Synthesis of CO_2-Soluble Poly(ether carbonate)s and Poly(ether ester)s by Step Growth Polymerization

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Abstract: In this paper, 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 CO_2 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 is more easily interpreted in combination with a quantitative gravimetric extraction method that we have developed. It was found that the CO_2 solubility of the PEC and PEE samples was strongly affected by both the polymer molecular weight and also by the chemical structure.

Key words: Poly(ether carbonate); poly(ether ester); supercritical fluids; carbon dioxide

INTRODUCTION

Supercritical carbon dioxide ($scCO_2$) is an inexpensive, non-toxic, and non-flammable solvent for chemical processes such as synthesis,[1] polymerization,[2,3] catalysis,[4,5] and extraction.[6] Until recently, the only polymers found to have significant solubility in CO_2 under moderate conditions (<100ºC, <400 bar) were amorphous fluoropolymers and to a lesser extent polysiloxanes.[7,8] A number of research groups have synthesised 'CO_2-philic' fluoropolymers or silicone-based materials for use as steric stabilisers in dispersion polymerization,[9-15] as phase transfer agents for liquid–liquid extraction,[16] as supports for homogeneous catalysis,[17,18] and as surfactants for the formation of water / CO_2 emulsions and microemulsions.[19-21] Unfortunately, the cost of these surfactants is usually very high, which may prohibit their use on an industrial scale for many applications. Fluoropolymers also have poor environmental degradability, and this could negate the environmental advantages associated with the use of $scCO_2$.

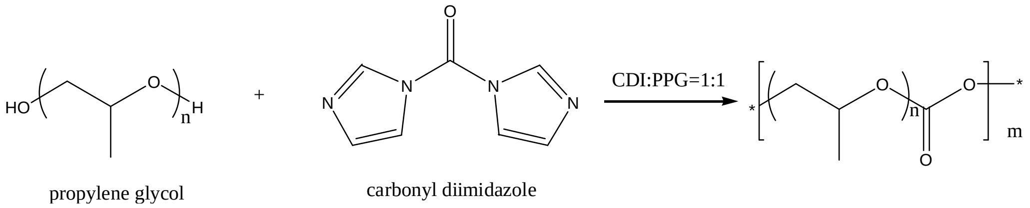
Recently, Beckman and co-workers reported that certain poly(ether carbonate) (PEC) copolymers are reasonably soluble in CO_2 under moderate conditions.[22,23] Beckman's hydrocarbon systems involve PECs synthesized by aluminium-catalysed copolymerization of cyclic ethers with CO_2 (*i.e.*, M_1 = ethylene oxide, propylene oxide, cyclohexene oxide; $M_2 = CO_2$). These copolymers were found to be soluble in liquid CO_2 at concentrations of 0.2–1.5% w/v at ambient temperatures and moderate pressures (120–160 bar; *i.e.*, significantly above the liquid vapour pressure for CO_2). The reported materials were all statistical copolymers which were generated from very inexpensive feed-stocks.

Step growth polymerization is a method that can be used to synthesize polymers with very well-defined chemical compositions; indeed, unlike most non-ideal statistical chain growth polymerizations, the composition of the polymer exactly mirrors 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 CO_2-philes.

RESULTS AND DISCUSSION

Synthesis of Poly(ether carbonate)s by Step-Growth Polymerization

A series of poly(ether carbonate)s was synthesized by condensation of oligomeric poly(propylene glycol) (PPG) diols with carbonyl diimidazole, as described in Scheme 1:

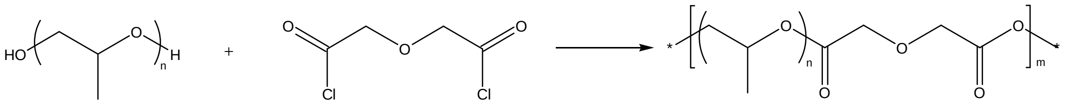


Scheme 1: Synthesis of poly(ether carbonate) by step growth polymerization

By using step growth polymerization, it is relatively easy to control the composition (*i.e.*, carbonate content) of the final products since it is defined by the alternating structure 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). Since these are step growth polymers, it is possible to estimate the percentage carbonate incorporation by knowing the average molecular weight of the PPG 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 (using the supplier's values for the molecular weights of the diols). The structure of both polymers was also analyzed by ^{1}H NMR in order to confirm the percentage carbonate incorporation. It was found that the carbonate incorporations were 12.5 % mol/mol and 8.75 % mol/mol, respectively, for the two materials.

