**Macromolecules**
ARTICLE

*Macromolecules* **2009**, *42*, 7945–7952 **7945**
DOI: 10.1021/ma901458a

# Fractionation of Poly(vinyl acetate) and the Phase Behavior of End-Group Modified Oligo(vinyl acetate)s in $CO_2$

**Bien Tan,*[†,‡] Christopher L. Bray,[‡] and Andrew I. Cooper*[‡]**

[†]*College of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan 430074, China, and* [‡]*Department of Chemistry, University of Liverpool, L69 7ZD, Liverpool, United Kingdom*

*Received July 5, 2009; Revised Manuscript Received August 14, 2009*

ABSTRACT: Poly(vinyl acetate) (PVAc) is an inexpensive, high-tonnage bulk commodity polymer which, unlike most vinyl polymers, is moderately biodegradable. PVAc has been shown to exhibit anomalously high solubility in $CO_2$ with respect to other vinyl hydrocarbon polymers. Understanding the phase behavior of PVAc in $CO_2$ and its variation with structure is very important for its potential application as suitable surfactant, ligand, or phase transfer agent in a $CO_2$ solvent process. In this article, PVAc has been fractionated using a supercritical fluid extraction method (SCFE) to provide low molecular weight fractions with narrow polydispersity. The phase behavior of hydroxyl terminated poly(vinyl acetate)s (PVAc-OH) were determined by a high throughput gravimetric extraction (HTGE) screening method and a cloud-point pressure method using a variable volume view cell (VVVC). The solubility of PVAc in $CO_2$ strongly depends on the molecular weight. Oligomer PVAc-OH ($M_w < 3000$ g·mol$^{-1}$) is soluble in $CO_2$ at low pressures but decreases in solubility with increasing molecular weight. End-group modification of oligomer PVAc-OH alters the phase behavior of the oligomers.

## Introduction

Supercritical carbon dioxide ($scCO_2$) has been promoted recently as a sustainable solvent because it is nontoxic, nonflammable, and naturally abundant.[1] In particular, $scCO_2$ has been shown to be a versatile solvent for polymer synthesis and processing.[2−8]

But carbon dioxide is a relatively weak solvent: for example, important classes of materials which tend to exhibit low solubility in $scCO_2$ include polar biomolecules, pharmaceutical actives, and high molecular weight polymers.[2−4] This problem is not unique to $CO_2$; indeed, an enormous variety of surfactants and phase transfer agents have been developed to disperse poorly soluble molecules in water. A technical barrier for the use of $scCO_2$ is the lack of an equivalent range of inexpensive $CO_2$-soluble (and preferably biodegradable) surfactants, ligands, and phase transfer agents. A number of research groups have synthesized $CO_2$-philic fluoropolymers or silicone-based materials for use as steric stabilizers in dispersion polymerization,[4,9−11] as phase transfer agents for liquid−liquid extraction,[12] as supports for homogeneous catalysis,[13,14] and as surfactants for the formation of water/$CO_2$ emulsions and microemulsions.[15,16]

Unfortunately, the high cost of fluorinated polymers may prohibit their use on an industrial scale for most applications. Fluoropolymers also tend to have poor environmental degradability, and this could negate the environmental advantages associated with the use of $scCO_2$. The lack of inexpensive $CO_2$-soluble polymers and surfactants is a significant barrier to the future implementation of this solvent technology.

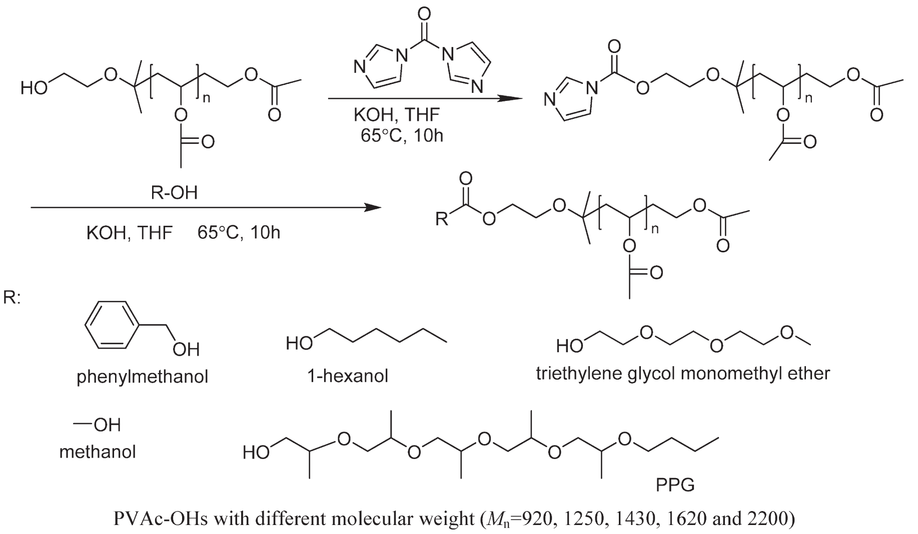
The discovery of inexpensive $CO_2$-soluble materials or $CO_2$-philes is therefore an important challenge.[17] One of the fundamental issues that one must consider when implementing $CO_2$ for polymer synthesis or processing is polymer solubility. There has been considerable research effort focused on discovering inexpensive biodegradable $CO_2$-soluble polymers from which inexpensive $CO_2$-soluble surfactants, ligands, and phase transfer agents could be developed. However, it is very difficult to predict which polymer structures would be $CO_2$-soluble, despite recent attempts to rationalize specific solvent−solute interactions by using *ab initio* calculations.[18] Only a few examples of $CO_2$-soluble polymers currently exist and, as such, there are a limited number of design motifs to draw upon. Moreover, it is clear that polymer solubility in $CO_2$ is influenced by a large number of interrelated factors[19,24] such as specific solvent−solute interactions,[18,20−23] backbone flexibility,[20,22,23] topology,[20] and the nature of the end groups.[20] Given the current limits of predictive understanding, the discovery of new $CO_2$-soluble polymers might be accelerated using parallel or high-throughput (HTP) methodology. The synthetic approaches for such a strategy are already well in place; for example, a growing number of methods exist whereby one may synthesize and characterize polymer libraries.[24] By contrast, there are no examples of techniques for the rapid, parallel determination of solubility for libraries of materials in $scCO_2$ or other supercritical fluids (SCFs). The conventional method for evaluating polymer solubility in SCFs is cloud point measurement,[19,20,23] which involves the use of a variable-volume view cell. This technique is not suitable for rapid solubility measurement and would be impractical for large libraries of materials.

