

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231700859>

Polymer CO₂ Solubility. Structure/Property Relationships in Polyester Libraries

ARTICLE *in* MACROMOLECULES · OCTOBER 2010

Impact Factor: 5.8 · DOI: 10.1021/ma1016055

CITATIONS

9

READS

46

4 AUTHORS, INCLUDING:



Bien Tan

Huazhong University of Science and Technol...

117 PUBLICATIONS 2,313 CITATIONS

SEE PROFILE

Polymer CO₂ Solubility. Structure/Property Relationships in Polyester Libraries

Christopher L. Bray,^{*,†} Bien Tan,^{*,†,‡} Sean Higgins,[†] and Andrew I. Cooper[†]

[†]Department of Chemistry and Centre for Materials Discovery, University of Liverpool, Crown Street, Liverpool L69 3BX, U.K., and [‡]School of Chemistry and Chemical Engineering, Huazhong University of Science & Technology Wuhan 4300074, China

Received July 16, 2010; Revised Manuscript Received October 3, 2010

ABSTRACT: There is a need for continuing development of CO₂-soluble polymers to be used as suitable surfactants, ligands, or phase transfer agents in CO₂ solvent processes. Identifying CO₂/polymer solubility trends will help to enhance the search for CO₂-soluble polymers. The synthesis and characterization of structurally diverse polyester libraries using high-throughput techniques combined with the use of a high-throughput gravimetric extraction (HTGE) technique for the measurement of polymer solubility in supercritical carbon dioxide has enabled the study of structure/CO₂ solubility relationships. Small structural changes in polyesters have significant effects on their CO₂ solubility. Branching in either the diacid moiety or diol moiety imparts a significant increase in solubility, and in particular, branching with acyl chains enhances solubility by as much as 20 times. The length of the acyl chain is significant with the solubility of the polymer increasing in a systematic way as the acyl chain length increases to 10 carbon atoms. There are odd/even effects on solubility relating to the number of carbon atoms in the diacid moiety of the polyester. The results provide pointers for the development of more soluble alkyl polymers useful as ligands for synthesis and polymerization in CO₂. The use of HTGE to examine the effect of small structural changes on the solubility of polymers in CO₂ suggests that a quantitative study of structure–property relationships of polymers is possible, leading to the understanding and ability to predict solubility properties.

Introduction

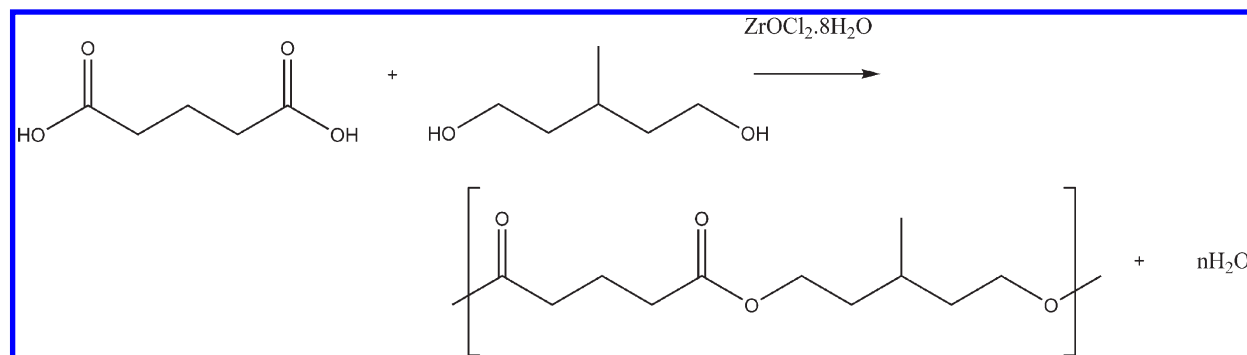
Carbon dioxide (CO₂) holds an ambivalent position for those who have concerns for the global environment. As a significant greenhouse gas there are those who are seeking to find a means to sequester it, and yet others, in seeking to reduce the impact of large-scale industrial processes, are looking for alternatives to volatile organic solvents. CO₂ (liquid or supercritical) may be an alternative to organic solvents.¹ It has the advantages of being nontoxic, nonflammable, and relatively inert; it does not form air-polluting daughter products and is relatively cheap and plentiful. CO₂ for supercritical fluid technologies is available in large quantities as a byproduct of fermentation, combustion, and ammonia synthesis.² Its use in industrial processes can be considered an effective way to sequester or even to continuously recycle; thus, there may be no net environmental impact.^{3,4} Supercritical carbon dioxide (scCO₂) has already been used as a solvent for a wide range of industrial processes, including synthesis and polymerization, materials processing, biomaterials fabrication, film deposition, lithographic processes, and catalysis.^{1,5–10} Until recently, the only polymers found to have significant solubility in CO₂ under moderate conditions (< 100 °C, < 400 bar) were amorphous fluoropolymers and to a lesser extent polysiloxanes. The associated costs and low biodegradability prohibit industrial-scale use in key applications.¹¹ Considerable research effort has gone into finding CO₂-philic alkyl polymers which can be used to form surfactants, and there has been some success, but a full understanding of the polymer/CO₂ solubility system remains elusive.^{12–20} Poly(vinyl acetate) has been shown to exhibit reasonably high solubility in carbon dioxide although recently

