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ARTICLE

Synthesis and Phase Behavior of CO_2-Soluble Hydrocarbon Copolymer: Poly(vinyl acetate-*alt*-dibutyl maleate)

Hyunsuk Lee, Ji Won Pack, Wenxin Wang,† Kristofer J. Thurecht,‡ and Steven M. Howdle*

School of Chemistry, University of Nottingham, Nottingham NG7 2RD, United Kingdom. †Current address: Network of Excellence for Functional Biomaterials, Department of Mechanical and Biomedical Engineering, National University of Ireland, Galway, Ireland. ‡Current address: Australian Institute for Bioengineering and Nanotechnology and Centre for Magnetic Resonance, The University of Queensland, St. Lucia, QLD 4072, Australia.

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ABSTRACT: We report the synthesis of a new hydrocarbon copolymer which is soluble in supercritical carbon dioxide. Poly(vinyl acetate-*alt*-dibutyl maleate) (PVAc-*alt*-PDBM) copolymer was synthesized by free-radical polymerization mediated by the RAFT technique. Liquid CO_2 extraction was performed to remove the residual monomer and solvent from the final product. The solubility of the copolymers was measured in a variable volume view cell at temperatures between 25 and 75 °C. The phase behavior of the copolymer in CO_2 was studied in terms of its molecular weight and concentration in the solvent. It was found that the copolymer shows good solubility in CO_2 approaching that of perfluoropolyether (PFPE) and poly(dimethylsiloxane) monomethacrylate (PDMS-mMA).

Introduction

The chemical industry has become increasingly aware of environmental issues over the use of volatile organic solvents in the manufacture of commercial polymer products. As a result of these environmental concerns, supercritical carbon dioxide ($scCO_2$) has emerged as a more environmentally friendly alternative to traditional solvents. Particularly, the use of $scCO_2$ as a polymerization medium has attracted much attention during the past decade.[1−6] However, the inherent insolubility of most polymers in CO_2 makes it critical to develop suitable surfactants that can stabilize the growing particles in CO_2. The major hurdle in the design of new CO_2 soluble stabilizers is to find high molecular weight polymers which have good CO_2-philicity. Fluorinated polymers show high solubility in CO_2 and have been extensively used as dispersing agents.[2,7−11] They have been synthesized with various types of topology, and their stabilizing ability has been broadly investigated in dispersion polymerization conducted in CO_2. A reactive silicone (methacrylate-terminated polydimethylsiloxane, PDMS-mMA) was also employed as a stabilizer in the polymerization of MMA in $scCO_2$. However, the use of fluorinated and/or siloxane polymers to prepare CO_2-philic stabilizers is relatively expensive.[12] Ultimately, stabilizers containing fluorine and silicone are not likely to be applied industrially. Therefore, the design and development of a CO_2-soluble hydrocarbon polymer with solubility comparable to that of fluorocarbons would allow production of much less expensive surfactants than their fluorinated counterparts.[13] It is suggested that the identification of highly CO_2 soluble polymers composed of only carbon, hydrogen, and oxygen could facilitate the design of safe, inexpensive, environmentally benign "CO_2-philes" and therefore enhance the performance and commercial success of CO_2-based technologies.[14]

In 2000, Beckman and co-workers synthesized highly CO_2-soluble ether−carbonate copolymers.[13] They showed that functionalization of polyethers with carbonyl groups in the side chain or incorporation of carbonyls into the backbone significantly lowers the cloud point pressures of such polyethers in CO_2. It was suggested that, by choosing the appropriate amount of carbonyl incorporation, they could generate propylene oxide−CO_2 copolymers that exhibit lower miscibility pressures than fluoroethers with the same number of repeat units. In 2002, they examined the effect of polyether structure on resultant phase behavior in CO_2 and found that the carbonyl oxygen, if placed in an accessible position, enhances the solubility of polymers in carbon dioxide through Lewis acid−Lewis base interactions.[14] In 2005, Cooper and colleagues introduced step growth polymerization routes to synthesize poly(ether carbonate) (PEC) and poly(ether ester) (PEE) materials as potential inexpensive hydrocarbon CO_2-philes.[15] Their results showed that the PEC and PEE materials prepared were soluble in CO_2 at moderately high pressure, but only up to modest molecular weights. Various other recent studies have investigated the solubility of hydrocarbon surfactants,[16−18] including the effect of end-groups on their solubility.[19,20]

Poly(vinyl acetate) (PVAc) has been recognized as one of the most CO_2-philic hydrocarbon materials.[21,22] It was reported that PVAc exhibits remarkable CO_2 solubility over a wide range of concentrations (∼15 wt %) and molecular weights (∼6800 repeat units) at 298 K and pressures ranging from 13.6 to 67.6 MPa. The highly CO_2-philic nature of PVAc is attributed to the favorable specific interaction between CO_2 and the acetate groups in PVAc. *Ab initio* molecular orbital calculations also indicated that the interactions between the carbonyl moieties of acetate functional groups and CO_2 are almost half as strong as the hydrogen bond interaction in a water dimer.[23] This specific interaction between CO_2 and carbonyl groups has been confirmed by IR spectroscopic studies.[24] In addition, it has been shown that a weak, but cooperative, C−H···O hydrogen bond, involving the hydrogen atom in the methyl group in the side chain of PVAc and one of the oxygen atoms in CO_2, reinforces the Lewis acid−Lewis base interactions.[25] In this study, we have synthesized a new PVAc-based

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*Corresponding author: e-mail Steve.howdle@nottingham.ac.uk; Ph +44 0115 9513486.