Inexpensive poly(ether carbonate) (PEC) copolymers have been reported to be soluble in $CO_2$ under moderate conditions.[22,23] These copolymers were found to be soluble in liquid $CO_2$ 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 $CO_2$. These statistical copolymers were generated from very inexpensive feed-stocks and are thus appealing as building blocks for cheap surfactants. The enhanced solubility of these copolymers with respect to poly(propylene oxide) is speculated to arise, at least in part, from specific Lewis acid−base interactions that exist between $CO_2$ and the carbonyl

---

*Corresponding author. E-mail: bien.tan@mail.hust.edu.cn (B.T.); aicooper@liv.ac.uk (A.I.C.).

**Scheme 1.**[a]



[a] PVAc-OHs with different molecular weight ($Mn$ = 920, 1250, 1430, 1620, and 2200).

groups of the carbonate moieties.[22,23,25] 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 exactly mirrors the composition of the monomer feed. We recently developed step-growth polymerization routes to synthesize PEC and also poly(ether ester) (PEE) materials as potential inexpensive hydrocarbon $CO_2$-philes.[26] These polymers are soluble in $CO_2$, but only up to moderate molecular weights (< 10,000 g/mol).

Similarly, sugar acetates are highly soluble and have been proposed as renewable $CO_2$-philes.[18,27] Such materials could, in principle, function as $CO_2$-philic building blocks for inexpensive ligands and surfactants, but this potential has not yet been realized, and numerous practical difficulties remain.

Poly(vinyl acetate) (PVAc) has been shown to exhibit anomalously high solubility in $CO_2$ with respect to other vinyl hydrocarbon polymers,[28,29] although the polymer is soluble only at relatively low molecular weights under conditions of practical relevance ($P < 300$ bar, $T < 100$ °C). Recently, end-functionalized poly(vinyl acetate) oligomers (OVAc) were used as $CO_2$-philic building blocks.[30,31]

We have also demonstrated a simple and generic method for producing inexpensive, functional hydrocarbon $CO_2$-philes for solubilization, emulsification, and related applications.[31] A range of $H_2O$-soluble diblock and triblock architectures were produced, and it was found that both types of architecture could stabilize highly concentrated emulsions. Almost at the same time, OVAc was used to generate $CO_2$-soluble ionic surfactants.[30,32] Recently, Howdle's group successfully conducted dispersion polymerization in supercritical $CO_2$ by using polyvinylalkylate hydrocarbon surfactants synthesized and anchored via RAFT.[33]

It is often considered that the end group on a polymer may have a significant effect upon the properties of the polymer. The significance is thought to be greater with lower molecular weight polymers. Fedors' work on solubility parameters for SCFs and polymers suggests that the end group should be considered for all molecular weights.[34] For solubility in poor solvents such as $scCO_2$, the effect is likely to be important, and therefore, an investigation of end-group effects is advisible.

PVAc is an inexpensive, high-tonnage bulk commodity polymer which, unlike most vinyl polymers, is moderately biodegradable and has been used in pharmaceutical excipient formulations.[35] Understanding the phase behavior of PVAc in $CO_2$ and its variation with structure is very important for its potential application as suitable surfactant, ligand, or phase transfer agent in a $CO_2$ solvent process. PVAc has some solubility in $scCO_2$,[28] and our initial work with HTP gravimetric extraction suggested that the end group of PVAc may have an effect on solubility at lower molecular weights.[36] Here, a study was conducted to test this hypothesis. A library of end-group modified PVAcs was synthesized (Scheme 1), and these were tested for solubility using the HTP gravimetric extraction technique.

## Experimental Section

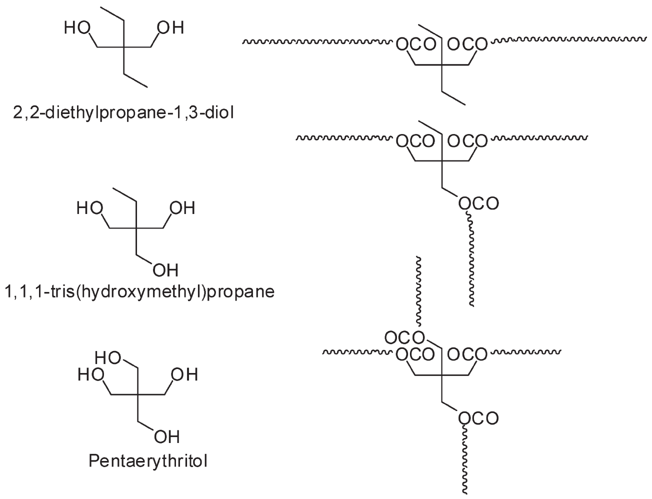
**Materials.** Vinyl acetate (VAc, Aldrich, 99+%) was freed from the inhibitor by passing through an alumina column. 2,2′-Azobis(isobutyronitrile) (AIBN, Fisher, 97%) was recrystallized twice from methanol and dried under vacuum before use. 2-Isopropoxyethanol (IPE, Aldrich, 99%), 1,1′-carbonyldiimidazole (CDI), phenylmethanol, 1-hexanol, triethylene glycol monomethyl ether (95%), methanol, poly(propylene glycol) monobutyl ether (average $M_n$ ~340), 2,2-diethylpropane-1, 3-diol, 1,1,1-tris(hydroxoymethyl) propane, pentaerythritol sodium sulfate, anhydrous tetrahydrofuran (THF), and dichloromethane were all from Aldrich and used as received. Deionized water was used throughout. High purity carbon dioxide (SFC grade, 99.9999%) was purchased from BOC Gases.

**Synthesis of PVAc-OH.** The synthetic strategy presented here was based on the preparation of monohydroxyl functionalized PVAc by free-radical polymerization in the presence of a chain-transfer agent, 2-isopropoxyethanol (IPE).[37] Briefly, VAc (64.07 g, 0.745 mol) was added to IPE (480 mL, 4.16 mol) containing AIBN (9.61 g, 15% w/w based upon monomer). The resulting solution was heated to 65 °C with stirring for 12 h. The solvent was removed under reduced pressure, and the polymer was reprecipitated into cold *n*-hexane. The product was then dissolved in acetone and was reprecipitated into cold *n*-hexane. This was repeated twice followed by drying under vacuum at 30 °C to afford the product as a viscous liquid (59.5 g, 93%). $M_n$ (GPC) = 3830 g/mol; $M_w$ = 6430 g/mol.

$^1$H NMR data (400 MHz, $CDCl_3$): $\delta$ 4.87−5.25, 50H; $\delta$ 4.02−4.18, 2H; $\delta$ 3.59−3.73, 2H; $\delta$ 3.34−3.52, 2H; $\delta$ 1.94−2.23, 150H; $\delta$ 1.54−1.94, 100H; $\delta$ 1.10−1.29, 6H.

**End-Group Modification and Topological Modification.** PVAc-OHs with different molecular weights ($M_n$ = 920, 1250, 1430, 1620, and 2200 g mol$^{-1}$) were synthesized and modified following the procedure[31] used to give a library of 30 polymers (Scheme 1).

