

Synthesis and CO₂ Solubility Studies of Poly(ether carbonate)s and Poly(ether ester)s Produced by Step Growth Polymerization

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ABSTRACT: Poly(ether carbonate)s (PEC) and poly(ether ester)s (PEE) were synthesized by step growth polymerization, and the reaction conditions were optimized. The solubility of the polymers in CO₂ was then evaluated using two methods: (i) observation of the cloud point and (ii) gravimetric extraction. Our results suggest that it is difficult to give an exact description of the solubility profiles for these polymers using cloud points alone, particularly in cases where there is a broad distribution of molecular weights. We suggest that the cloud point data are more easily interpreted in combination with a quantitative gravimetric extraction method that we have developed. It was found that the CO₂ solubility of the PEC and PEE samples was strongly affected by both the polymer molecular weight and the chemical structure.

Introduction

Supercritical carbon dioxide (scCO₂) is an inexpensive, nontoxic, and nonflammable solvent for polymer synthesis and processing.^{1–3} Until recently, the only polymers found to have significant solubility in CO₂ under moderate conditions (<100 °C, <400 bar) were amorphous fluoropolymers² and to a lesser extent polysiloxanes.⁴ A number of research groups have synthesized “CO₂-philic” fluoropolymers or silicone-based materials for use as steric stabilizers in dispersion polymerization,^{3,5–8} as phase transfer agents for liquid–liquid extraction,⁹ as supports for homogeneous catalysis,^{10,11} and as surfactants for the formation of water/CO₂ emulsions and microemulsions.^{12,13} Unfortunately, the high cost of fluorinated polymers may prohibit their use on an industrial scale for some applications. Fluoropolymers also tend to have poor environmental degradability, and this could negate the environmental advantages associated with the use of scCO₂. The lack of inexpensive CO₂-soluble polymers and surfactants is a significant barrier to the future implementation of this solvent technology.¹⁴

Beckman and co-workers reported that certain poly(ether carbonate) (PEC) copolymers are reasonably soluble in CO₂ under moderate conditions.^{15,16} Beckman’s hydrocarbon systems involve PECs synthesized by aluminum-catalyzed copolymerization of cyclic ethers with CO₂ (i.e., M₁ = ethylene oxide, propylene oxide, cyclohexene oxide; M₂ = CO₂). These copolymers were found to be soluble in liquid CO₂ at concentrations of 0.2–1.5% w/v at ambient temperatures and pressures in the range 120–160 bar, that is, significantly above the liquid vapor pressure for CO₂. These statistical copolymers were generated from very inexpensive feedstocks and are thus appealing as “building blocks” for cheap surfactants. The enhanced solubility of these copolymers with respect to poly(propylene oxide) is believed to arise, at least in part, from specific Lewis acid–base interactions that exist between CO₂ and the carbonyl groups of the carbonate moieties.^{15–19}

Step growth polymerization is a method that can be used to synthesize polymers with well-defined chemical compositions; indeed, unlike nonideal statistical chain growth polymerizations, the composition of step growth polymers mirrors exactly the composition of the monomer feed. In this study, we have developed step growth polymerization routes to synthesize PEC and also poly(ether ester) (PEE) materials as potential inexpensive hydrocarbon CO₂-philes. We have shown that these polymers are soluble in CO₂, but only up to moderate molecular weights (<10 000 g/mol).

Experimental Section

Materials. Poly(propylene glycol) (PPG, 425 and 725 g/mol), 1,1'-carbonyldiimidazole (CDI), sodium sulfate, diglycolyl chloride, anhydrous tetrahydrofuran (THF), and dichloromethane were all purchased from Sigma-Aldrich Chemical Co. and used as received. Deionized water was used. High-purity carbon dioxide (SFC grade, 99.9999%) was purchased from BOC Gases.

Synthesis of Poly(ether carbonate)s. In a typical preparation, dry solvent (THF, 50 mL) was added to a round-bottom flask or Radleys reaction tube fitted with a dry N₂ inlet and a magnetic stirrer. CDI (6.48 g, 40 mmol) was added followed by PPG (425 g/mol, 17.00 g, 40 mmol) and KOH (0.224 g, 4 mmol). The mixture was heated at 60 °C with constant stirring for 5 h. The clear, pale-yellow solution formed was allowed to cool and was then concentrated under vacuum. The crude product was dissolved in dichloromethane (50 mL) and washed three times with water (3 × 100 mL). The solution was then dried over anhydrous Na₂SO₄ and concentrated in vacuo to obtain the polymer as a colorless, viscous liquid (16.4 g, 89%). The PEC materials (which have only moderate thermal stability) were stored in a freezer (–20 °C) until use.

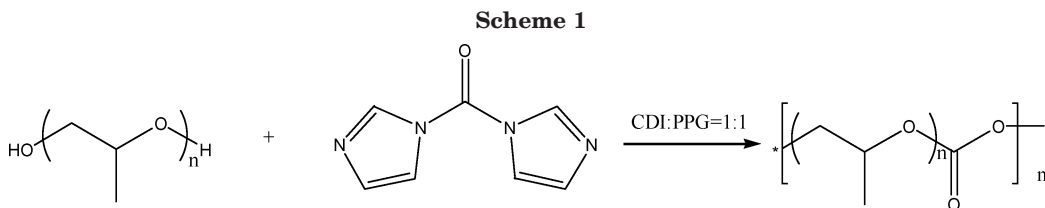
Synthesis of Poly(ether ester). PPG-725 (3.625 g, 5 mmol) and diglycolyl chloride (0.855 g, 5 mmol) were added into a reaction tube equipped with a N₂ inlet and magnetic stirrer. Polycondensation was carried out in bulk at 100 °C, initially at normal pressure for 2 h, then under reduced pressure for 2 h, and finally under high vacuum for 12 h.²⁰ The PEE was isolated as a viscous liquid in >95% yield and was not purified further.