CO_2 soluble hydrocarbon copolymer by free radical polymerization and by RAFT. The phase behavior of the copolymer was observed, and its solubility in CO_2 was compared to that of commercially available fluorinated and siloxane polymers.

Experimental Section

Materials. Vinyl acetate (VAc, 99.9%, Fluka), dibutyl maleate (DBM, 96%, Aldrich), and high-purity carbon dioxide (SFC grade, BOC gases) were used as received. 2,2′-Azobis(isobutyronitrile) (AIBN, Fisher Chemicals) was purified via recrystallization from methanol before use. Tetrahydrofuran (THF, HPLC grade), isopropyl alcohol (IPA), toluene, and benzene were purchased from Fisher Scientific and used without further purification.

Synthesis of Poly(vinyl acetate-*alt*-dibutyl maleate). Poly(vinyl acetate-*alt*-dibutyl maleate) (PVAc-*alt*-PDBM) copolymer was synthesized by free radical polymerization in organic solvent and by RAFT polymerization using xanthate in bulk. For the free radical polymerization, equimolar amounts of vinyl acetate (VAc) and dibutyl maleate (DBM) were added to a 100 mL round-bottom flask followed by AIBN (1.0 wt % based on the total weight of monomer). The monomer mixture was then dissolved in 20 mL of either IPA, toluene, or benzene. The mixture was then degassed with argon for 10 min and heated up to 70 °C. The polymerization was left to proceed for 24 h with stirring and then cooled down to room temperature. For the RAFT polymerization, the reaction was carried out in bulk with a desired amount of xanthate at 60 °C for 48 h.

Purification. After the polymerization, the final solution was poured into a 60 mL high-pressure autoclave, which was then sealed. Liquid CO_2 was then introduced into the autoclave to a final pressure of 1500 psi (10.34 MPa). The liquid CO_2 was then allowed to gently flow through the autoclave while maintaining a pressure of 1500 psi with a flow rate of 10 mL/min over a period of 6 h. The purification process was monitored every 2 h by ^1H NMR.

Characterization Techniques. The monomer conversion and copolymer composition were calculated from ^1H NMR spectra which were recorded in $CDCl_3$ using a Bruker DPX-300 spectrometer. Molecular weight and molecular weight distribution of polymers were obtained by gel permeation chromatography (PL-120, Polymer Laboratories) with an RI detector. The columns (30 cm PLgel Mixed-C, 2 in series) were eluted by THF and calibrated with polystyrene standards. All calibration and analysis was performed at 40 °C and at a flow rate of 1 mL/min. MALDI-TOF MS was employed to analyze the end-groups of the polymer chains which were polymerized by the RAFT technique.

Solubility Measurement in CO_2. The cloud point curves were obtained using the hydraulic variable volume view cell which has been described previously.[26] In a typical experiment, an accurate amount of polymer was weighed by difference into the main chamber of the cell along with a magnetic stirrer, and the cell was sealed. CO_2 (~20.0 g) was transferred into the main chamber of the cell from a high-pressure stainless steel bomb. The exact composition (wt/wt %) of polymer/CO_2 was calculated using the weight of CO_2 and polymer added to the cell. The system was then heated to the desired temperature (25−75 °C) and was left to equilibrate for 30 min. At a particular temperature, the volume of the view cell was steadily decreased to compress the CO_2 phase to higher pressure and density without altering chemical composition of the mixture until a homogeneous mixture is obtained. The cloud point was observed by slowly lowering the pressure inside the cell. The cloud point pressure was taken as the point at which it was no longer possible to see the three LED lamps behind the view cell through the CO_2/polymer mixture. At a particular temperature, the average of the three repeated measurements was recorded as the cloud point pressure.

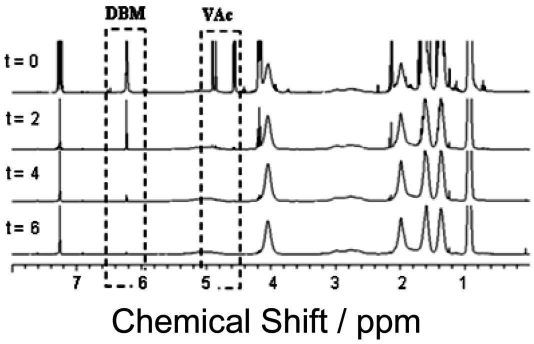

Figure 1. ^1H NMR spectra of PVAc-*alt*-PDBM during liquid CO_2 extraction over a period of 6 h. The low molecular weight VAc monomer was first extracted out, and then DBM monomer was also almost completely removed after 6 h.