a 50:50 random copolymer of vinyl acetate and vinyl butyrate (PVAc–PVB) and a copolymer of vinyl acetate and dibutylmaleate (PVAc-*alt*-PDBM) have been shown to exhibit higher solubility.^{21,22}

Carbon dioxide is a nonpolar solvent characterized by a low polarizability per volume, a low Hildebrand solubility parameter, and a low dielectric constant.^{1,2} These values suggest similarities with saturated organic solvents. Near the critical point, there is a significant change in density with pressure although the change in the absolute value is small. Because of these properties, it was commonly thought that only volatile or relatively nonpolar compounds would be soluble in CO₂. But because of structural symmetry, CO₂ also possesses a significant quadrupole moment and the ability to act as a weak Lewis base or a weak Lewis acid. This quadrupole moment operates over a much shorter distance than dipolar interactions. Because CO₂ is a dense solvent at modest temperatures and pressures, the quadrupolar interactions are magnified and scale with inverse molar volume to the ⁵/₆ power.²³ This has implications for its solvent power in that it needs close access to polar parts of potential solutes in order to have effective interaction. Kauffman has suggested that the solvent properties of this quadrupolar solvent are not easily predicted.²⁴ But in general, the solvent power of scCO₂ depends chiefly on its density, the temperature, and the intermolecular interaction between the solvent and solute. The pressures and temperatures needed to dissolve a polymer in CO₂ depend on the intermolecular forces between solvent–solvent, solvent–polymer segment, and polymer segment–segment pairs in solution as given by the interchange energy and on the free volume difference between the polymer and CO₂.²⁵ CO₂ is a weak solvent for nonpolar polymers since CO₂ quadrupolar interactions dominate the interchange energy as the temperature is lowered. Conversely,

*To whom correspondence should be addressed.

Scheme 1



CO₂ is a feeble solvent for very polar polymers since dipole interactions outweigh quadrupole interactions, especially at low temperatures where polar interactions are magnified. Finding a favorable balance for the interaction of polymers with CO₂ is difficult, and it remains a challenge to predict the solvent properties of CO₂ quantitatively since solution theories that describe intermolecular interactions between solvents and solutes in a dense fluid state are still poorly developed.²³

The creation of libraries of polymers enables the study of structure/SCF solubility trends. Until recently, the lack of a rapid solubility testing technique has prevented much systematic study of structure/SCF solubility relationships.^{26,27} Three polyester libraries are examined in this paper: (1) A library of 300+ linear alkyl polyesters. (2) A library of 35 poly(glycerol adipate)s acylated with different degrees of C8 or C18 acyl chains and with varying degrees of acylation; 0%, 20%, 40%, 60%, 80%, and 100% poly(glycerol adipate)s with three different molecular weights were used. The starting structures were based on approximately 52, 40, and 20 repeat units, giving molecular weights of 10 400, 8000, and 4000 g mol⁻¹, respectively. Exact stoichiometric amounts of acid chlorides were used to vary the degree of acylation. (3) A library of six poly(glycerol adipate)s acylated with C0, C2, C4, C6, C8, and C10 acyl branches with 100% acylation. The starting poly(glycerol adipate) structure has ~54 repeat units (*M_w* 10 900 g mol⁻¹).