Characterization. ¹H NMR spectra were recorded in CDCl₃ on a Bruker Analytic GmbH 400 MHz spectrometer using tetramethylsilane (TMS) as an internal reference. ¹³C NMR spectra were recorded at 400 MHz in CDCl₃ solution on

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a Bruker Analytic GmbH 400 MHz spectrometer using solvent carbon signal as standard. Gel permeation chromatography (GPC) was performed using a Polymer Laboratories system equipped with a PL-ELS 1000 evaporative light scattering detector and a series of PC mix gel columns 5 μm MIXED C and D. THF was used as the eluent at a flow rate of 1.0 mL/min at 40 $^{\circ}\text{C}$. Calibration was carried out using EasiCal polystyrene standards (Polymer Laboratories).

Solubility Measurements in CO_2 : (a) **Cloud Point Curve Determinations.** Cloud points were recorded using a high-pressure, variable volume view cell, the full details of which have been published in a recent article.²¹ An accurately weighed amount of polymer was added to the view cell along with a magnetic stirrer bar, and the cell was sealed. CO_2 was then passed into the cell using a weighed, high-pressure, stainless steel bomb. After addition of the CO_2 , the bomb was reweighed in order to calculate the exact composition of the polymer/ CO_2 mixture (recorded in w/w %). The cell was heated to a given temperature and allowed to equilibrate with stirring. Pressure inside the cell was then increased by slowly reducing the volume of the cell until a single polymer/ CO_2 homogeneous phase was observed. The cloud point pressure of the mixture was recorded by slowly lowering the pressure inside the cell until the polymer phase separated from solution. The cloud point was taken as the point at which it was no longer possible to see the back of the cell through the polymer- CO_2 mixture. This process was repeated three times and an average of the results taken as the cloud point pressure. We estimate that the cloud point pressures measured in this way were accurate to at least ± 4 bar (~ 60 psi). Cloud point pressures were recorded between 25 and 65 $^{\circ}\text{C}$ for a given polymer/ CO_2 mixture.

(b) **Gravimetric Extraction Method.** (i) **View Cell Method.** About 0.25 g of polymer was weighed accurately by difference into a 10 mL stainless steel view cell equipped with a sapphire view window.⁷ CO_2 was flowed through the vessel at a constant pressure (delivered using a NWA PM-101 compressor) for a fixed period, and then the pressure was increased. The extracts were collected in THF, and the collection vial was exchanged after predetermined time intervals, thus producing a series of extracted fractions.

(ii) **Extraction Column Method.** About 0.25 g of polymer was weighed accurately by difference into the bottom of a vertically mounted 4.5 mm i.d. stainless steel HPLC column. CO_2 was allowed to flow from the bottom of the column at a certain pressure and flow rate as controlled by an Isco Series D syringe pump. The extracts were collected in THF, as described before.

Results and Discussion

Synthesis of Poly(ether carbonate)s by Step Growth Polymerization. A series of PECs were synthesized by condensation of oligomeric poly(propylene glycol) (PPG) diols with carbonyldiimidazole (CDI),^{22–24} as described in Scheme 1. By using step growth polymerization, one can precisely control the composition of the products since it is defined by the alternating microstructure of the copolymers. One sample (PEC-PPG-425) was synthesized using PPG-diol with an average molecular weight of 425 g/mol (PPG-425) while the other sample (PEC-PPG-725) was synthesized using PPG-diol with an average molecular weight of 725 g/mol (PPG-725). The evolution of molecular weight over time was monitored by taking small aliquots (~ 50 μL)

of the reaction mixture and analyzing by GPC. A plot of the degree of polymerization vs reaction time for the two aliphatic PEC samples is shown in Figure 1. For both samples PEC-PPG-425 and PEC-PPG-725, it was observed that the molecular weight increased over the first 600 min or so, after which no further increase in molecular weight was observed. The molecular weight distribution (M_w/M_n) broadened during the course of the reaction and reached the typical value for step growth polymerization (~ 2) at the end of the reaction. The monomer PPG-725 gave rise to a slightly higher degree of polymerization than the PPG-425 under analogous conditions. Despite attempts to optimize the reaction conditions with respect to the CDI-to-PPG ratio, the nature of the base (e.g., KOH, K_2CO_3), the temperature, and the solvent, we did not achieve much higher degrees of polymerization than those shown in Figure 1. A potential complication here is the asymmetric nature of the CDI coupling reaction: the intermediate imidazolidone reacts much faster with primary alcohols than with secondary alcohols and will indeed functionalize the former with complete selectivity in mixed primary–secondary systems.^{23,24} As such, the PPG-to-CDI stoichiometry may be perturbed by preferential depletion of the primary PPG alcohol end groups. This would lead to a preponderance of mutually unreactive secondary alcohols and secondary imidazolides which would not contribute to further molecular weight buildup. The use of a less discriminate and more reactive coupling agent such as phosgene would likely give higher molecular weights, although the CDI route is convenient in terms of safety and ease of handling of the reagents.