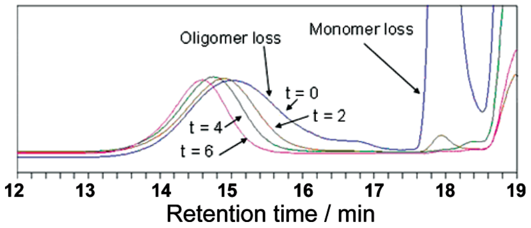

Figure 2. GPC traces of PVAc-*alt*-PDBM during the liquid CO_2 extraction over a period of 6 h. VAc monomers and oligomers are gradually removed as the extraction proceeds.

Results and Discussion

Synthesis of PVAc-*alt*-PDBM Copolymer by Free-Radical Polymerization. The PVAc-*alt*-PDBM copolymers were first synthesized by free radical copolymerization at 70 °C for 24 h using AIBN as initiator in IPA, toluene, and benzene. In the purification of the final product, a problem was encountered. While the solvents (THF, IPA) were easily removed from the final solution using rotary evaporator under reduced pressure, the unreacted monomers were not completely removed. This is due to the high boiling point of dibutyl maleate monomer (bp = 276 °C). The use of antisolvent to separate polymers from monomers was not successful either. When the final solution was poured dropwise into a large excess of hexane (as antisolvent), the polymer solution settled to the bottom of the flask as viscous droplets rather than as a powder. This is ascribed to the low molecular weight of the polymers and also possibly to their partial solubility even in hexane.

In order to overcome this difficulty in purification, liquid CO_2 was used to dissolve and extract the residual monomers. This method is based on the fact that most vinyl monomers are soluble in liquid CO_2, but their polymers are not.[20,27] After the polymerization, the final product was purified by liquid CO_2 extraction and the extraction was monitored by ^1H NMR. VAc monomer was extracted out first, and after 6 h the less soluble DBM monomer was also almost completely removed (Figure 1).

The molecular weight of PVAc-*alt*-PDBM increased from 2400 to 3800 g/mol through extraction, and the PDI narrowed from 1.39 to 1.26, indicating that that low molecular weight oligomers were also removed along with residual monomers. This led to a narrower molecular weight distribution of polymer, which was manifest in a more well-defined cloud point. The GPC traces at each interval demonstrate that the VAc monomers and oligomers are gradually removed as the extraction proceeds (Figure 2).

Table 1. Synthesis of PVAc-*alt*-PDBM by Free Radical Copolymerization

sample[a]	[VAc]/[DBM][b]	AIBN (wt %)	solvent	C_s[c] ($\times 10^4$)	conversion[d]	PVAc:PDBM[d]	M_n[e] (g/mol)	PDI[e]
F1	1	1.0	IPA	44.6	0.47	52:48	3800	1.3
F2	1	1.0	IPA	44.6	0.52	51:49	7000	1.2
F3	1	1.0	toluene	21.1	0.48	43:57	10 700	1.5
F4	1	1.0	benzene	5.27	0.79	51:49	15 400	1.6

[a] The polymerization was conducted at 70 °C for 24 h with stirring. [b] The two monomers were used in equimolar feed ratio. [c] The chain transfer constant to the solvent.[28] [d] Calculated from ^{1}H NMR spectrum recorded in $CDCl_3$. [e] Measured by GPC in THF against PS standards.

