydrous conditions (e.g., entry 6) did appear to yield rather higher molecular weight products than those where no special precautions were undertaken (entries 5, 7–12). The dependence of both yield and number-average molecular weight on reaction time was modest (Table 2, entries 8–10). No further increase in polymer yield was observed after around 8 h, perhaps suggesting that an equilibrium between monomer and polymer was established rather quickly under these conditions.

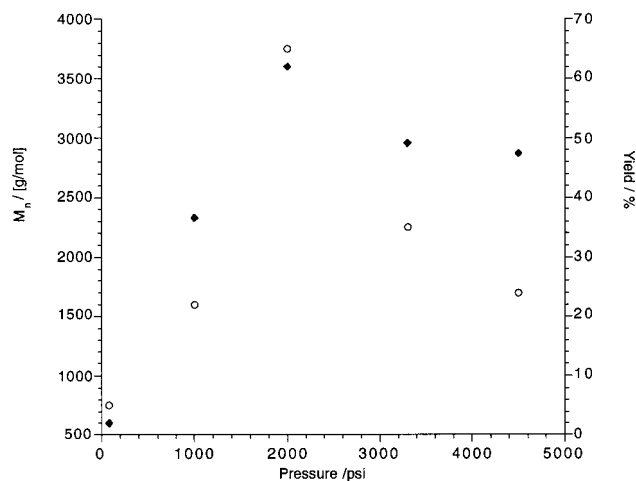
In a separate series of reactions, the molar ratio of catalyst to monomers was varied while the remaining variables were kept constant (Table 3). There was no obvious trend in the variation of molecular weights. The highest molecular weight material was isolated from reactions carried out at 110 °C when the molar ratio was in the range *N*_{CHO}/*N*_{CrTFPPCl} = 1360–4275 (entry 18), but there was essentially no dependency of number-average molecular weight on the catalyst-to-monomer ratio. This fact again suggests that molecular weight may have been limited by equilibrium processes. The catalyst-to-monomer ratio also had no effect on the molecular weight distribution, which remained low (<1.4) in all cases.

In another series of reactions, the CO₂ pressure was varied while the temperature (95 °C) and reaction time (18 h) were kept constant (Table 4). This in turn led to variations in both the density of the reaction mixture and the molar ratio of CHO to CO₂. When the bulk

Table 4. Effect of Pressure on the Copolymerization of Cyclohexene Oxide and CO₂ in scCO₂^a

entry	press. [psi]	yield [%]	<i>m</i> [%]	<i>M_n</i> [g/mol]	<i>M_w/M_n</i>	phase behavior
19	80	5	50	600		CO ₂ atmos
20	1000	22	93	2330	1.11	biphasic
21	2000	65	95	3600	1.16	biphasic
22	3300	35	95	2960	1.12	one phase
23	4500	24	93	3870	1.27	one phase

^a Conditions: [CHO] = 13% w/v, *T* = 95 °C, *t* = 18 h, *N*_{CrTFPPCl}/*N*_{CHO} ≈ 2.6 × 10⁻³.

**Figure 1.** Effect of pressure on molecular weight and yield for the polymerization shown in Scheme 2 (■ for *M_n* and ○ for yield dependency).

polymerization was conducted in a low-pressure CO₂ atmosphere (80 psi), only oligomeric material could be isolated in very poor yield and with a low CO₂ incorporation (Table 4, entry 19). This result contrasts with recent studies by Coates, whose catalyst system led to good polymer yields in bulk polymerizations of this type.^{23,24} By increasing the pressure to 2000 psi (Table 4, entry 21), both yield and number-average molecular weight were increased significantly. A further increase in pressure to 3300 psi led to a pronounced depression in yield (Table 4, entry 22; Figure 1). This effect is almost certainly due to the phase behavior in this set of experiments and is in general agreement with previous studies by Super and Beckman.¹³ Under our conditions ([CHO] = 13% w/v, *T* = 95 °C) polymerizations conducted at 95 °C/2000 psi occurred initially in the two-phase regime; that is, the reaction mixture consisted of a lower CHO-rich phase (which was swollen with CO₂) and an upper CO₂-rich phase (in which was dissolved a relatively small amount of CHO monomer). Since the green color was much more intense in the monomer-rich phase, it seems likely that most of the catalyst resided there. Under these conditions, the effective concentration of CHO in the CHO-rich phase would be much higher than the "nominal" concentration of 13% w/v as calculated from the amount of CHO added to the reaction vessel. By contrast, the polymerizations conducted at 3300 and 4500 psi (entries 22 and 23) commenced in the single-phase regime. Under those conditions, the effective concentration of CHO would be equivalent to the nominal concentration of 13% w/v. We therefore attribute the abrupt decrease in yield and molecular weight (Figure 1) to this sudden reduction in effective CHO concentration, which occurs when the phase boundary for the system is crossed. This dilution effect seems to strongly outweigh any advantage that