Since these are step growth polymers, it is possible to estimate the percentage carbonate incorporation by knowing the average molecular weight of the PPG-diol monomers. For the polymer formed from PPG-425, the nominal percentage carbonate incorporation was calculated to be 14.3% mol/mol, compared to 8.2% mol/mol for the polymer synthesized from PPG-725. (Supplier values for the molecular weights of the diols were used

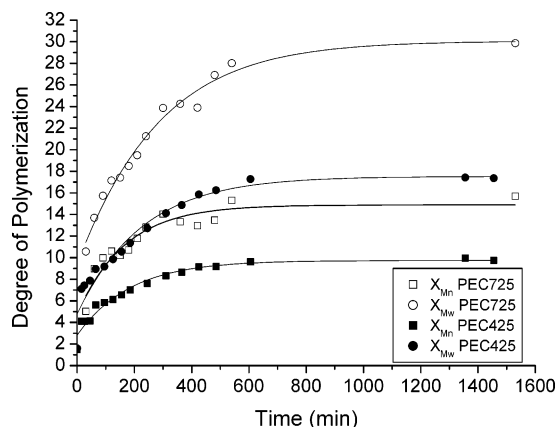
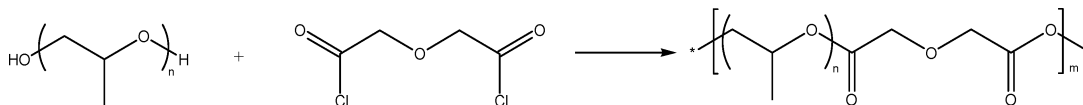


Figure 1. Kinetics of molecular weight increase for poly(ether carbonate)s synthesized by step growth polymerization. Reaction conditions: PPG-425 (■, ●) or PPG-725 (□, ○) (40 mmol), CDI (40 mmol), KOH (40 mmol), THF (50 mL), 65 $^{\circ}\text{C}$, 24 h.

Scheme 2



in both cases.) Both PECs were also analyzed by ^1H NMR in order to confirm the percentage carbonate incorporation. The carbonate percentage was determined from the integrals of the $-\text{CH}_2-\text{O}-$ peaks at 3.4–3.6 ppm and the carbonate resonances ($-\text{CH}_2-\text{O}(\text{CO})-\text{O}-$) at 4.87 ppm. The carbonate incorporations were found to be 12.4% mol/mol and 8.75% mol/mol, respectively, for the two materials, that is, within error, quite close to the nominal calculated values. The ^{13}C NMR spectrum of the PEC samples also exhibited a dominant $\text{C}=\text{O}$ signal at δ 154.4 ppm, thus confirming that the carbonyl group had been introduced into the polymer. The thermal stability of the PECs was found to be limited: the samples degraded at room temperature over a period of days to weeks, leading to a gradual reduction in the molecular weight. This could be avoided by storing the samples at -20 °C. Tests showed that heating the polymers in air at 100 °C for 48 h degraded the polymers completely to yield products which had $M_w < 800$ g/mol.

Synthesis of Poly(ether ester)s by Step Growth Polymerization. Poly(ether ester)s (PEEs) were synthesized by step growth polymerization of PPG-diols and diglycyl chloride (Scheme 2). The resulting polyesters had broadly similar structure to the PEC materials, that is, a polyether backbone punctuated at regular intervals with carbonyl groups. The spacing of these groups along the chain, however, is quite different in the PEE materials since the carbonyls in the diglycyl chloride monomer are separated by just three connecting atoms.

Cloud Point Observations in CO_2 : PEC-PPG-425, 12.4% mol/mol Carbonate, $M_w = 7800$ g/mol, $M_n = 3680$ g/mol. We attempted to measure the cloud point in CO_2 for this material over a range of different concentrations. At a concentration of 0.367% w/w, it was observed that the material did not dissolve completely, even at low temperatures (35 °C) and high pressures (345 bar), that is, at high CO_2 densities. At a lower concentration (0.173%), the sample was fully soluble at 35 °C and 263 bar but could not be solubilized completely at temperatures above 45 °C at pressures within the safe working range for the equipment (<380 bar). In Beckman's studies,¹⁵ a 250-repeat-unit copolymer of PO and CO_2 ($M_n \approx 16\,000$ g/mol) with 15.4% mol/mol carbonate incorporation was reported to exhibit a much lower miscibility pressure of ~ 125 bar at 22 °C (1800 psi) at a somewhat higher concentration (0.8 wt %) than used in our studies. Our sample (PEC-PPG-425, $M_n = 3680$ g/mol, ~ 60 repeat units) was not fully miscible with CO_2 under similar conditions up to pressures of 380 bar.

PEC-PPG-725: 8.75% mol/mol Carbonate, $M_w = 8590$ g/mol, $M_n = 3520$ g/mol. Despite the fact that this PEC sample has a similar number-average molecular weight to PEC-PPG 425 (~ 55 repeat units vs ~ 60 repeat units, see above), this material did not dissolve fully in CO_2 at low concentrations (0.193%) and high CO_2 densities (25 °C, 345 bar), and it proved impossible to form a single, homogeneous phase under any conditions that we investigated. This supports Beckman's observation that the solubility of PEC materials is strongly dependent on the level of carbonate incorpora-

tion,^{15,16} since a fairly subtle change in structure leads to a substantial change in phase behavior.

Fractionated PEC-PPG-425 Samples. Since neither of the as-produced PEC materials exhibited particularly high solubility in CO_2 , a sample of PEC-PPG-425 (original $M_w = 8740$ g/mol) was fractionated using supercritical fluid extraction (SFE) with CO_2 as the mobile phase. A series of lower M_w PEC fractions were thus obtained. Figure 2 shows the relationship between cloud point pressure and molecular weight for three of these fractions at a concentration ca. 0.19 wt %. It is clear that the cloud point pressure rises as the molecular weight of the sample is increased, even over a relatively small molecular weight range (3800–5700 g/mol). For example, the 5670 g/mol fraction (~ 90 repeat units) exhibits a cloud point curve that is approximately 20–25 bar higher than the same curve for the 3780 g/mol fraction (~ 60 repeat units) over the temperature range 25–45 °C.

These results show that there is a marked variation in solubility for these PEC materials over the range of molecular weights studied. Given the typical molecular weight distributions for the unfractionated polymers ($M_w/M_n \sim 2$), it is not clear that cloud point measurements alone will lead to a full description of solubility profiles for these materials. This is because a significant weight fraction appears to be insoluble in CO_2 over the measurable pressure range for our equipment. For this reason, we have coupled the cloud point observations with a series of gravimetric extraction tests.