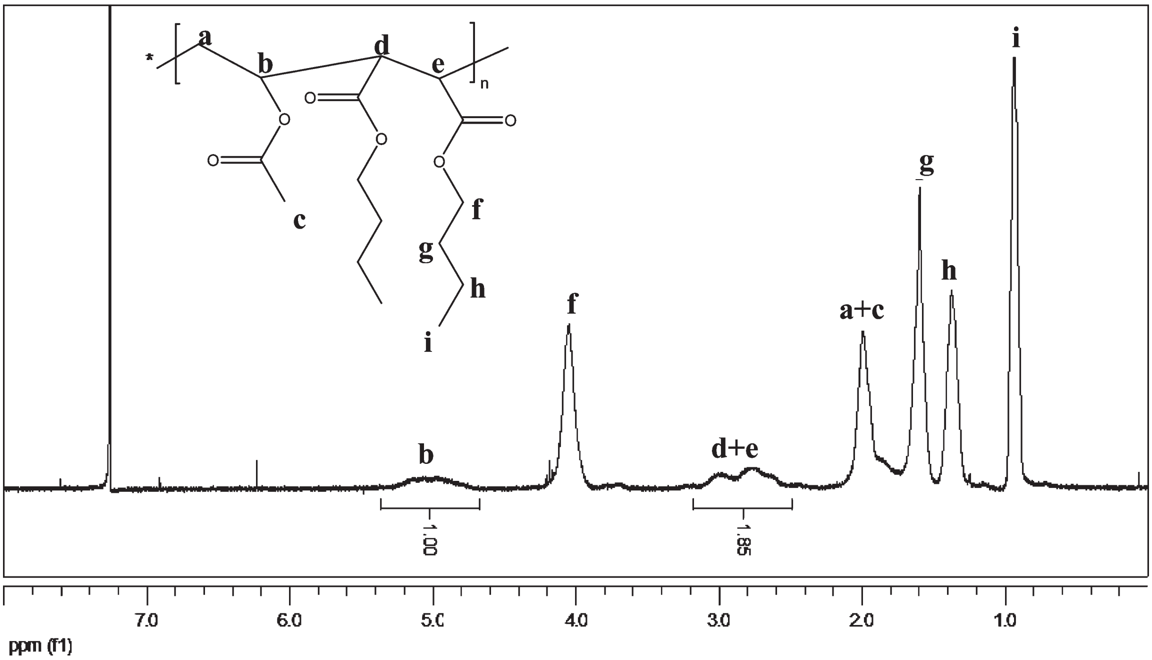

Figure 3. ^{1}H NMR spectrum for a purified PVAc-*alt*-PDBM copolymer. PVAc:PDBM = b:(d + e)/2 = 1:1.85/2 = 1:0.95 = 51:49.

The characteristics of the final copolymer products after purification are summarized in Table 1. The molecular weight (M_n) of PVAc-*alt*-PDBM synthesized in IPA ranges from 3800 to 7000 g/mol, and the monomer conversion was lower than 52%. Poor control over the molecular weights is typical for free radical polymerization. When toluene and benzene were used as solvents, the molecular weight increased up to 21 400 g/mol. This is attributed to the difference in chain transfer constant of vinyl acetate to each solvent. The higher the chain transfer constant to solvent, the lower the molecular weight of the polymer.

This PVAc-*alt*-PDBM copolymer was anticipated to form an alternating structure because maleate esters tend to undergo negligible homopolymerization because of structural hindrance. In addition, the reactivity ratios of this pair are assumed to be very similar to those for VAc and diethyl maleate (DEM), for which r_1(VAc) is 0.17 and r_2(DEM) is 0.043, and the product r_1r_2 is 0.007, suggesting an alternating structure.[29]

The ^{1}H NMR spectrum of PVAc-*alt*-PDBM shows that the final copolymer is free of monomer and solvent residue (within the detection limits of ^{1}H NMR) after purification by CO_2 extraction (Figure 3). ^{13}C NMR of the copolymer was also examined to detect for VAc homopolymer (Figure 4).

A comparison with homopolymer shows that peaks a and b for the PVAc homopolymer (spectrum A in Figure 4) are shifted to a′ and b′ because of the different chemical environment in the copolymer structure (spectrum B in Figure 4). No peaks for PVAc homopolymer were found in ^{13}C NMR of PVAc-*alt*-PDBM copolymer indicating that any PVAc homopolymer blocks are likely very short and the concentration of such blocks is not significantly high. Thus, the data support the underlying hypothesis based on monomer reactivity ratios, that an alternating polymer architecture of PVAc-*alt*-PDBM copolymer (∼ABABABABAB∼) predominates.

Synthesis of PVAc-*alt*-PDBM Copolymer via RAFT Technique. Free-radical polymerization in different solvents with different chain transfer constants (C_s) allowed for the synthesis of a series of PVAc-*alt*-PDBM copolymers having various molecular weights. However, it was still difficult to synthesize low molecular weight ($M_n < 10\,000$ g/mol) copolymers with good reproducibility via this free radical method. It is particularly important to prepare a series of low molecular weight copolymers having specifically targeted chain lengths for the phase behavior study because high molecular weight copolymers ($M_n > 10\,000$ g/mol) were found to show limited solubility in $scCO_2$ and were also very difficult to purify. For this reason, we extended our study to prepare PVAc-*alt*-PDBM copolymers using xanthate[30,31] as a RAFT agent to control the molecular weight and give narrow PDI.

The RAFT polymerizations of PVAc-*alt*-PDBM-X are summarized in Table 2. The molecular weights (M_n) of PVAc-*alt*-PDBM-X synthesized using different amounts of xanthate range from 2900 to 6400 g/mol. The PDI values (PDIs = 1.10−1.22) are lower than those of PVAc-*alt*-PDBM prepared by free radical polymerization (PDIs = 1.2−1.6), indicating that RAFT provides a well-controlled molecular weight distribution.