Table 5. Effect of Mole Fractions of CHO at 3300 psi^a

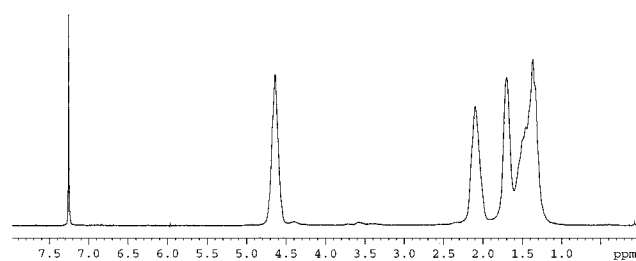
entry	χ (CHO) [% w/v]	yield [%]	<i>m</i> [%]	<i>M_n</i> [g/mol]	<i>M_w/M_n</i>
24	13	35	95	2960	1.12
25	25	74	95	3430	1.16
26	35	62	93	2910	1.14

^a Conditions: *T* = 95 °C, *t* = 18 h, *N*_{CrTFPPCl}/*N*_{CHO} ≈ 2.6 × 10⁻³.

Table 6. Effect of Mole Fractions of CHO at 2000 psi^a

entry	χ (CHO) [% w/v]	yield [%]	<i>m</i> [%]	<i>M_n</i> [g/mol]	<i>M_w/M_n</i>
27	13	65	95	3600	1.16
28	25	70	94	6960	1.32
29	35	65	94	3970	1.50

^a Conditions: *T* = 95 °C, *t* = 18 h, *N*_{CrTFPPCl}/*N*_{CHO} ≈ 2.6 × 10⁻³.

**Figure 2.** ¹H NMR spectrum of the copolymer (Table 1, entry 6).

might be gained from increased ceiling temperatures/ lowered equilibrium monomer concentrations that are associated with increased reaction pressures.¹³

Even though a constant volume of CHO and a constant amount of catalyst were used for this series of polymerizations, the effective mole fraction of CHO decreased with increasing pressure, since more moles of CO₂ was present in reactions at higher pressures. Since the relative concentrations of the two monomers may be an important variable (e.g., due to differences in the propensity of CHO and CO₂ toward depolymerization), a separate series of polymerizations were carried out where the mole fraction of monomer, χ (CHO), was varied (Table 5).

The effect of varying monomer concentration at constant pressure in the single-phase regime was explored, as shown in Table 5. At lower monomer concentrations (<15 w/v %), the polymer yield was low (entry 24). At monomer concentrations above 25 w/v %, the yields were significantly higher (entries 25 + 26).

In a further series of experiments, the concentration of monomer was varied, but the polymerizations were carried out at a lower pressure (2000 psi) in the two-phase regime (Table 6). The variation in monomer concentration had a less pronounced effect on polymer yield in this case, probably because the effective concentration of CHO in the CHO-rich phase did not vary so greatly.

¹H NMR spectroscopy of **4** (Figure 2) confirmed that the polymers were comprised mostly of carbonate linkages and contained only a very small percentage of ether linkages. A strong signal was assigned to the methine proton (H₁ in **4**) of the repeating oxycarbonyloxy (1,2-cyclohexene) unit at δ 4.6, while the singlet corresponding to the repeating oxy (1,2-cyclohexene) units at δ 3.5 (H₂ in **4**) was barely discernible. A very high percentage (≈95%) of carbonate linkages was estimated to be

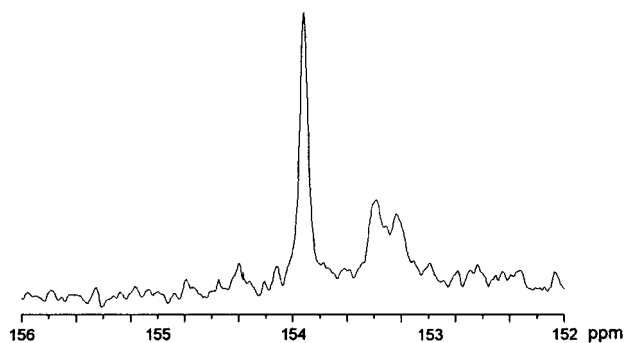


Figure 3. ¹³C NMR spectrum of the copolymer (Table 1, entry 6).