Gravimetric Extraction Method. The polymer was placed into a stainless steel vessel, and CO_2 was flowed through the vessel at a constant pressure and at 25 °C. The various extracts (and the residue in the reactor at the end of the extraction process) were analyzed by GPC. Figure 3 shows the molecular weight distributions for a PEC-PPG-425 sample (12.4% mol/mol carbonate) before extraction (a) and for the residue at the end of the extraction process (f). The other GPC traces (b–e) correspond to the fractions collected during extraction at increasing CO_2 pressures. The first fraction to be collected ((b) 30 min CO_2 flow at 170 bar) had a much

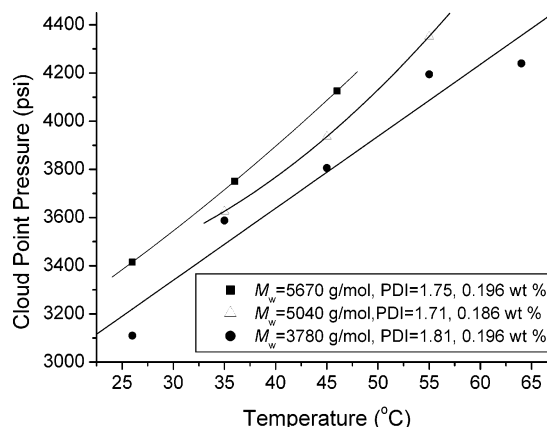


Figure 2. Cloud point curves for fractionated PEC-PPG-425 samples with different molecular weights: (■) $M_w = 5670$ g/mol, $M_w/M_n = 1.75$; (△) $M_w = 5040$ g/mol, $M_w/M_n = 1.71$; (●) $M_w = 3780$ g/mol, $M_w/M_n = 1.81$.

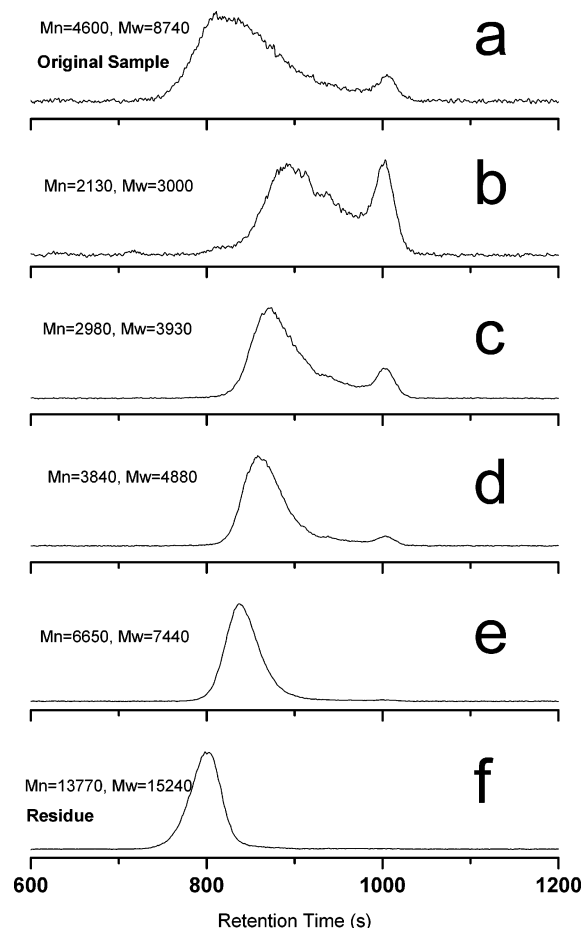


Figure 3. Molecular weight distributions for PEC-PPG-425 (a) before and (f) after extraction by CO₂ at 25 °C (CO₂ flow rate = 1.0 mL/min). (b–e) Fractions collected during extraction (see Table 1 for details of extraction conditions).

lower number-average molecular weight than the starting material (2130 vs 4600 g/mol), suggesting that the lower molecular weight oligomers were extracted from the material first. This first fraction represented 33.9 wt % of the total sample (see Table 1). More prolonged extraction at 170 bar led to further fractions (c, d) of somewhat higher M_n (up to 3840 g/mol) with smaller amounts of material being extracted as the extraction proceeded (16 and 6 wt %, respectively). After around 120 min at 170 bar, little further material was extracted at this pressure: a total of 55.9% of the sample mass had been extracted. The extraction pressure was then ramped to 272 bar for 120 min, whereupon a further 19.6% of the sample mass was recovered (e) with a higher M_n (6650 g/mol) than that previously extracted at 170 bar.

A significant proportion (24.5 wt %) of the sample remained in the vessel at the end of the experiment which was not extracted under these conditions and which had a much higher molecular weight than the starting material ($M_n = 13\,770$ g/mol, $M_w = 15\,240$ g/mol; see Figure 3f). To verify that the remaining polymer had the same chemical composition as that of the original sample, the structure was analyzed by ¹H NMR and was found to have a structure which was identical to the original bulk sample (12.4% mol/mol carbonate). Taken together, these data suggest that PEC-PPG-425 is moderately soluble in CO₂ at low molecular weights but has limited solubility in CO₂ at $M_n > 10\,000$ g/mol at 25 °C and pressures up to 272 bar. These findings are in agreement with the cloud point observations described above.