The solubility of these libraries has been tested using a high-throughput gravimetric extraction technique (HTGE),²⁶ and the structure–solubility relationships were examined within and among the libraries.

Experimental Section

Materials. For the polyester library, diacids, diols, and zirconium(IV) oxychloride octahydrate from Sigma-Aldrich were used as received. For the acylated poly(glycerol adipate)s, novozyme 435 (a lipase derived from *Candida antarctica* and immobilized on an acrylic macroporous resin) from Novozyme Co., Denmark, was stored over P₂O₅ at 5 °C prior to use. Divinyl adipate (Fluorochem, UK) was used as received. Acid chlorides were synthesized, by standard procedures, from the parent carboxylic acid using thionyl chloride and distilled prior to use. All other chemicals and reagents (Sigma-Aldrich) were used as received except tetrahydrofuran (THF), which was freshly distilled from sodium/benzophenone ketyl prior to use, and pyridine, which was distilled from KOH prior to use. Carbon dioxide used was BOC N5.5 SFC carbon dioxide DIN 6, 285970-AK-C.

Polyester Synthesis. Polyesters were synthesized by direct condensation of diacids with diols using small amounts of catalyst. Scheme 1 shows a typical reaction.

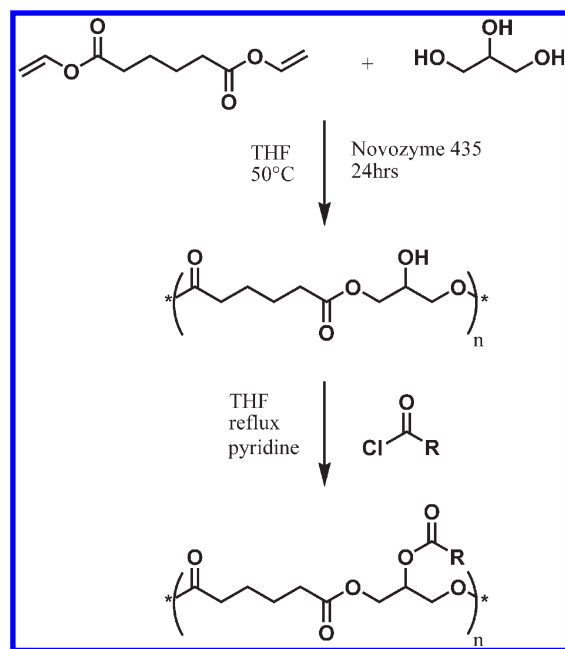
1. *Library of 300+ Linear Alkyl Polyester Preparation.* For the linear alkyl polyester library, two methods of synthesis were employed: (a) using a Büchi Syncore 24 well reactor and

(b) using a CEM Discover microwave reaction station. Both systems were suitable for making linear alkyl polyesters, the CEM Discover was used particularly for library members which presented particular synthetic difficulty.

a. *Using a Büchi Syncore 24 Well Reactor.* A typical procedure using the Büchi Syncore 24 well reactor is as follows. Glutaric acid (1.321 g, 10 mmol) was weighed into a flame-dried custom boiling tube. The catalyst, zirconyl chloride (ZrOCl₂·8H₂O) (25 mg, 0.8 mol %), was added, and then 3-methyl-1,5-pentanediol (1.181 g, 10 mmol) was added. 1,4-Dioxane, anhydrous (4 mL), was added using the Syncore filtration unit, and the mixture was agitated on the reaction stage for 30 min at 400 rpm at 50 °C to ensure thorough mixing. The mixture was placed under increasing vacuum for up to 2 h to remove the solvent, and then the temperature was increased to 150 °C at < 2 mbar pressure for 12 h. Twenty-four reactions were performed in parallel. The reaction was returned to atmospheric pressure and allowed to cool. The products were dissolved in chloroform with the solvent being added using the Syncore filtration unit and precipitated into diethyl ether. The precipitate was dried in parallel in a Genevac personal evaporator and dried overnight at 40 °C in a vacuum oven.