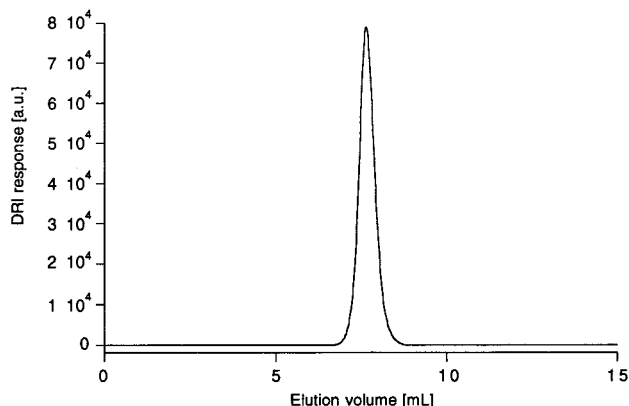


Figure 4. Gel permeation chromatogram of the copolymer (Table 1, entry 6).

present from the ¹H NMR. Compared with the percentage of carbonate units in polycarbonate–polyether copolymers reported by Super et al.,¹¹ our catalyst system appears to be at least as effective in this respect.

The ¹³C NMR spectrum of the polymer **4** (Figure 3) contains a dominant C=O signal at δ 153.9 with minor resonances at δ 153.2 and 153.4. The cyclohexane ring carbons are evident at δ 29.1 and 23.0. Coates²³ reported that hydrolysis of the polycarbonate produced by copolymerization of CHO in CO₂ afforded 1,2-*trans*-dihydroxycyclohexane. We therefore also assign the stereochemistry of the polycarbonate **4** as 1,2-*trans* at the cyclohexane substituents.^{8,26} Further studies on the tacticity of the polymer **4** are currently under investigation.

Static light scattering analysis and the Casassa–Holtzer²⁷ plot revealed that polymer **4** behaves like a typical coil in CHCl₃, and therefore gel permeation chromatography (GPC) in CHCl₃ calibrated against polystyrene was used to characterize the materials. The number-average molecular weights of the copolymers were in the range of 3500 g/mol (Tables 1–3). However, considering that the copolymerization is a precipitation process, the GPC chromatograms (Figure 4) for all the polymers showed sharp elution curves and remarkably narrow unimodal distributions. The molecular weight distribution (M_w/M_n) was calculated to be less than 1.4 in all cases and could be as low as 1.08 (Table 1, entry 6). This represents a very significant improvement over the distributions (M_w/M_n = 2.4–27) reported previously for other scCO₂-based systems.^{8,9,11}

Thermal gravimetric analysis (TGA) of **4** revealed a maximum decomposition temperature T_{max} of 310 °C, without any prior decomposition steps. No remarkable changes were observed until 280 °C; at temperatures

close to 300 °C, the copolymer began to decompose rapidly. These values corresponded well with literature TGA data for PCHC.²⁴ Differential scanning calorimetry (DSC) revealed a glass transition temperature (T_g) of 117 °C (entry 5) (literature²⁸ T_g = 135 °C). The slight deviation between the measured glass transition temperature and the literature value may be due to the presence of a small percentage of ether linkages in our samples.

Conclusions

Metalloporphyrin complexes bearing fluorinated aryl substituents in the *meso*-positions are soluble in both neat liquid and supercritical CO₂, as well as in mixtures of CO₂ and CHO. Tetrakis(pentafluorophenyl)porphyrin chromium(III) chloride showed catalytic activity for the alternating copolymerization of cyclohexene oxide and CO₂ in the presence of an organic base. It was found that the pressure affected the CO₂/monomer phase behavior, which in turn strongly affected the outcome of the reaction. In all cases, the polymers formed showed very narrow molecular weight distributions ($M_w/M_n \leq 1.4$), and high carbonate contents (90–97%) were determined by ¹H NMR. In addition, greatly improved catalyst efficiencies were obtained (3.9 kg of polymer/g of Cr) in comparison to previous catalyst systems.^{8–11} The main limitation to our method is that relatively low number-average molecular weights are obtained in the polycarbonate products. This is possibly due to the fact that the reaction is an equilibrium process and that the temperatures needed to achieve polymerization with this catalyst are fairly close to the ceiling temperature for this particular polymer. It is also possible that the molecular weight was limited by chain transfer to protic impurities in the reaction mixture. Nevertheless, the range of potential uses for CO₂-soluble catalysts of this type is quite broad, in both the areas of polymerization and homogeneous catalysis. A variety of novel applications for these porphyrin complexes is currently under investigation.

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References and Notes

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