A poly(ether ester) (PEE) sample with very similar molecular weight ($M_w = 8430$ g/mol) and a slightly higher carbonyl incorporation in the backbone (14.3% mol/mol, as estimated by ¹H NMR) was extracted in the same fashion (see Figure 4 and Table 1). The general trends were similar; the lower molecular weight oligomers were extracted first, and then higher molecular weight species were extracted at increased pressures. Again, a residue was left in the extraction vessel which had higher molecular weight (and narrower molecular weight distribution) than the starting material (Figure 4f, $M_n = 7760$ g/mol, $M_w = 10\,380$ g/mol). A significantly higher percentage of the PEE remained after extraction (55.1%) compared with the PEC sample (24.5%), despite the fact that the molecular weights of the two samples before extraction were very similar. The molecular weight of the PEE residue after extraction was also closer to that of the starting material, and the molecular weight distribution was broader than in the case of the PEC material. All of these facts suggest that the PEE sample was less soluble in CO₂ than the PEC sample and that the extraction process had “eaten in” to the molecular weight distribution of the material to a lesser degree, as is clear from a comparison of Figure 3f and Figure 4f. Again, these observations are in agreement with the attempted cloud point measurements using the variable volume view cell; that is, the PEE sample was not fully miscible in CO₂ within the operational pressure range of our equipment.

Effect of CO₂ Pressure. To evaluate the effect of extraction pressure, our gravimetric extraction method was adapted to use a syringe pump such that precise volumes of CO₂ could be delivered at controlled flow rates. It was thus possible to carry out comparable quantitative experiments where the only variable was the CO₂ pressure.

Table 1. Characterization Data for PEC and PEE Fractions Collected by SFE

		PEC (12.4% mol/mol carbonate)				PEE (14.3% mol/mol ester)			
		M_n (g/mol)	M_w (g/mol)	M_w/M_n	wt % ^a	M_n (g/mol)	M_w (g/mol)	M_w/M_n	wt % ^a
a	original sample	4600	8740	1.90		4530	8430	1.98	
b	30 min/170 bar ^b	2130	3000	1.40	33.9	3700	4190	1.13	18.7
						1360	1590	1.17	
c	90 min/170 bar ^b	2980	3930	1.32	16.0	3160	3880	1.23	8.7
d	120 min/170 bar ^b	3840	4880	1.27	6.0	3840	4750	1.27	7.8
e	120 min/272 bar ^b	6640	7440	1.12	19.6	5710	6710	1.18	9.7
f	residue	13700	15240	1.11	24.5 ^c	7760	10380	1.34	55.1 ^c

^a Percentage of total sample weight. ^b Flow rate = 1 mL/min (average), $T = 25$ °C. ^c As determined gravimetrically by weighing extraction column before and after extraction. The mass of the residue was further confirmed by extraction of the material from the vessel with dichloromethane, followed by evaporation of the solvent and gravimetric determination of the solids residue. Both measurements (i.e., mass balance of fractions and physical determination of solids residue) agreed to within 5%.

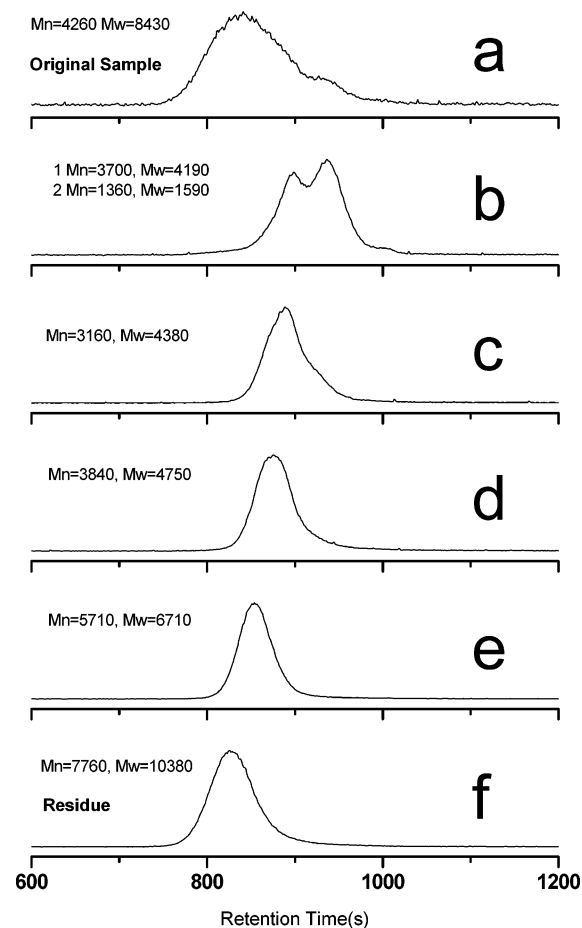


Figure 4. Molecular weight distributions for PEE-PPG-725 (a) before and (f) after extraction by CO₂ at 25 °C (CO₂ flow rate = 1.0 mL/min). (b–e) Fractions collected during extraction (see Table 1 for details of extraction conditions).

Table 2. Three Types of Polymer Used in Gravimetric Extraction Experiments

	M_n (g/mol)	M_w (g/mol)	carbonyl (% mol/mol)	total extracted (%)
PEC-PPG-725	3520	8590	8.75	30
PEC-PPG-425	4600	8740	12.4	70
PEE-PPG-725	4530	8430	14.3	35

Figure 5a shows the weight percentage of PEC-PPG-425 ($M_n = 4600$ g/mol, $M_w = 8740$ g/mol) extracted as a function of the CO₂ volume passed through the vessel (normalized to the unit mass of starting material in the vessel) at three different CO₂ pressures (flow rate = 1.0 mL/min in all cases, initial mass of sample = 0.25 g). At all three pressures, the initial extraction rate is higher but then levels off over time. It is clear that a much higher percentage of the sample is extracted at 300 bar than at 100 bar and that the overall rate of extraction is higher at increased CO₂ density. Nonetheless, even the maximum extraction rates observed are not particularly high; for example, in the initial extraction period at 300 bar, around 0.1 g of the sample (40%) is extracted after flowing 100 mL of CO₂ through the vessel. This corresponds to an average extraction rate of around 1 mg polymer/mL CO₂ at this flow rate (1 mL/min) and pressure (300 bar).