Scheme 2



Different topological structures of PVAc with similar molecular weights were prepared by combining VAc oligomers of different molecular weights (2000, 1300 and 1000) with diols, triols, and tetraols: 2,2-diethylpropane-1,3-diol, 1,1,1-tris(hydroxoymethyl) propane, and pentaerythritol. These give three shapes: a linear polymer, a branched polymer, and a star-shaped polymer with similar molecular weight. (Scheme 2)

**Solubility Measurements in $CO_2$.** (*a*). *Cloud Point Curve Determinations*[38]. Cloud points were recorded using a high-pressure, variable volume view cell (VVVC). 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 the addition of $CO_2$, 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. The pressure inside the cell was 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 estimated in this way were accurate to at least ± 4 bar (~60 psi). Cloud point pressures were recorded between 25−65 °C for a given polymer/$CO_2$ mixture.

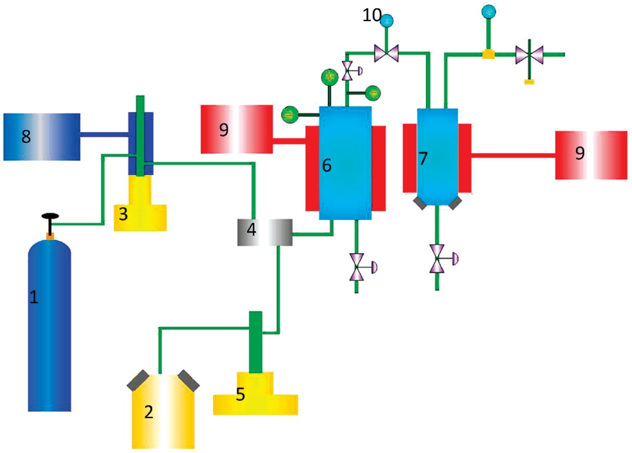


**Figure 1.** Schematic of fractionation equipment $CO_2$ (1, cylinder; 2, solvent reservoir; 3, $CO_2$ pump; 4, mixer; 5, cosolvent pump; 6, 500 mL pressure vessel; 7, collection vessel; 8, cooling bath; 9, heating bath; 10, automated back pressure regulator).

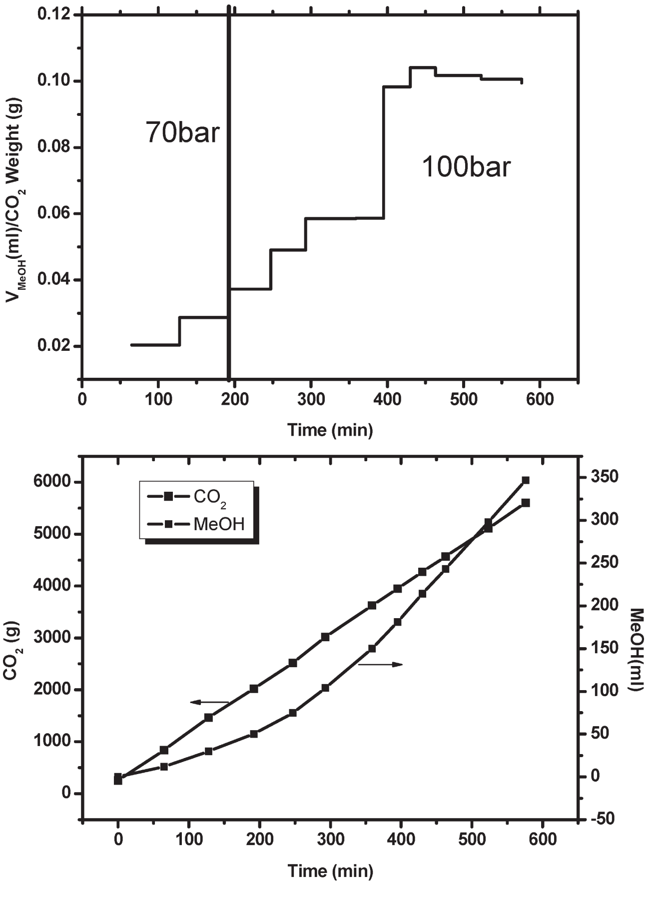


**Figure 2.** Variations of the ratio of MeOH to $CO_2$ in the fractionation process.

(*b*). *High Throughput Gravimetric Extraction* (*HTGE*) *Screening Method*. The method has been described in a previous publication.[36] Briefly, polymer samples (ca. 100 mg) were accurately weighed into 42 mm open borosilicate glass sample tubes with an i.d. of 6 mm. Each tube was double wrapped with Milliwrap and loaded into a specially designed sample holder which will accept up to 72 tubes on this scale. This holder was then placed into a custom-built (Thar Designs) SCF extractor (Figure 1) consisting of a vertically mounted 500 $cm^3$ extraction vessel and computer-controlled syringe pump/back pressure regulator. $CO_2$ was then passed through the vessel at a controlled pressure, temperature, and flow rate for a predetermined period of time. Thus, all 72 samples were subjected, in parallel, to precisely the same extraction conditions. The $CO_2$ was then slowly vented, controlled by an automated script at 5 bar/min, the sample holder removed from the vessel, and the samples reweighed individually to determine the sample mass loss (if any) under those extraction conditions. The procedure was then repeated (typically at progressively higher $CO_2$ pressures) in order to build a cumulative extraction profile for the library of samples. A low molecular weight material (e.g., AIBN) of known $CO_2$-solubility was added as an internal standard for each run.

**HTGE Fractionation of PVAc-OH.** Fractionation of PVAc-OH was performed using the same Thar SCF extraction apparatus as described above. Aproximately 100 g of PVAc-OH ($M_n$ = 3830 g/mol; $M_w$ = 6430 g/mol) was weighed accurately into the 500 $cm^3$ stainless steel extraction vessel. Compressed $CO_2$ was allowed to flow into the bottom of the vessel at a predetermined pressure and constant flow rate ($CO_2$ flow rate = 10 mL/min for all pressures) as controlled by a syringe pump.

The extraction pressure was varied over the range 70−300 bar. The lower molecular weight oligo(vinyl acetate) (OVAc) fractions were extracted using pure $CO_2$. In order to collect higher $M_w$ fractions, a modifier, MeOH, was coinjected into the system (MeOH is a good solvent for PVAc). (Figure 2) During the fractionation process, the MeOH flow rate was increased from 0 to 1.0 mL/min. Extracts were collected after predetermined time intervals to produce a series of OVAc fractions with different molecular weights. When $M_n$ of the extract is close to 4000 (determined by gel permeation chromatography (GPC)), the extraction process was stopped.