Synthesis of Poly(ether ester)s by Step-Growth Polymerization

Poly(ether ester)s were synthesized by step growth polymerization of PPG-diols and diacrylol chlorides (Scheme 2). The resulting polyesters had broadly similar structure to the PEC materials (*i.e.*, a polyether backbone punctuated at regular intervals with carbonyl groups).



Scheme 2: Synthesis of poly(ether ester) by step growth polymerization

Cloud Point Observations in CO_2

PEC-PPG-425, 12.5 % 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 wt. %, it was observed that the material did not dissolve completely, even at low temperatures (35°C) and high pressures (5000 psi). At a lower concentration (0.173%), the sample was fully soluble at 35°C and 3820 psi, but could not be solubilized completely at temperatures above 45°C at pressures within the safe range for the equipment (< 5500 psi). In Beckman's studies,[22] a 250-repeat-unit copolymer of PO and CO_2 (M_n ~ 16,000 g/mol) with 15.4% mol/mol carbonate incorporation was reported to exhibit a lower miscibility pressures (~1800 psi) at a higher concentration (0.8 wt %) than used in our studies. It should be noted, however, that Beckman's materials were statistical copolymers, while our new polymers have a more regular, alternating structure that may influence the solubility.[24]

PEC-PPG-725, 8.75 % mol/mol carbonate, M_n = 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 (see above), this material did not dissolve fully in CO_2 even at low concentrations (0.193%) and high CO_2 densities (*e.g.*, 25°C, 5000 psi), and it proved impossible to form a single, homogeneous phase. This is in agreement with Beckman's observation that the solubility of PEC materials is strongly dependent on level of carbonate incorporation.[22,23]

Since neither of the 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 was thus obtained. Figure 1 shows the relationship between cloud point pressure and molecule weight for three of these fractions. It is clear that the cloud point pressure increases significantly as the molecular weight of the sample is increased, even over a relatively small molecular weight range (3780–5670 g/mol).