Figure 5b plots M_w for the recovered PEC extracts against the volume of CO₂ flowed through the vessel (normalized to the unit mass of starting material in the vessel). While there is significant scatter in these data,

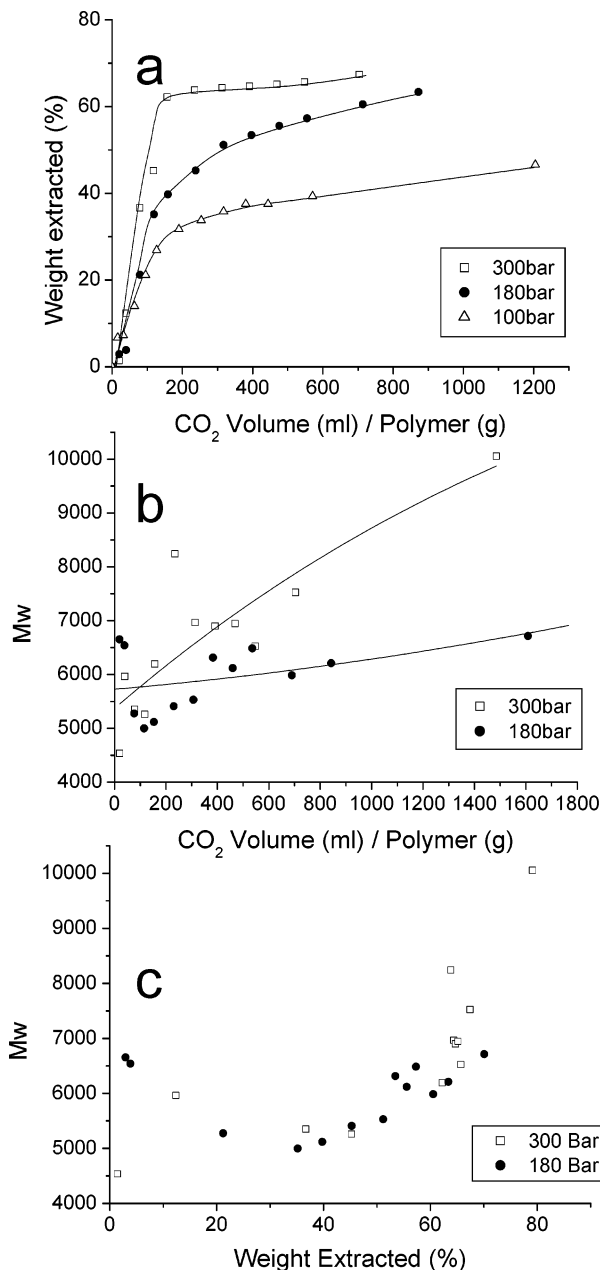


Figure 5. (a) Weight percentage of PEC-PPG-425 ($M_n = 4600$ g/mol, $M_w = 8740$ g/mol) extracted at different pressures (CO₂ flow rate = 1 mL/min for all pressures; $T = 25$ °C). (b) Corresponding plot of M_w for extracts of this PEC-PPG-425 sample at two different pressures (180 and 300 bar) as a function of CO₂ volume. (c) Plot of M_w for PEC-PPG-425 extracts as a function of sample weight extracted.

the overall trend is, again, that the lower molecular weight fractions are extracted earlier in the process. When M_w for the extracts is plotted as a function of sample mass extracted, the trend observed is very similar at both 180 and 300 bar (Figure 5c). Figure 5c effectively normalizes the data with respect to the overall extraction rate. This plot, and Figure 5b, confirm that while the overall extraction rate is higher at 300 bar than at 180 bar, the kinetic “profiles” of molecular weights extracted are similar at these two pressures: the lower molecular weight species are extracted more readily from the sample.

The GPC chromatograms in Figure 6a and the graph in Figure 6b demonstrate clearly that the molecular weight of the PEC residue increases as the extraction

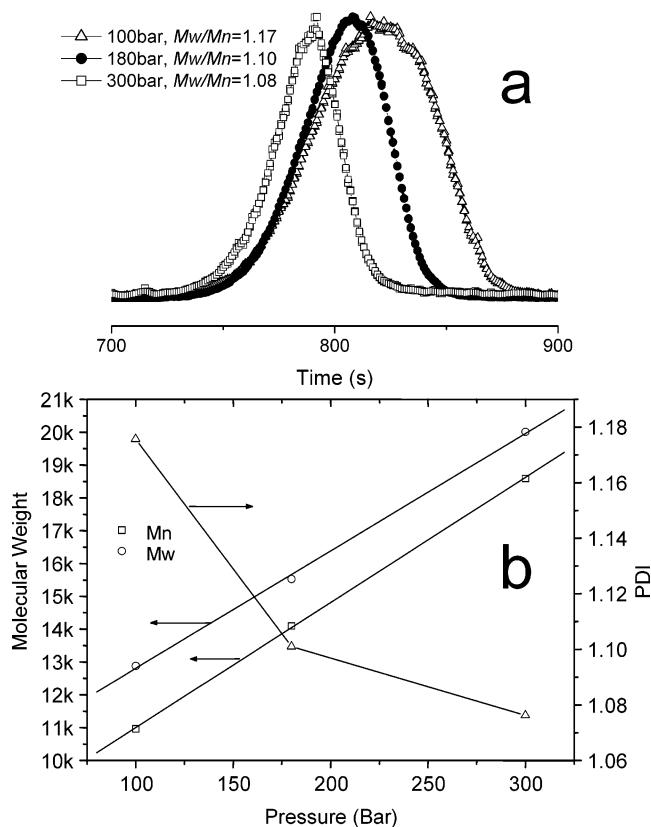


Figure 6. (a) Molecular weight distribution of the PEC-PPG-425 residue at end of extraction at three different pressures (100, 180, and 300 bar; flow rate = 1 mL/min; $T = 25\text{ }^{\circ}\text{C}$). (b) Corresponding plot of M_w (\circ), M_n (\square), and polydispersity index (Δ) for PEC-PPG-425 residues after extraction at these three different pressures.

pressure increases and also that the molecular weight distribution of the residue decreases. This is because an increasingly high fraction of the lower molecular weight distribution is removed by extraction as the CO_2 pressure is increased. Nonetheless, it is clear from these data that the PEC sample is only significantly soluble at rather low molecular weights. Even at the highest extraction pressure (300 bar), 30 wt % of the sample remained as unextracted residue after passing 700 g CO_2/g polymer through the vessel. Once again, these data suggest a molecular weight “cutoff” in terms of CO_2 solubility of around 10 000 g/mol.