**Polymer Characterization.** $^1$H NMR spectra were recorded in $CDCl_3$ on a Bruker Analytic GmbH 400 MHz spectrometer using tetramethylsilane (TMS) as an internal reference. $^{13}$C NMR spectra were recorded at 400 MHz in $CDCl_3$ solution on a Bruker Analytic GmbH 400 MHz spectrometer using solvent carbon signal as the standard. GPC was performed using a Polymer Laboratories system equipped with a PL-ELS 1000 evaporative light scattering detector and a series of PL mix gel columns (5 $\mu$m MIXED C and D). THF was used as the eluent at a flow rate of 1.0 mL/min at 40 °C. Calibration was carried out using EasiCal polystyrene standards (Polymer Laboratories).

## Results and Discussion

**PVAc Fractionation.** Fractionation of the bulk PVAc-OH material has produced a series of end-functionalized PVAc-OH materials with number average molecular weights, $M_n$, ranging from 800−4000 g/mol (Figure 3). The fractionated PVAc-OH samples exhibited relatively narrow molecular weight distributions ($M_w/M_n$) in the range 1.14−1.40 (Table 1). These will be suitable for a range of applications where the molecular weight of the oligomer is important, for example, modification into surfactants. The oligomeric fractions were soluble in $CO_2$ up to significant concentrations, for example, a PVAc-OH fraction with a $M_n$ of 840 g/mol and a $M_w$ of 1048 g/mol was soluble at 10% w/v in liquid $CO_2$ (25 °C) at a pressure of 100 bar.

**High Through-put Screening Reproducibility.** In order for the method to be useful for screening and for solubility measurements, a high level of reproducibility is required. A number of questions with a HTP system must be faced. Will the presence of other samples affect the extraction of the samples around them? Will the position on the sample holder rack affect extraction?

Studies were carried out to test and to maximize reproducibility. Samples were placed throughout the holder, varying from top to bottom and from inside to out on the holder. With the conditions outlined above, good reproducibility could be achieved. Measurements within 5% were achieved for a wide range of polymers. Figure 4 provides typical reproducibility results. Variations in measurements are generally less than ±2 (wt.%) (Figure 4b, error bars). This is similar for all samples regardless of the level of extraction, which means that this is the measurement error arising from weighing uncertainties and so forth. In general, errors increased with multiple extractions resulting from (a) wear and tear on the wrap material and (b) cumulative measurement errors. Standard deviations (SDs) (Table 1) are within a few percent of the total extraction for reasonably soluble samples but are much higher for poorly extracted samples. For samples with a very low of extraction, this represents a high % SD, but these samples are virtually insoluble in $CO_2$ at reasonable pressures, and this technique is the only technique that can provide any measurement of the variation of the solubility of these polymers.

These tests suggest that the method is reproducible enough to make rapid high, medium, and low solubility judgments for libraries of materials at various pressures and will allow quantitative structure−property relationship (QSPR) approaches to be employed.

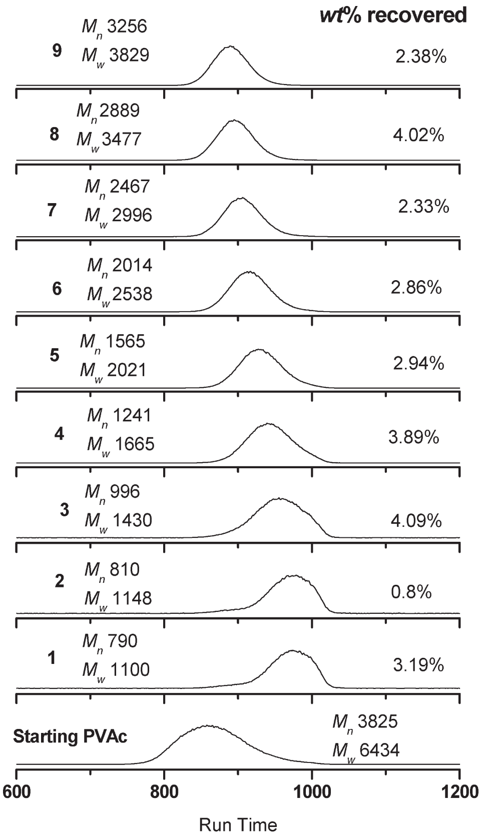


**Figure 3.** Representative series of nine OVAc fractions collected by supercritical fluid extraction of PVAc-OH. The data on the right refer to the weight percentage of the total original sample represented by that fraction.

In summary, this new technique has broad potential for the rapid solubility mapping for libraries of new materials in SCFs. We believe that this method is at least 50 times faster than other techniques in terms of the rate of useful information that is obtained. A powerful combined approach in the future will be to screen libraries of materials using our new HTP methodology followed by further validation of $CO_2$ solubility for candidate materials using conventional cloud point measurements. While our preliminary experiments have involved polymer libraries, this parallel methodology is equally applicable to the discovery of novel SCF-soluble ligands, catalysts, biomolecules, fragrances, dyes, or pharmaceuticals for a wide range of material applications.

**PVAc Phase Behavior.** *Effect of Molecular Weight on $CO_2$ Solubility*. Our previous research[36] has already revealed that a clear global relationship exists between molecular weight and solubility, that is, the solubility in $CO_2$ drops off sharply as a function of moleculra weight, and none of the polymers tested shows significant solubility for moleculra weight > 20 000 g mol$^{-1}$ (100−300 bar, 35 °C). More detailed examination of this relationship using HTGE and cloud point measurement confirms this. Figure 5a shows the cumulative extraction percentage in $CO_2$ after extraction at 100 bar (1450 psi) and 35 °C for 4 h as a function of $M_n$ for the polymers in the library. Figure 5b shows the cloud point pressure curves for the same library of polymers. Extraction of PVAc falls rapidly with increasing molecular weight so that very little is extracted at 100 bar when $M_n$ exceeds 2000 g mol$^{-1}$. The more detailed cloud point curves reveal a similar pattern and also that solubility increases with increasing temperature. Small increases in molecular weight produce