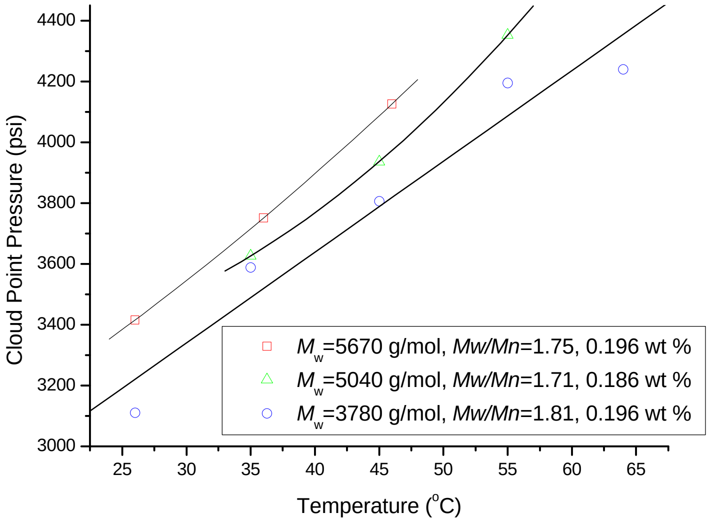


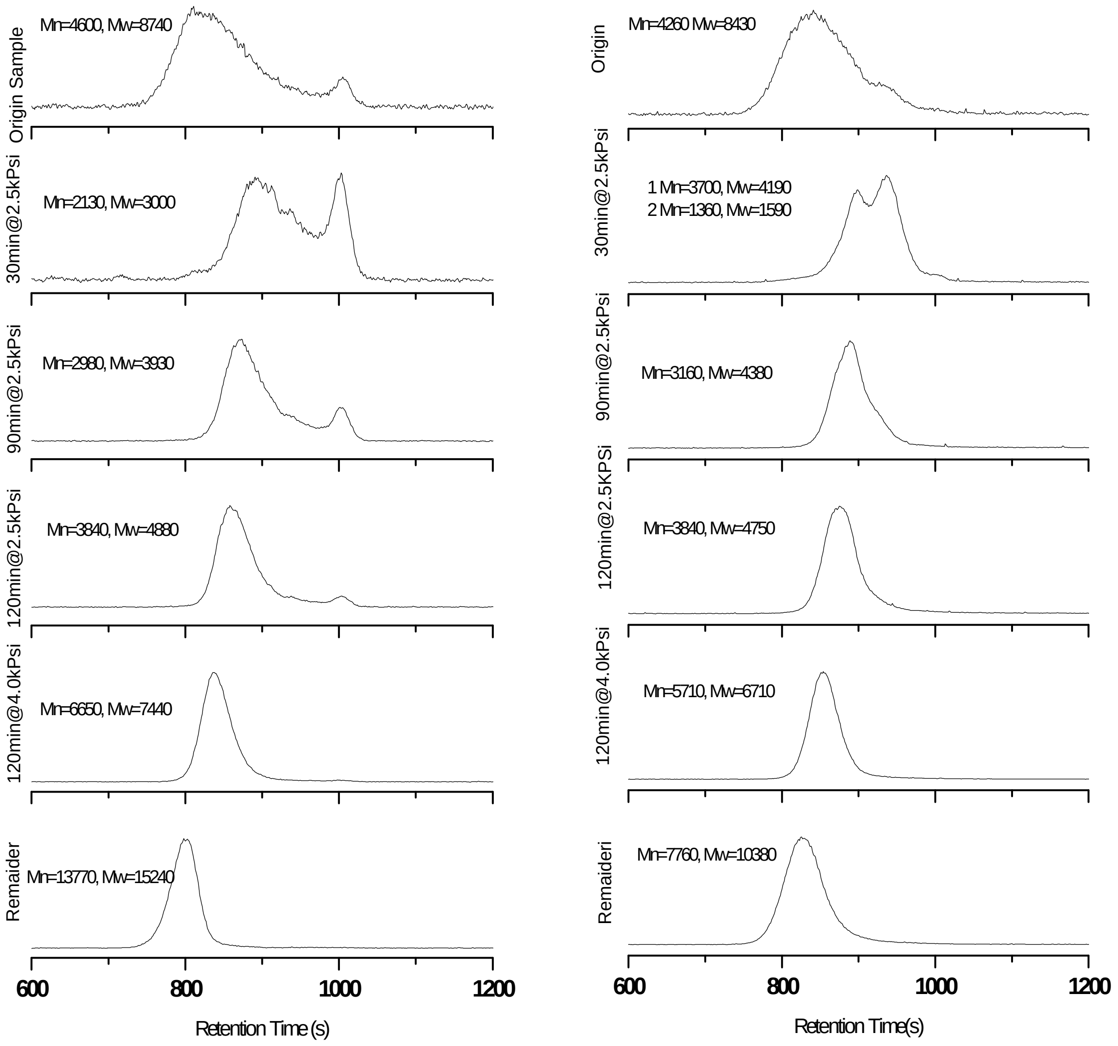
Figure 1: Cloud point curves for fractionated PEC-PPG-425 with three different molecule weights

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 ~ 2), it is not clear that cloud point measurements alone will lead to a full description of solubility profiles for these materials in CO_2. A significant weight fraction of these samples appears to be insoluble in CO_2 over the measurable pressure range for our equipment. As such, we have coupled these cloud point observations with a series of gravimetric extraction tests.

Gravimetric Extraction Method

The polymer was placed into a pressure vessel and CO_2 was flowed through the vessel at a constant pressure. The various extracts (and the residue in the reactor at the end of the extraction process) were analyzed by GPC. Figure 2a shows the molecular weight distributions for a PEC-PPG-425 sample (12.5 % mol/mol carbonate) before extraction (top) and the residue after extraction (bottom). The other GPC traces were recorded for the fractions collected during extraction at increasing CO_2 pressure. The first fraction to be collected (30 min CO_2 flow at 2500 psi) had a much 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 2500 psi led to further fractions of somewhat higher M_n (up to 3840 g/mol) with smaller amounts of material being extracted as the extraction proceeded. After around 120 min at 2500 psi, 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 4000 psi for 120 min, whereupon a further 19.6% of the sample mass was recovered with a significantly higher M_n (6650 g/mol) than the material extracted at 2500 psi.

A 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 much higher molecular weight than the starting material (M_n = 13,770 g/mol, M_w = 15,240 g/mol, see Fig. 2a, bottom GPC trace). In order to verify that the remaining polymer had the same chemical composition as that of original sample, the structure of the remainder was analyzed by ^{1}H NMR and found to have identical composition to the original sample (12.5 % mol/mol carbonate). Taken together, these data suggest that this polymer is moderately soluble in CO_2 at low molecular weights, but has very limited solubility in CO_2 at M_n > 10,000 g/mol at 25°C and pressures up to 4000 psi.



a. PEC-PPG-425 **b. PEE-PPG-725**

Figure 2: Change in M. Wt. of PEC and PEE before and after extraction by CO_2 at 25°C

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) was extracted in the same fashion (see Fig. 2b & Table 2). The general trends were very similar; the lower molecular weight oligomers were extracted first, and then higher molecular weight species were extracted at higher pressures. Again, a residue was left in the extraction vessel which had higher molecular weight (and narrower molecular weight distribution) than the starting material. A significantly higher percentage of the PEE remained after extraction (55.1 %) compared with the PEC sample (24.5 %). The molecular weight of the PEE remainder was also closer to that of the starting material and the molecular weight distribution was broader. All of these facts suggest that the PEE sample was less soluble in CO_2 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 Fig. 2.