Effect of Polymer Structure on Solubility in CO_2 . Three polymers (PEC-PPG-725, PEC-PPG-425, and PEE-PPG-725) having different chemical structures were tested for solubility in CO_2 by the gravimetric extraction method (Table 2). The two PEC samples (PEC-PPG-725 and PEC-PPG-425) had relatively similar molecular weights and differed mostly in carbonyl content (8.75% mol/mol and 12.4% mol/mol, respectively). The PEE sample (PEE-PPG-725) had a very similar carbonyl content compared to PEC-PPG-425 and a comparable molecular weight but contained ester rather than carbonate linkages in the polymer backbone.

Extraction studies support our view cell and cloud point observations and suggest that these three polymers differ significantly in terms of their solubility profiles in CO_2 (Figure 7). The total amount of polymer extracted by CO_2 was found to be around 70, 25, and 30 wt % for PEC-PPG-425, PEC-PPG-725 and PEE-PPG-725, respectively, under equivalent extraction

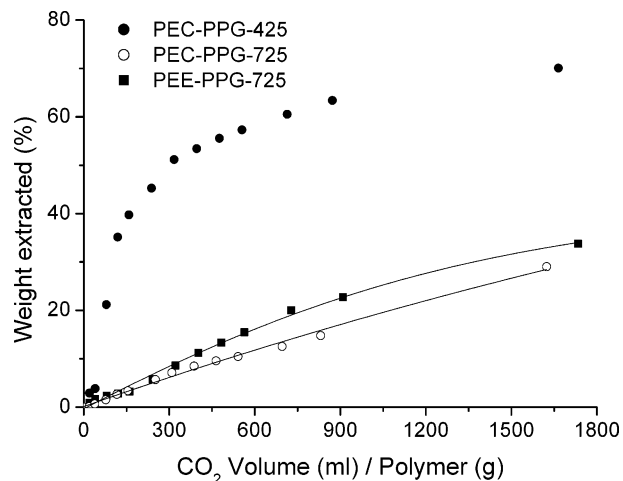


Figure 7. Plot of weight extracted vs CO_2 volume for three related polymer structures (CO_2 flow rate = 1 mL/min; $P = 180\text{ bar}$; $T = 25\text{ }^{\circ}\text{C}$): (\bullet) PEC-PPG-425 ($M_n = 4600\text{ g/mol}$, $M_w = 8740\text{ g/mol}$; carbonyl content = 12.4% mol/mol); (\circ) PEC-PPG-725 ($M_n = 3520\text{ g/mol}$, $M_w = 8590\text{ g/mol}$; carbonyl content = 8.75% mol/mol); (\blacksquare) PEE-PPG-725 ($M_n = 4530\text{ g/mol}$, $M_w = 8430\text{ g/mol}$; carbonyl content = 14.3% mol/mol).

conditions (Table 2; 180 bar, $25\text{ }^{\circ}\text{C}$, CO_2 flow rate = 1 mL/min, total CO_2 volume = 420 mL = 1680 mL/g polymer). The PEC sample with 12.4% mol/mol carbonate (PEC-PPG-425) was found to be the most soluble in CO_2 , although again only up to modest molecular weights (<10 000 g/mol). The PEC sample with lower carbonate content (PEC-PPG-725, 8.75% mol/mol) was significantly less soluble, despite having a similar molecular weight. Our new PEE material (PEE-PPG-725) appeared to be much less soluble than the PEC sample with comparable carbonyl incorporation (PEC-PPG-425) and slightly more soluble than the PEC sample with lower carbonyl content (PEC-PPG-725), although this latter difference may not be significant within the accuracy of the experiments. These data suggest that either the ester unit itself or the periodicity of the ester units along the polymer chain was less effective in solubilizing the PEE in CO_2 in comparison with the carbonate units in the PEC materials.

Comparison of Solubility with Statistical Polypropylene Oxide- CO_2 Copolymers. Taken as a whole, these results suggest that our PEC and PEE materials are significantly less soluble in CO_2 than the PECs reported by Beckman.¹⁵ For example, a 250-repeat-unit copolymer of propylene oxide and CO_2 ($M_n \approx 16\text{ }000\text{ g/mol}$) with 15.4% mol/mol carbonate incorporation was shown to exhibit a miscibility pressure of 122 bar ($\sim 1800\text{ psi}$) at 0.8 wt %.¹⁵ Our most closely analogous sample (PEC-PPG-425, 12.4% mol/mol carbonate, $M_n = 3680\text{ g/mol}$, $M_w = 7800\text{ g/mol}$, ~ 60 repeat units) was not fully miscible with CO_2 up to pressures of 375 bar. A fractionated sample of PEC-PPG-425 ($M_w = 5670\text{ g/mol}$, ~ 50 repeat units) exhibited a cloud point pressure (Figure 2) that was almost twice as high as that observed for Beckman’s material.¹⁵