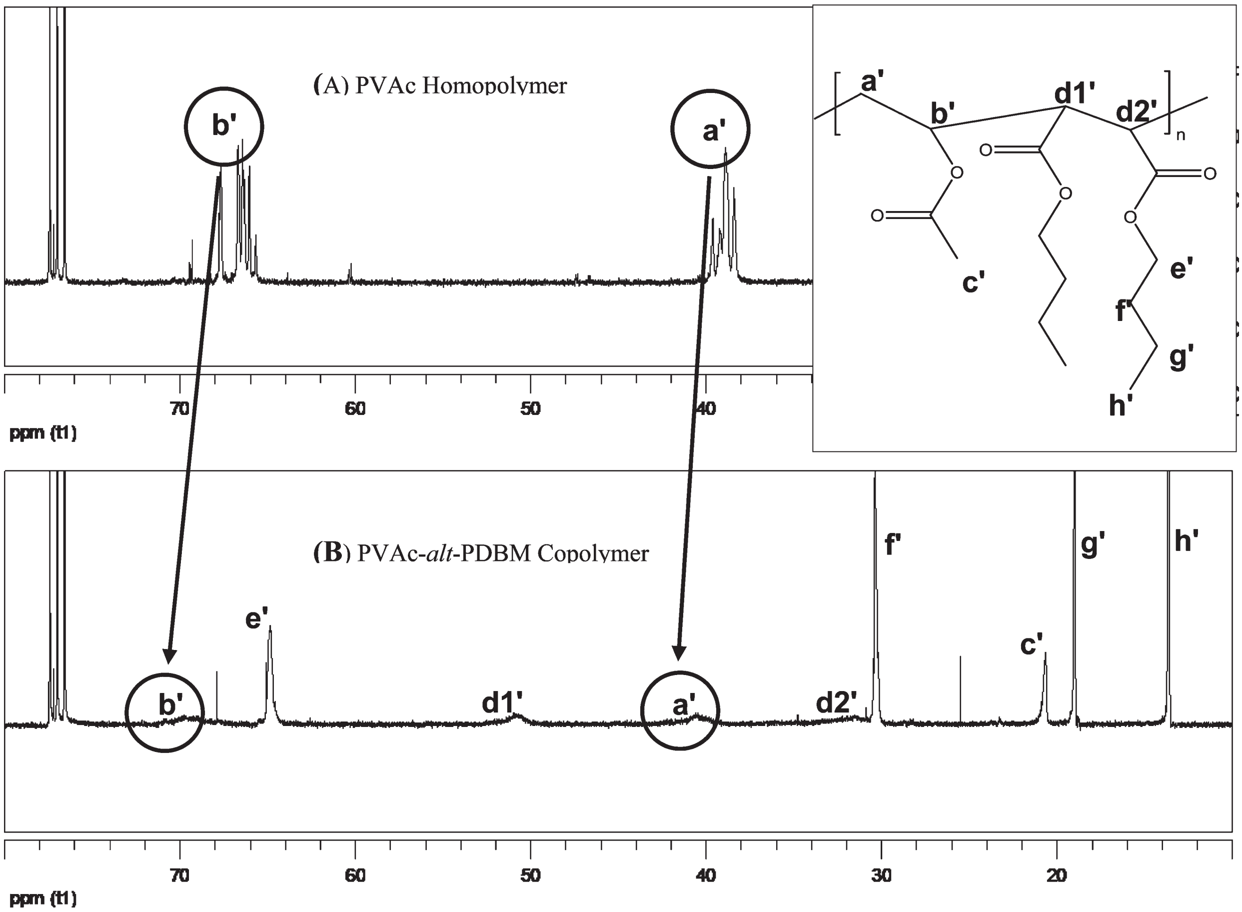

Figure 4. ^{13}C NMR spectra of (A) PVAc−homopolymer and (B) PVAc-*alt*-PDBM copolymer. The peaks a and b for PVAc homopolymer (A) have been shifted to a′ and b′ because of the different chemical environment in the copolymer structure (B). No peaks for PVAc homopolymer were found in ^{13}C NMR of PVAc-*alt*-PDBM copolymer.

Table 2. Synthesis of PVAc-*alt*-PDBM-X Copolymers Using Xanthate as a RAFT Agent

entry	[VAc]/[DBM]	M:R:I[a]	M_n[b] (g/mol)	M_w[b] (g/mol)	PDI[b]
R1	1	12:1:0.1	2900	3200	1.10
R2	1	24:1:0.1	3200	3600	1.12
R3	1	36:1:0.1	4200	5000	1.17
R4	1	48:1:0.1	5300	6300	1.18
R5	1	60:1:0.1	6400	7800	1.22

[a] M:R:I = monomer:RAFT (xanthate):initiator (AIBN). [b] Determined by GPC (THF as eluent).

This copolymer was analyzed by MALDI-TOF to determine that the RAFT agent (xanthate) was actually incorporated at the polymer chain end. The MALDI-TOF spectrum (Figure 5) for the PVAc-*alt*-PDBM-X (M_n = 3200 g/mol, PDI = 1.12) (entry R2, Table 2) shows that several series are present. In every series, the peaks are separated by 314.38 m/z, which is equivalent to one (VAc-DBM) unit. The four main series are separated by 86.09 m/z, which corresponds to the mass of VAc monomer.