Table 1: Characterization data for PEC and PEE fractions collected by SFE

	PEC				**PEE**			
	M_n	M_w	M_w/M_n	Wt. %	M_n	M_w	M_w/M_n	Wt. %
Origin Sample	4600	8740	1.90	–	4530	8430	1.98	–
30 min @ 2.5kPsi	2130	3000	1.40	33.9	3700 1360	4190 1590	1.13 1.17	18.7
90 min @ 2.5kPsi	2980	3930	1.32	16.0	3160	3880	1.23	8.7
120 min @ 2.5kPsi	3840	4870	1.27	6.0	3840	4750	1.27	7.8
120 min @ 4.0kPsi	6640	7440	1.12	19.6	5710	6710	1.18	9.7
Remainder	13700	15240	1.11	24.5	7760	10380	1.34	55.1

Effect of CO_2 Pressure

In order to evaluate the effect of extraction pressure, the method was adapted to use a syringe pump such that precise volumes of CO_2 could be delivered at controlled flow rates. It was thus possible to carry out strictly comparable experiments where the only variable was the CO_2 pressure.

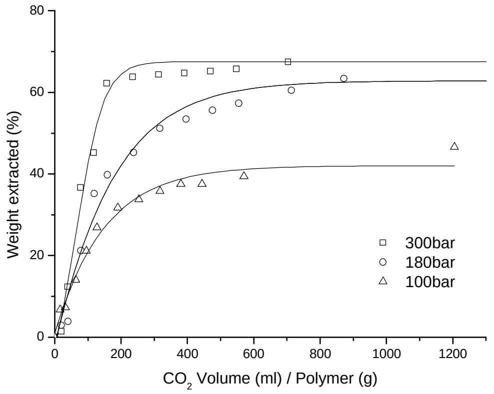


Figure 3: Weight percentage of PEC extracted at different pressures

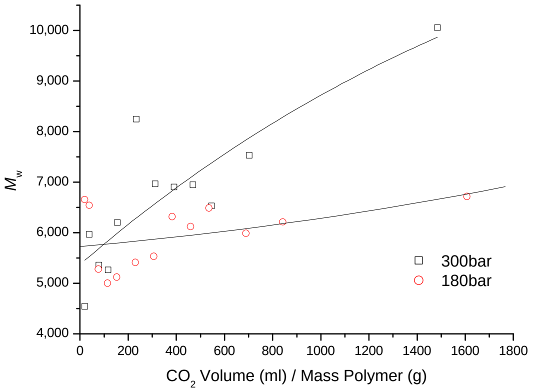


Figure 4: M_w (g/mol) of PEC-PPG-425 fractions extracted at two different CO_2 pressures

Figure 3 shows the weight percentage of PEC-PPG-425 (M_n = 4600 g/mol, M_w = 8743 g/mol) extracted as a function of the CO_2 volume passed through the vessel at three different CO_2 pressures (flow rate = 1.0 ml/min in all cases, mass of sample = 0.25 g). At all three pressures, the initial extraction rate is quite high and 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 CO_2 density. Figure 4 plots M_w for the recovered PEC extracts against the volume of

CO_2 flowed through the vessel (normalized to the unit mass of starting material in the vessel). While there is a large degree of scatter in this data, the overall trend is, again, that the lower molecular weight fraction tends to be extracted earlier in the process.

CONCLUSIONS

1) PEC and PEE materials may be synthesized by step growth polymerization to give materials with well-defined and controllable carbonyl incorporations.
2) The solubility of these materials in CO_2 is more fully understood by using a combination of cloud point measurements and gravimetric extraction experiments.
3) PEC and PEE materials synthesized by this route have moderate solubility in CO_2 up to modest molecular weights (< 10,000 g/mol), but the data suggests that, at higher degrees of polymerization, the polymers are not nearly as soluble in CO_2 as amorphous fluoropolymers such as PFOA.[7]

ACKNOWLEDGEMENTS

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[24] The PPG-diols themselves have a distribution of molecular weights; as such, the spacing of the

carbonate units along the polymer chain is not expected to be completely uniform.