Extraction studies support this conclusion; for example, PEC-PPG-425 ($M_n = 4600\text{ g/mol}$, $M_w = 8740\text{ g/mol}$) was found to be extracted by CO_2 up to around 70 wt % at 180 bar and $25\text{ }^{\circ}\text{C}$ (Figure 7) after flowing 1500 mL CO_2/g polymer, but further extraction of the higher molecular weight species (>10 000 g/mol) appeared to be extremely slow at this pressure. We attempted to estimate the limit of solubility for these

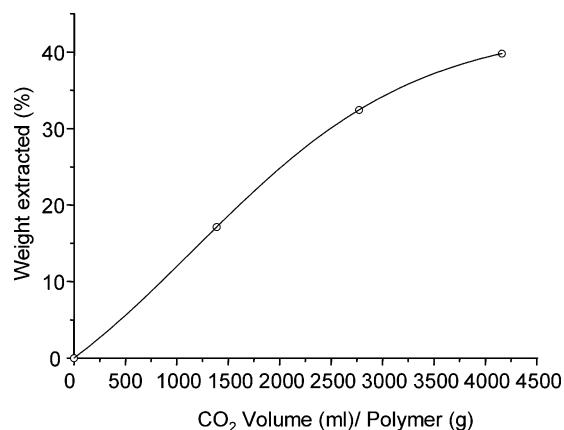


Figure 8. Plot of weight extracted vs CO₂ volume for second extended extraction of sample PEC-PPG-425 (0.1442 g, M_w = 13 080 g/mol; M_n = 10 920 g/mol before second extraction).

PEC materials by carrying out more prolonged extraction experiments. A portion (0.1442 g) of a PEC-PPG-425 sample which had already been extracted at 100 bar (1200 mL CO₂/g polymer; M_w and M_n after extraction = 13 080 g/mol and 10 920 g/mol, respectively) was placed again in the extraction vessel and submitted to further prolonged extraction at 300 bar (4200 mL CO₂/g polymer). This additional extraction led to a further weight loss of 0.0574 g (40 wt %, Figure 8). This corresponds, for the additional period, to a very low average extraction rate of around 0.014 mg polymer/mL CO₂. Moreover, the M_w values for the fractions collected during this extended period were found to be lower than 9000 g/mol, suggesting that even prolonged extraction did not lead to solubilization of the higher M_w species (> 10 000 g/mol). M_w and M_n for the residue at the end of the extraction were found to be 16 410 g/mol and 13 650 g/mol, respectively.

Very few of the extraction experiments that we have carried out have shown an extracted fraction with M_w greater than ~10 000 g/mol (see for example Figure 5), even after long periods of extraction at elevated CO₂ pressures. In most cases, the final residue in the extraction vessel had M_w of > 10 000 g/mol (Figures 3 and 4). All of our data are consistent with the conclusion that these PEC and PEE materials are moderately soluble in CO₂ up to around 10 000 g/mol but that the solubility is very low above this molecular weight threshold.

The carbonyl content in our PEC-PPG-425 sample (12.4% mol/mol) was slightly lower than that reported in Beckman's study (15.4% mol/mol),¹⁵ but it would be surprising if this alone could account for such large differences in phase behavior, despite the fact that both this study and Beckman's^{15,16} suggest that the percentage carbonyl incorporation does indeed affect solubility significantly.

It could be argued that our materials are less soluble in CO₂ because the molecular weights are lower and that unfavorable effects arising from the hydroxyl end groups²⁵ become more pronounced at lower molecular weights. This explanation would seem unlikely on both thermodynamic and kinetic grounds: first because the cloud point for PEC-PPG-425 increases steadily with molecular weight (Figure 2) and second because the lower molecular weight species were invariably extracted earlier in the gravimetric extraction experiments (Figure 5c).

A more likely explanation for the differences observed is perhaps the microstructure of the materials. Beckman's materials were statistical copolymers,^{15,16} while our new polymers have a more regular, alternating structure that is imposed by the step growth mechanism. The microstructure in our polymers is not perfectly regular and periodic because the PPG diols themselves have a (narrow) distribution of molecular weights (M_w/M_n = 1.04 for both PPG-425 and PPG-725). Nonetheless, the distribution of the carbonate groups along the polymer backbone in our PECs is likely to be more ordered than in Beckman's materials, and this may account for the large difference in phase behavior that is observed, for example, by promoting increased self-interaction in the polymer.

Conclusions

This study has shown that it is possible to synthesize potential CO₂-philes via a step growth mechanism rather than by the various chain growth routes reported previously.^{1,2,15,16} Two important conclusions may be drawn. First, to understand fully the phase behavior of these materials in CO₂, it is useful to perform complementary gravimetric studies in addition to cloud point measurements. This is particularly helpful in the case of polymers with broad molecular weight distributions (> 1.5) and which may contain higher molecular weight fractions that are significantly less soluble than the bulk material. Second, our results suggest that the PEC and PEE samples synthesized by step growth polymerization are soluble in CO₂ at moderately high pressures (> 150 bar), but only up to modest molecular weights. Our combined data suggest that the solubility in CO₂ for these materials is very low for M_w > 10 000 g/mol; that is, these materials are considerably less soluble at comparable molecular weights than fluorinated polyacrylate^{2,3} and perfluoropolyether⁹ materials reported previously. The apparent low solubility of these materials in comparison with statistical CO₂-propylene oxide copolymers^{15,16} highlights the importance, as noted by others,²⁵ of considering not only molecular composition but also topology when designing polymeric CO₂-philes. Nevertheless, the synthetic approach described here has a number of potential advantages for the discovery of CO₂-soluble polymers. For example, we envisage a combinatorial strategy^{26,27} to produce diverse, well-defined libraries of carbonyl-containing copolymers with heteroatoms in the backbone structure. We propose to combine this approach with rapid solubility screening²⁸ in order to facilitate the "high-throughput" discovery of novel, inexpensive CO₂-philes.

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