b. *Using a CEM Discover Microwave Reaction Station.* A typical procedure using the CEM Discover microwave reactor is as follows. Glutaric acid (1.321 g, 10 mmol) was weighed into a flame-dried custom boiling tube. The catalyst, zirconyl chloride (ZrOCl₂·8H₂O) (25 mg, 0.8 mol %), was added and then 3-methyl-1,5-pentanediol (1.181 g, 10 mmol) was added. A Teflon-coated magnetic stirrer bar was added, and the tube placed in the reactor with a fitting through which N₂ could be passed. The system was flushed with N₂ for 1 min before the reaction was started. The CEM microwave system was set in Open Vessel mode at 250 W and temperature at 200 °C. The run time (during which the temperature reached its set temperature) was set at 5 min, and the hold time was set at 20 min. After air cooling ≈ 150 s, the polymer was dissolved in chloroform and precipitated into diethyl ether. The polymer was dried in parallel in a Genevac personal evaporator and dried overnight at 40 °C in a vacuum oven.

2. *Acylated Poly(glycerol adipate) Libraries Synthesis.* Polymers were synthesized following a literature procedure.²⁸ For the backbone poly(glycerol adipate), a typical procedure was as follows. An oven-dried 500 mL three-necked RB flask, equipped with a center stirrer guide, and an open topped condenser, to act as an outlet for the acetaldehyde produced, was charged with divinyl adipate (49.55 g, 250 mmol), glycerol (23.38 g, 250 mmol), and anhydrous THF (20 mL). The mixture was stirred for 30 min to allow the reactants to warm to the water bath temperature (50 °C). The enzyme complex (1.45 g (2% monomer weight)) was then added, and the mixture was stirred for 24 h (200 rpm using an overhead stirrer fitted with a Teflon stirrer paddle). The enzyme complex was then removed by filtration, washing with a further 50 mL of THF. The solvents were removed by rotary evaporation (final bath temperature set at

Scheme 2. Synthesis of Poly(glycerol adipate) and Its Subsequent Acylation Reaction

100 °C to deactivate any free enzyme) to yield ca. 45 g of the polyester as a pale viscous liquid, which was used without further purification. Enzyme contact time was varied to achieve various molecular weights.

3. Acylation of Poly(glycerol adipate) Library Preparations. Acylation of poly(glycerol adipate) was achieved by reaction of a percentage of the pendant hydroxyl groups with acid chlorides using pyridine as a catalyst and acid scavenger.²⁸ A typical procedure for 100% C2 acylated poly(glycerol adipate) is as follows. A 250 mL Radleys round-bottom flask was charged with poly(glycerol adipate) (9.55 g, 47.23 mmol) and anhydrous THF (100 mL). The contents were warmed to reflux to ensure the entire polymer was dissolved. A solution of ethanoyl chloride (4.45 g, 57.00 mmol, 1.2 equiv) in 5 mL of THF was added to the colorless refluxing solution. A further 50 mL of THF was added followed by the slow addition of 10 mL of pyridine, which initiated the formation of a white precipitate. The reaction was left to stir, at reflux, overnight and then poured into a 500 mL separating funnel containing 100 mL of water, 2 mL of concentrated HCl, and 150 mL of chloroform. After careful mixing, the organic layer was collected. The upper aqueous layer was extracted with a further 50 mL of chloroform. The combined organics were washed with a mixture of 100 mL of water and 2 mL of concentrated HCl, followed by 2 × 200 mL of water. The organic layer was dried over MgSO₄, and the chloroform was removed by rotary evaporation to yield the title product as a yellow viscous liquid 8.78 g (76%). Scheme 2 shows the synthesis of poly(glycerol) adipate and subsequent acylation.