The masses of the peaks obtained from the spectrum are in good agreement with the calculated values (Table 3), providing strong evidence for the coordination of xanthate on the end of each polymer chain. The existence of chains with additional VAc units (or very short blocks of VAc) is not entirely unexpected since VAc will always show some propensity to homopolymerize based on the reactivity ratios observed for DEM and VAc.[29]

Phase Behavior of PVAc-*alt*-PDBM in CO$_2$. The solubility of PVAc-*alt*-PDBM copolymers (M_n = 3800−21 400 g/mol)

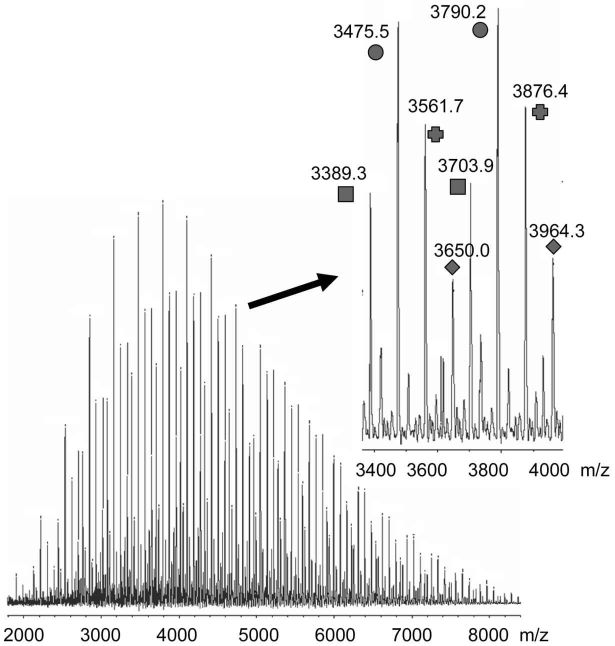

Figure 5. MALDI-TOF spectrum of PVAc-*alt*-PDBM-X (M_n = 3200 g/mol, PDI = 1.12) (entry R2, Table 2) measured with Na cation: (■) poly(VAc-DBM)-xanthate; (●) poly(VAc-DBM)-VAc-xanthate; (+) poly(VAc-DBM)-VAc-VAc-xanthate; (◆) poly(VAc-DBM)-VAc-VAc-VAc-xanthate. Each peak in the series is separated by 314.38 m/z, equivalent to one (VAc-DBM) unit.

synthesized by free radical method (entries F1−F5, Table 1) was first examined in pure CO_2. The cloud point curves measured are shown in Figure 6.

The low molecular weight samples PVAc-PDBM-3800 (F1) and PVAc-PDBM-7000 (F2) were found to fully dissolve in the CO_2 phase below 4300 psi within the temperature range 35−75 °C at a concentration of 0.2 wt %. The sample PVAc-PDBM-3800 exhibited comparatively high solubility in CO_2 with a miscibility pressure of 2640 psi (182 bar) at 35 °C. As expected, higher molecular weight PVAc-PDBM-7000 showed a higher cloud point pressure than PVAc-PDBM-3800.

The samples with molecular weights over 10 000 g/mol (entries F3−F5, Table 1) were not fully miscible with CO_2 within the safe working pressure (~6000 psi) of the variable volume view cell. Nonetheless, it is clear that incorporating the PDBM into PVAc significantly increased their solubility in CO_2 compared to PVAc homopolymer of a similar molecular weight.

Table 3. Comparison of Molecular Weights Calculated and Those Obtained from the MALDI-TOF Spectrum for PVAc-*alt*-PDBM-X (M_n = 3200 g/mol, PDI = 1.12) (Entry R2, Table 2)[a]

polymer chains	*m*/*z* (calculated)	*m*/*z* (detected)
poly(VAc-DBM)$_{10}$-xanthate + Na[b]	3389.1	3389.3
poly(VAc-DBM)$_{10}$-VAc-xanthate + Na	3475.2	3475.5
poly(VAc-DBM)$_{10}$-VAc-VAc-xanthate + Na	3561.3	3561.7
poly(VAc-DBM)$_{10}$-VAc-VAc-Vac-xanthate + Na	3649.4	3650.0
poly(VAc-DBM)$_{11}$-xanthate + Na	3703.5	3703.9
poly(VAc-DBM)$_{11}$-VAc-xanthate + Na	3789.6	3790.2
poly(VAc-DBM)$_{11}$-VAc-VAc-xanthate + Na	3875.7	3876.4
poly(VAc-DBM)$_{11}$-VAc-VAc-Vac-xanthate + Na	3963.8	3964.3

[a] The data confirm the coordination of xanthate into each polymer chain. [b] Na is from sodium trifluoroacetate (CF_3CO_2Na) which is the MALDI ionization salt.