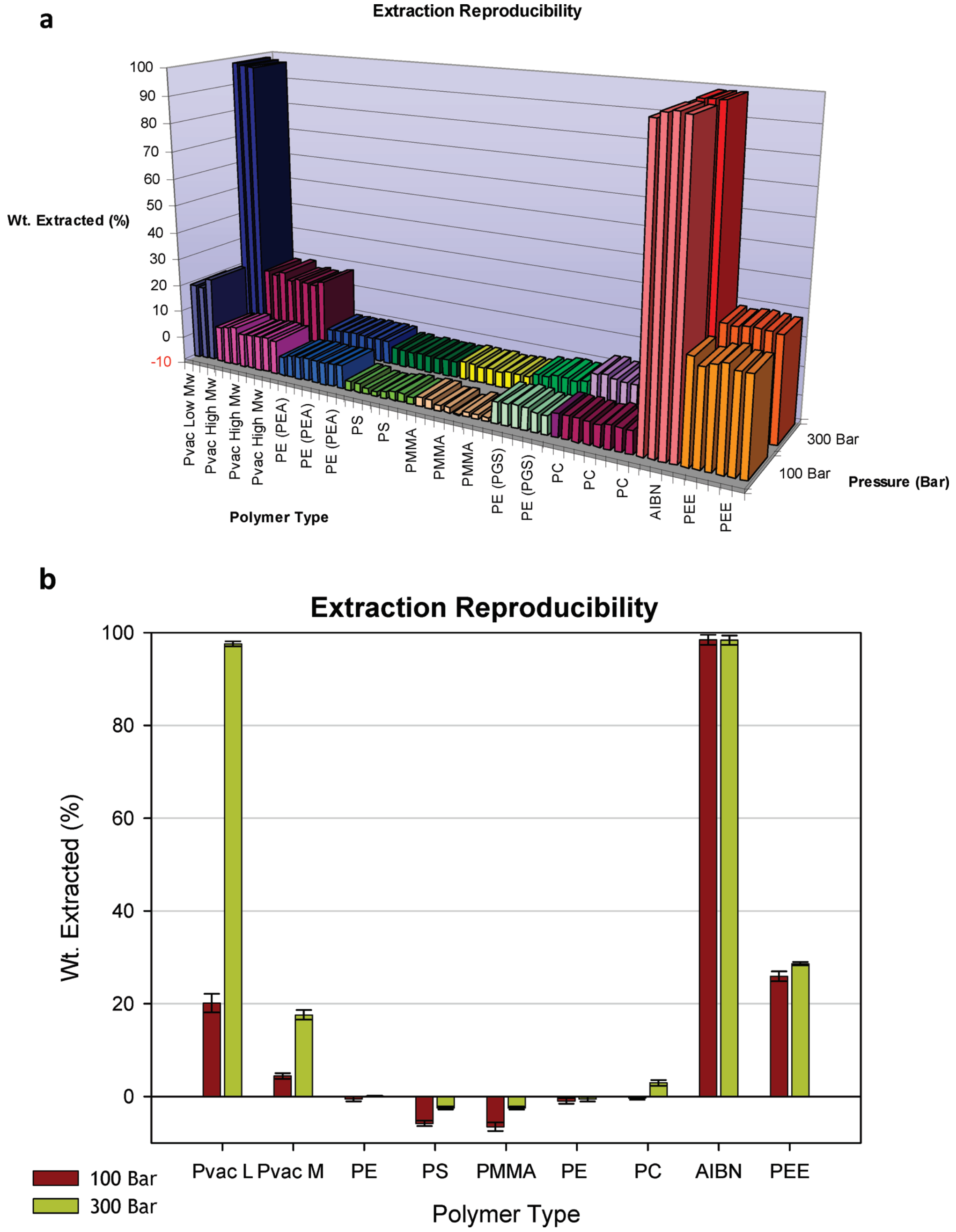


**Figure 4.** (a) Reproducibility measurements showing that a variety of polymers and molecular weights can be distinguished by their different solubilities. (b) Extraction of nine samples, 5 repeats with error bars at both 100 and 300 bar showing good reproducibility.

**Table 1. Molecular Weight of Fraction Parts**

| | extraction condition | | | molecular weight | | |
|---|---|---|---|---|---|---|
| sample name | pressure (bar) | duration (min) | amount (g) | $M_n$ | $M_w$ | PD |
| orgin sample | | | 134.58 | 9893 | 17456 | 1.7645 |
| EX-1 | 80 | 260 | 0.9768 | 909 | 1329 | 1.462 |
| EX-2 | | 180 | 0.4551 | 947 | 1304 | 1.377 |
| EX-3 | | 360 | 1.1365 | 1074 | 1524 | 1.419 |
| EX-4 | | 720 | 2.3848 | 1369 | 1958 | 1.4302 |
| EX-5 | 120 | 480 | 2.576 | 2503 | 3201 | 1.2789 |
| EX-6 | | 300 | 4.6617 | 5059 | 6345 | 1.2542 |
| EX-7 | 150 | 720 | 2.5414 | 4004 | 4781 | 1.1941 |
| EX-8 | 200 | 435 | 1.0126 | 4613 | 5528 | 1.1984 |
| EX-9 | 250 | 1000 | 4.4985 | 5994 | 7265 | 1.212 |

significant increases in cloud point pressure across the range of temperatures.

*Effect of End Group and Topology on PVAc Solubility in $CO_2$.* Examination of GPC results (Table 2) shows that modification of the end groups has been successful with $M_n$ and $M_w$ increasing proportionally with end-group size. The increase in $M_n$ and $M_w$ is greater than theoretical calculations would predict, but the measurement calibration uses polystyrene standards, and the end groups will not necessarily respond in exactly the same way in the GPC column. Nevertheless, the trend observed is what would be expected.

Proton NMR spectra of the end-group modified PVAc (see Supporting Information) reveal little additional information but confirm a small amount of contamination from the imidazole end group, which suggests that end-group modification has been successful.

Figures 6 and 7, and Table 3 summarize the solubility results. There are typical declines in polymer solubility,

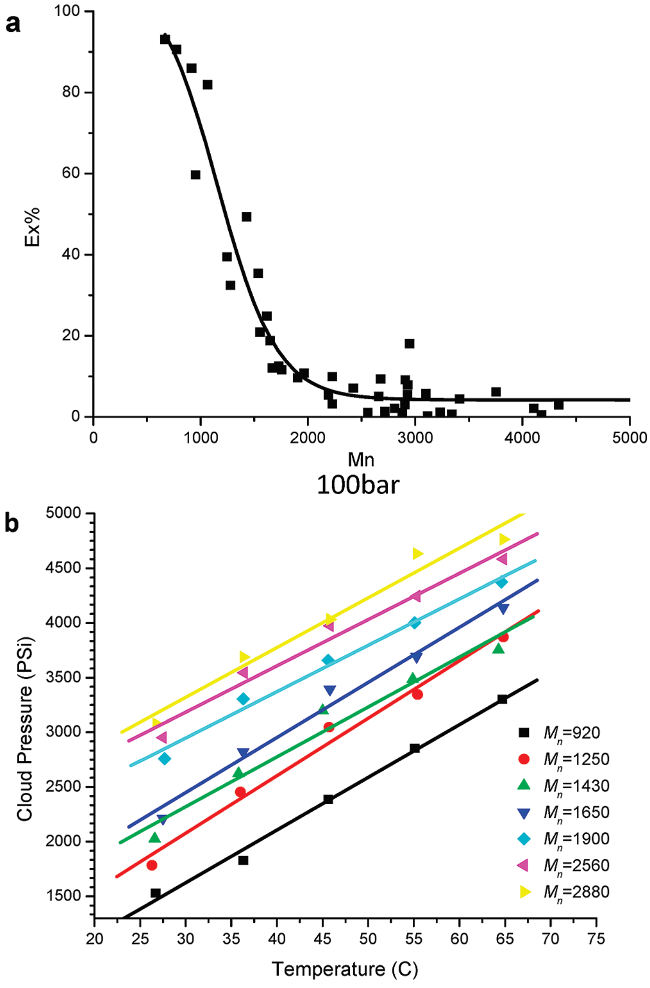


**Figure 5.** (a) Solubility of PVAc which have different molecular weights. (b) Cloud point pressure curves determined by a variable volume view cell.

**Table 2. GPC Results**[a]

| | 1 | | 2 | | 3 | | 4 | | 5 | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $M_n$ | $M_w$ | $M_n$ | $M_w$ | $M_n$ | $M_w$ | $M_n$ | $M_w$ | $M_n$ | $M_w$ |
| -OH | 920 | 1170 | 1250 | 1570 | 1430 | 1780 | 1620 | 2030 | 2230 | 2740 |
| -Im | 1060 | 1360 | 1390 | 1790 | 1580 | 2030 | 1730 | 2230 | 2320 | 3140 |
| a | 1130 | 1410 | 1580 | 1970 | 1840 | 2270 | 1980 | 2460 | 2640 | 3270 |
| b | 1220 | 1500 | 1690 | 2060 | 1910 | 2340 | 2080 | 2530 | 2880 | 3470 |
| c | 1240 | 1540 | 1870 | 2230 | 2070 | 2510 | 2230 | 2640 | 2900 | 3510 |
| d | 1314 | 1600 | 1700 | 2090 | 1910 | 2370 | 2190 | 2620 | 2930 | 3520 |
| e | 1539 | 1910 | 1970 | 2400 | 2330 | 2870 | 2640 | 3190 | | |

[a] a = methyl; b = benzyl; c = hexyl; d = polyethylene glycol; and e = polypropylene glycol end groups.

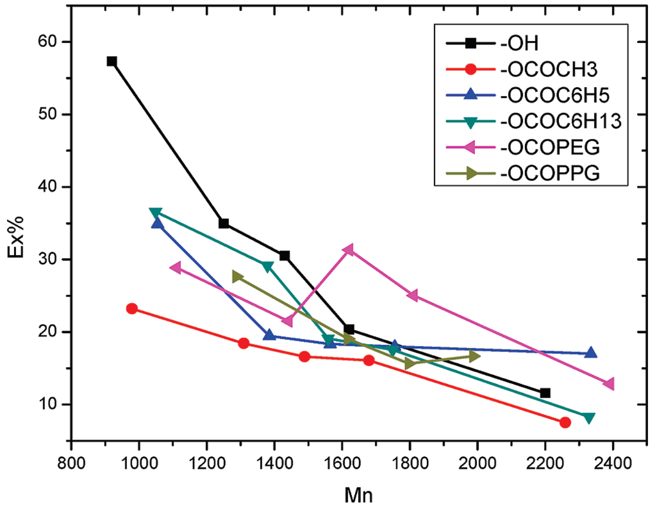


**Figure 6.** Solubility determination of PVAc by the HT screening method: extraction vs $M_n$ and end group at 100 bar. Solubility of PVAc-methyl is the poorest, and the solubility of PVAc−OH is highest at lower molecular weights, while at higher molecular weights, PVAc-PEG, PVAc-PPG, and PVAc-Benzyl show enhanced solubility.

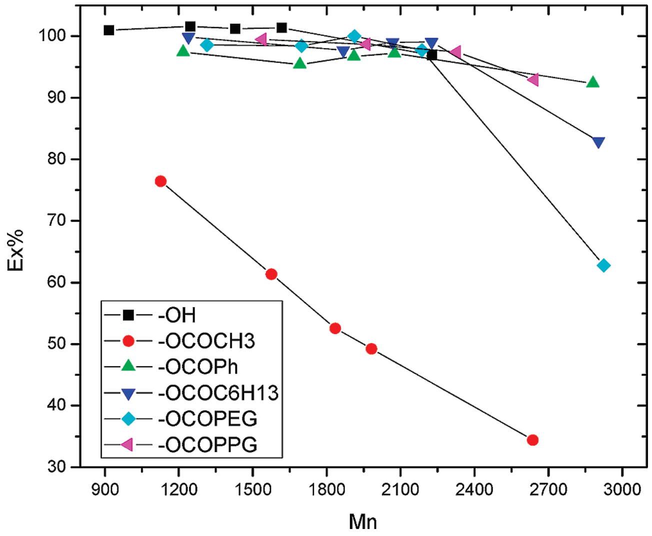


**Figure 7.** Solubility determination of PVAc by the HTP screening method at 300 bar: extraction v. $M_n$ and end group at 300 bar. The poor solubility of PVAc-methyl (red points) suggests that an exposed carbonate group is very deleterious to solubility. The rapid decline in extraction between molecular weights 2000−2300 g mol$^{-1}$ suggests that this is the location of the cloud point for these conditions.

**Table 3. Effect of Topology on PVAc's Solubility in CO$_2$**

| | | molecular weight | | |
|---|---|---|---|---|
| | | $M_n$ | $M_w$ | PD |
| A | PVAc-DIOL | 1678 | 2137 | 1.27 |
| B | PVAC-3OL | 1741 | 2282 | 1.31 |
| C | PVAc-4OL | 1489 | 2080 | 1.40 |

irrespective of end group, with increasing $M_n$. End group modification produces significant changes in solubility. The effect is most noticeable at the lowest molecular weights but is still significant when $M_n$ is 2200 g mol$^{-1}$ with extraction at 100 bar. Surprisingly, PVAc-OH is significantly more soluble at the lower molecular weights than any of the other end groups. The hydroxyl group is a very polar group which, would not be expected to interact favorably with CO$_2$. But in this case, the linker for the end-group modified members of the library is a carbonate linker. It is often suggested that carbonate groups will enhance the solubility of a polymer in CO$_2$,[22,23,26,31,39] although there are other views.[40,41] This study seems to reflect this conflicting evidence. In the two polymers with the lowest molecular weight, the poorest solubility is found where the tail of the end group is the shortest (methyl) (Figures 6 and 7); this is where the effect of the carbonate linker would be felt most strongly.