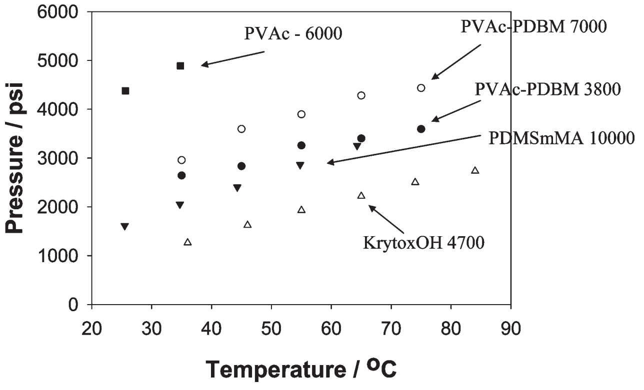

Figure 6. Phase behavior of PVAc-*alt*-PDBM (●, ○) along with PVAc (■), PDMS-mMA (▼), and PFPE (Krytox-OH) (△) in pure CO_2. The cloud point pressures of all samples were measured at the concentration of 0.2 wt % with respect to CO_2. The cloud point pressure of PVAc-PDBM is still higher but not far from those of PFPE (Krytox-OH 4700) and PDMS-mMA.

For comparison, the cloud point pressures of commercially available PFPE (Krytox-OH, M_n = 4700 g/mol) and PDMS-mMA (M_n = 10 000 g/mol) were also measured (Table 4) and plotted (Figure 6) at a concentration of 0.2 wt % with respect to CO_2. The cloud point pressure of PVAc-*alt*-PDBM is still higher than these polymers, but a significant improvement in solubility of the VAc-based polymers has been observed compared to previous studies.

The effect of polymer concentration on the phase behavior in CO_2 was studied, and the representative cloud point curves for PVAc-PDBM-3800 are shown (Figure 7). As expected, it is clear that higher pressure is required for CO_2 to completely dissolve the polymer as the concentration of copolymer increases from 0.2 to 0.6 wt %.

The solubility of PVAc-*alt*-PDBM was also compared to those of PEC−PPG hydrocarbon copolymers which were synthesized by Cooper et al.[15] The cloud point curves

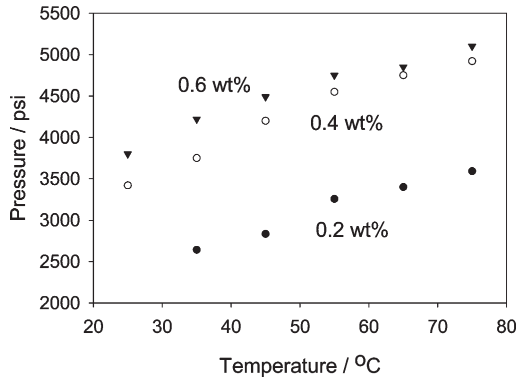

Figure 7. Cloud point curves of PVAc-PDBM-3800 at three different polymer concentrations (0.2 (●), 0.4 (○), and 0.6 wt % (▼)) in pure CO_2. As expected, higher densities are required to dissolve higher concentrations.

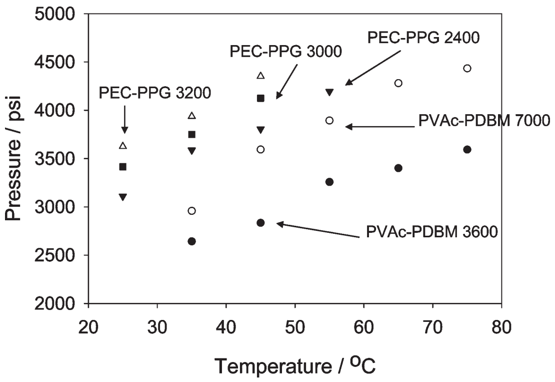

Figure 8. Phase behavior of two PVAc-PDBM alternating copolymers (M_n = 3600 (○), M_n = 7000 (●)) showing lower cloud point pressures than the previously published PEC−PPG-425 fractions[15] in pure CO_2 (M_n = 2400 (▼), M_n = 3000 (■), M_n = 3200 (△)). Number following label denotes the M_n.

Table 4. Cloud Point Data for PVAc-PDBM, PDMS-mMA, and Krytox-OH

		cloud point pressure (psi)						
entry	sample	25 °C	35 °C	45 °C	55 °C	65 °C	75 °C	85 °C
1	PVAc-PDBM-7000		2960	3590	3890	4280	4430	
2	PVAc-PDBM-3800		2640	2830	3260	3400	3590	
3	PDMS-mMA-10000	1620	2050	2410	2870	3260		
4	Krytox-OH-4700		1270	1620	1930	2220	2500	2730