With increasing $M_n$, PVAc-PEG shows better solubility at 100 bar. This provides an end group where the carbonate linker is sufficiently embedded in the chain to eliminate any deleterious effect by reducing overall polarity and also is long enough and flexible enough with the inclusion of ether groups to enhance solubility. With extraction at 300 bar,

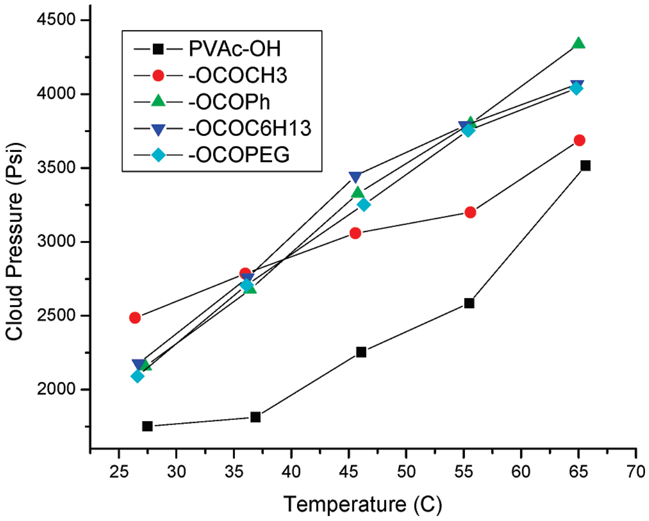


**Figure 8.** Cloud point pressure curve determination by VVVC ($M_n$ for PVAc-OH is 1620).

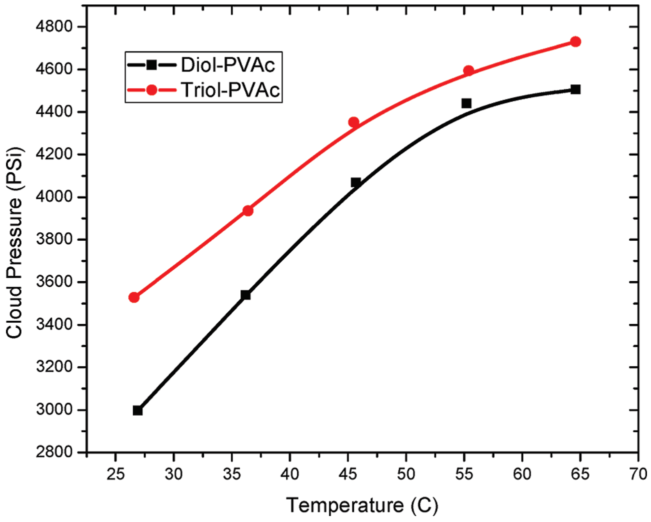


**Figure 9.** Cloud point pressure curve determination by VVVC.

the polymers are effectively completely soluble except at $M_n$ = 2300. This study again confirms the peculiar solubility of PVAc among the hydrocarbon polymers.[28] The methyl carbonate end group still provides reduced solubility compared to that of the other end–groups. PVAc-OH provides the highest overall solubility at all molecular weights when extracted at 300 bar. PVAc-PEG is also effective except at the highest $M_n$ where it begins to show a sharp decline compared to that of other end groups, although this may be an effect of the polymer having the highest molecular weight and marks the point of solubility decline. It equates with the polymer cloud point. PVAc-benzyl retains solubility to the highest molecular weights suggesting that this is a relatively favorable end group.

Cloud point measurements for these end-group modified polymers show that the unmodified polymer has a lower cloud point than the modified polymers (Figure 8). PVAc-$OCOCH_3$ shows less temperature dependence than the other end groups and at lower temperatures has a higher cloud-point pressure in line with the extraction measurements.

The picture (Figures 6–8) presented is a complex one demonstrating that small changes in the structure of a polymer can have significant if not dramatic effects on solubility in a supercritical fluid. The effect of the end group is still very significant at the highest $M_n$, and the methyl carbonate end group still dominates the solubility characteristics of the polymer. With a poor solvent such as $scCO_2$, tuning the polymer and the solvent may well change the solubility characteristics significantly, and this has a bearing on the development of $CO_2$-compatible surfactants.

The significance of the carbonate linker is also revealed in the topologically altered PVAc samples. Contrary to expectations, where branching consistently reduces cloud-point pressures, in this case solubility decreases with increased branching (Figure 9). With each increase in branching, a carbonate linker is added to relatively low molecular weight oligomers so that the diol-PVAc has a lower cloud-point pressure curve than the triol-PVAc sample, which is lower than the tetraol-PVAc sample whose cloud-point curve was above the pressure which could be achieved with our instrumentation. This confirms the observations with the end-group modified PVAcs that a carbonate linker has a deleterious effect upon solubility in $scCO_2$. For PVAc, end groups connecting the end group with a less polar linker than carbonate might have a positive effect upon solubility. An ether linkage with a short chain flexible end group, or better still an acetate end group, might be advantageous. The effect of end-group linker may also have a bearing on the performance of $CO_2$-philic surfactants with better performance resulting from $CO_2$-neutral linkers.

## Conclusions

It has been possible to fractionate PVAc with $scCO_2$ in order to produce a series of low molecular weight monofunctionalized fractions with narrow polydispersity. These may prove useful for applications where specific molecular weight $CO_2$ soluble oligomers are necessary.

The solubility of PVAc-OH is chiefly dependent upon molecular weight. End-group modification has an important effect upon solubility while the carbonate linker used to attach the end group and to alter topology has an even greater effect. The poor solubility of the methyl carbonate end group PVAc demonstrates the importance of using an optimal linker to the end group. Using an ether linkage with a short chain flexible end group or better still an acetate end group might be advantageous.

PVAc has the potential to act as the $CO_2$-philic moiety of a surfactant which will enable the use of $CO_2$ as a solvent, but the method of linking to this moiety should be carefully considered to ensure maximum $CO_2$ solubility. The solubility with end groups, discovered in this study, suggest that the nature of the end group should be carefully examined when seeking to discover $CO_2$-philic polymers. Certainly, low molecular weight polymers exhibit strong end-group effects.

**Acknowledgment.** We thank EPSRC for supporting this research (GR/R/26252 & GR/R/26276). A.I.C. thanks the Royal Society for a University Research Fellowship. B.T. thanks to National Natural Science Foundation of China for financial support (Nos. 20774032).

**Supporting Information Available:** $^1$H NMR of end-group modified oligo(vinyl acetate)s. This material is available free of charge via the Internet at http://pubs.acs.org.

## References and Notes

(1) DeSimone, J. M. *Science* **2002**, *297*, 799–803.
(2) Cooper, A. I. *J. Mater. Chem.* **2000**, *10*, 207–234.
(3) Desimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science* **1992**, *257*, 945–947.

(4) Desimone, J. M.; Maury, E. E.; Menceloglu, Y. Z.; McClain, J. B.; Romack, T. J.; Combes, J. R. *Science* **1994**, *265*, 356–359.

(5) Nalawade, S. P.; Picchioni, F.; Janssen, L. *Prog. Polym. Sci.* **2006**, *31*, 19–43.

(6) Wood, C. D.; Cooper, A. I.; DeSimone, J. M. *Curr. Opin. Solid State Mater. Sci.* **2004**, *8*, 325–331.

(7) Wood, C. D.; Tan, B.; Zhang, H.; Cooper, A. I. Supercritical Carbon Dioxide As a Green Solvent for Polymer Synthesis. In *Thermodynamics, Solubility and Enviromental Issues*; Letcher, T., Ed.; Elsevier: Amsterdam, 2007; pp 383−396.

(8) Wood, C. D.; Tan, B.; Lee, J.-Y.; Cooper, A. I. Emulsion-templated Porous Materials Using Concentrated Carbon Dioxide-in-Water Emulsions and Inexpensive Hydrocarbon Surfactants. In *Gas-Expanded Liquids and Near-Critical Media*; Hutchenson, K. W.; Scurto, A. M.; Subramaniam, B., Eds.; ACS Symposium Series1006; Oxford University Press: New York, 2008; pp 243−258.

(9) Cooper, A. I.; Hems, W. P.; Holmes, A. B. *Macromolecules* **1999**, *32*, 2156–2166.

(10) Lepilleur, C.; Beckman, E. J. *Macromolecules* **1997**, *30*, 745–756.

(11) Shaffer, K. A.; Jones, T. A.; Canelas, D. A.; DeSimone, J. M.; Wilkinson, S. P. *Macromolecules* **1996**, *29*, 2704–2706.

(12) Cooper, A. I.; Londono, J. D.; Wignall, G.; McClain, J. B.; Samulski, E. T.; Lin, J. S.; Dobrynin, A.; Rubinstein, M.; Burke, A. L. C.; Frechet, J. M. J.; DeSimone, J. M. *Nature* **1997**, *389*, 368–371.

(13) Chen, W. P.; Xu, L. J.; Hu, Y. L.; Osuna, A. M. B.; Xiao, J. L. *Tetrahedron* **2002**, *58*, 3889–3899.

(14) Kani, I.; Omary, M. A.; Rawashdeh-Omary, M. A.; Lopez-Castillo, Z. K.; Flores, R.; Akgerman, A.; Fackler, J. P. *Tetrahedron* **2002**, *58*, 3923–3928.

(15) Johnston, K. P. *Curr. Opin. Colloid Interface Sci.* **2000**, *5*, 351–356.

(16) Johnston, K. P.; Harrison, K. L.; Clarke, M. J.; Howdle, S. M.; Heitz, M. P.; Bright, F. V.; Carlier, C.; Randolph, T. W. *Science* **1996**, *271*, 624–626.

(17) Beckman, E. J. *Chem. Commun.* **2004**, 1885–1888.

(18) Raveendran, P.; Wallen, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 12590–12599.

(19) Kirby, C. F.; McHugh, M. A. *Chem. Rev.* **1999**, *99*, 565–602.

(20) Drohmann, C.; Beckman, E. J. *J. Supercrit. Fluids* **2002**, *22*, 103–110.

(21) Kazarian, S. G.; Vincent, M. F.; Bright, F. V.; Liotta, C. L.; Eckert, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 1729–1736.

(22) Sarbu, T.; Styranec, T.; Beckman, E. J. *Nature* **2000**, *405*, 165–168.

(23) Sarbu, T.; Styranec, T. J.; Beckman, E. J. *Ind. Eng. Chem. Res.* **2000**, *39*, 4678–4683.

(24) Hoogenboom, R.; Meier, M. A. R.; Schubert, U. S. *Macromol. Rapid Commun.* **2003**, *24*, 16–32.

(25) Tsukahara, T.; Kayaki, Y.; Ikariya, T.; Ikeda, Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 3719–3722.

(26) Tan, B.; Woods, H. M.; Licence, P.; Howdle, S. M.; Cooper, A. I. *Macromolecules* **2005**, *38*, 1691–1698.

(27) Raveendran, P.; Wallen, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 7274–7275.

(28) Shen, Z.; McHugh, M. A.; Xu, J.; Belardi, J.; Kilic, S.; Mesiano, A.; Bane, S.; Karnikas, C.; Beckman, E.; Enick, R. *Polymer* **2003**, *44*, 1491–1498.

(29) Tapriyal, D.; Wang, Y.; Enick, R. M.; Johnson, J. K.; Crosthwaite, J.; Thies, M. C.; Paik, I. H.; Hamilton, A. D. *J. Supercrit. Fluids* **2007**, *46*, 252–257.

(30) Fan, X.; Potluri, V. K.; McLeod, M. C.; Wang, Y.; Liu, J.; Enick, R. M.; Hamilton, A. D.; Roberts, C. B.; Johnson, J. K.; Beckman, E. J. *J. Am. Chem. Soc.* **2005**, *127*, 11754–11762.

(31) Tan, B.; Cooper, A. I. *J. Am. Chem. Soc.* **2005**, *127*, 8938–8939.

(32) Tan, B.; Lee, J.-Y.; Cooper, A. I. *Macromolecules* **2006**, *39*, 7471–7473.

(33) Lee, H.; Terry, E.; Zong, M.; Arrowsmith, N.; Perrier, S.; Thurecht, K. J.; Howdle, S. M. *J. Am. Chem. Soc.* **2008**, *130*, 12242–12243.

(34) Fedors, R. F. *Polym. Eng. Sci.* **1974**, *14*, 147–154.

(35) Shao, Z. J.; Farooqi, M. I.; Diaz, S.; Krishna, A. K.; Muhammad, N. A. *Pharm. Dev. Technol.* **2001**, *6*, 247–254.

(36) Bray, C. L.; Tan, B.; Wood, C. D.; Cooper, A. I. *J. Mater. Chem.* **2005**, *15*, 456–459.

(37) Wood, C. D.; Cooper, A. I. *Macromolecules* **2003**, *36*, 7534–7542.

(38) Licence, P.; Dellar, M. P.; Wilson, R. G. M.; Fields, P. A.; Litchfield, D.; Woods, H. M.; Poliakoff, M.; Howdle, S. M. *Rev. Sci. Instrum.* **2004**, *75*, 3233–3236.

(39) Wick, C. D.; Siepmann, J. I.; Theodorou, D. N. *J. Am. Chem. Soc.* **2005**, *127*, 12338–12342.

(40) Heller, J. P.; Dandge, D. K.; Card, R. J.; Donaruma, L. G. *Soc. Pet. Eng. J.* **1985**, *25*, 679–686.

(41) Kilic, S.; Michalik, S.; Wang, Y.; Johnson, J. K.; Enick, R. M.; Beckman, E. J. *Ind. Eng. Chem. Res.* **2003**, *42*, 6415–6424.