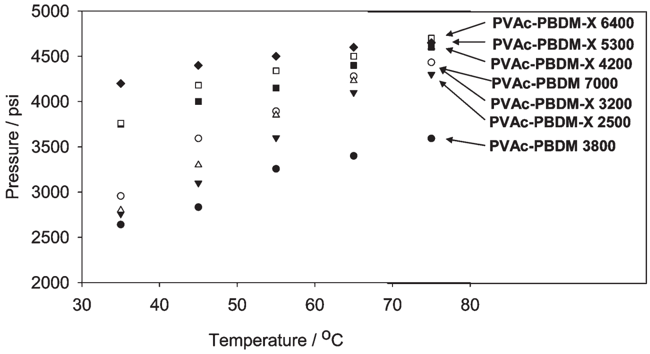

Figure 9. Cloud point curves for PVAc-*alt*-PDBM-X copolymers (synthesized using xanthate; M_n of 2500 (▲), 3200 (△), 4200 (■), 5300 (□), and 6400 kDa (◆)) and PVAc-*alt*-PDBM (synthesized by free radical polymerization; M_n of 3600 (●) and 7000 kDa (○)) in pure CO_2. The cloud point pressures of all samples were measured at the concentration of 0.2 wt % with respect to CO_2.

for the three PEC−PPG-425 fractions (at a concentration ca. 0.19 wt %) are plotted with those of PVAc-*alt*-PDBM copolymers (at a concentration ca. 0.20 wt %) in Figure 8.

Both PVAc-PDBM-3800 and PVAc-PDBM-7000 exhibited lower cloud point pressure (higher solubility) at each temperature than any of three PEC−PPG-425 fractions. Of particular interest is PVAc-PDBM-7000, which has a molecular weight (M_n = 7000 g/mol) of more than twice that of PEC−PPG-425 (M_n = 2100−3200 g/mol) but still shows higher solubility in CO_2. This considerably higher solubility of PVAc-PDBM can be explained by a combination of two possible factors: the addition of carbonyl groups in the side chain, which has been reported to give a favorable specific interaction with CO_2, and high chain flexibility provided by dibutyl groups, leading to low polymer−polymer interactions and therefore enhancing favorable polymer−CO_2 interaction.

The solubility of PVAc-*alt*-PDBM-X copolymers synthesized via RAFT (entries R1−R5, Table 2) were then examined in pure CO_2 at a concentration of 0.2 wt % with respect to CO_2. The cloud point curves for these PVAc-*alt*-PDBM-X polymers can then be compared with those of PVAc-*alt*-PDBM (entries F1 and F2, Table 1) which were synthesized by standard, noncontrolled free radical polymerization (Figure 9).

All of the PVAc-*alt*-PDBM-X copolymers were found to be fully dissolved in the CO_2 phase below 4650 psi within the temperature range 35−75 °C. The slope of the cloud point curves becomes less steep for the higher molecular weight polymers which indicate that the solubility of the polymers with longer chain length is affected less by changes in temperature (or CO_2 density) compared to the effect upon polymers with shorter chain length. This also means that the solubility of high molecular weight polymers is less easily tuned by simply varying the temperature.

The cloud point pressures of PVAc-*alt*-PDBM synthesized by free radical polymerization were also plotted for comparison. In all cases, the polymers synthesized by RAFT showed much higher cloud-points than polymers synthesized in the absence of RAFT agent of comparable molecular weight. Indeed, PVAc-PDBM-7000 exhibited a much lower cloud point curve than even PVAc-PDBM-X-4200. This was quite surprising, but the significantly lower solubility of PVAc-*alt*-PDBM-X compared to that of PVAc-*alt*-PDBM can be rationalized by noting the effect of the xanthate moiety at the end of polymer chains. In a recent report, we showed that xanthate-terminated PVAc-X is slightly less soluble in $scCO_2$ than the equivalent polymer formed by free radical polymerization.[32] Likewise, for example in this study, the PVAc-PDBM-X-4200 shows higher cloud point pressure by 800−900 psi compared to PVAc-PDBM-3800. It seems most likely that the dithioester group of the xanthate may have unfavorable interactions with CO_2. However, this could prove to be advantageous if the end group is designed to anchor to another environment, for example, in a dispersion polymerization.[32]

Conclusions

A range of new CO_2-soluble hydrocarbon copolymers PVAc-*alt*-PDBM-X having specifically targeted molecular weights with narrow PDIs were successfully synthesized via RAFT polymerization using xanthates as the controlling agent. MALDI-TOF analysis clearly showed that the xanthate was present on the end of each polymer chain. The cloud point observation revealed that the solubility of PVAc-*alt*-PDBM was strongly dependent on the molecular weight and on the polymer loadings. PVAc-*alt*-PDBM showed good solubility, much higher than that of PVAc homopolymer and approaching that of PFPE and PDMS-mMA—this is presumably due to the increase in free volume of the polymer upon incorporation of the highly branched DBM monomer. Phase behavior data also clearly showed that the solubility of PVAc-*alt*-PDBM-X (xanthate-terminated) copolymers is lower compared to that of PVAc-*alt*-PDBM synthesized by standard free radical polymerization following purification by CO_2 extraction. This lower solubility of PVAc-*alt*-PDBM-X is ascribed to the presence of the dithioester group of xanthate at the end of the polymer chains. However, this study suggested that it is possible to synthesize a new hydrocarbon-based copolymer having high solubility in CO_2 and established a prospective platform for further development of inexpensive hydrocarbon materials for use in $scCO_2$.

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