Polymer Characterization. Characterization of the polyester libraries was performed using gel permeation chromatography (GPC) to determine molecular weight. Measurements were confirmed using a Polymer Labs GPC with a PL-ES 1000 evaporative light scattering detector with a series of PC mix gel columns 5 μm Mixed C and D using THF as eluent at a flow rate of 1.0 mL min⁻¹ at 40 °C. Calibration was performed with Polymer Labs EasiCal polystyrene standards in the range MW 580–7 500 000 g mol⁻¹. For the polyester library NMR, ¹H and ¹³C were recorded on a Bruker Avance 400 MHz. For the acylated poly(glycerol adipate) libraries, MALDI-TOF data were collected on an Applied Biosystems QSTAR (Q-ToF) mass spectrometer. Samples were dissolved at a concentration of 10 mg mL⁻¹ using a matrix of dithranol and silver trifluoroacetate.²⁹ The NMR spectra were recorded on a Bruker DPX 250 MHz

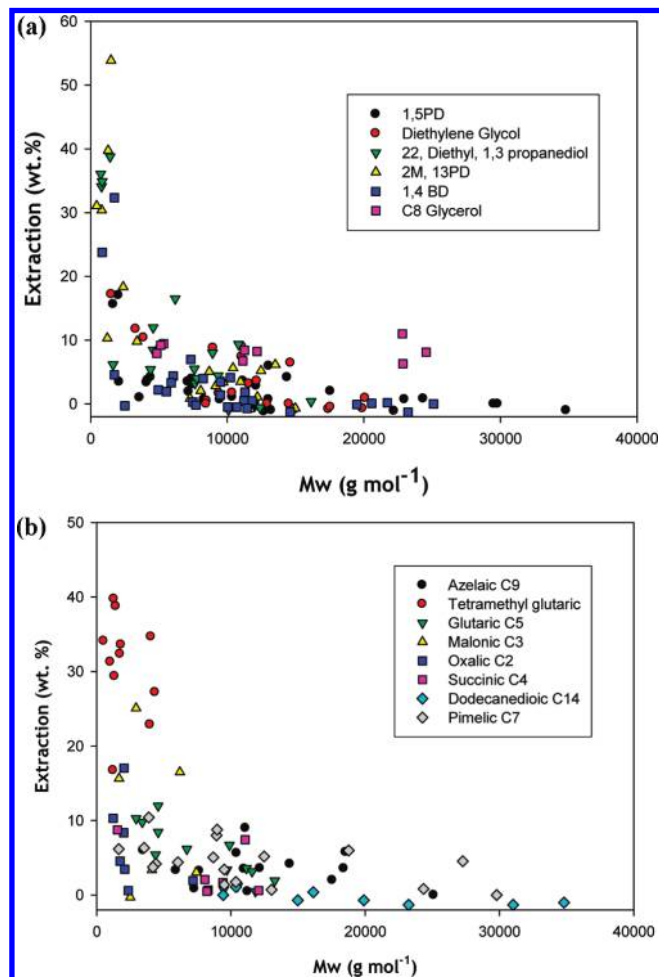


Figure 1. (a) Effect of diol moiety on extraction at 200 bar in scCO₂. (b) Effect of diacid moiety on extraction at 200 bar in scCO₂. The rapid decline in extractability with increasing *M_w* shows the most that it is the most significant factor for polymer solubility. For structures of the diacid and diol moieties, see Supporting Information Figure S1.

spectrometer. FT-IR spectra were collected using a Perkin-Elmer Spectrum BX spectrometer fitted with a PIKE Technologies MIRacle sampling accessory and using Spectrum v 5.0.1 for data storage and processing. The samples were scanned over 4000 to 600 cm⁻¹.

Solubility Measurement in scCO₂. The solubility of the polymers was determined using the high-throughput gravimetric extraction method (HTGE) described elsewhere.²⁶ Briefly, polymer samples (ca. 100 mg) were weighed into flame-dried open tubes and double wrapped with Milliwrap and loaded into a specially designed sample holder which will accept up to 72 tubes on this scale. These were extracted using a Thar supercritical fluid extractor at 100 and 300 bar for 4 h at 10 g min⁻¹ CO₂ at 35 °C for part a and at 200 and 400 bar for 6 h at 20 g min⁻¹ CO₂ at 35 °C for part b. Depressurization was controlled using a computer-programmed automated script and maintained at 5 bar min⁻¹. After each extraction samples were stored overnight in a desiccator before the samples were reweighed individually to determine percentage mass loss. This provides a measure of solubility of the polymer samples. Unlike cloud point measurements, this HTGE technique does not give an absolute measure of the miscibility pressure of the samples with CO₂. Indeed, one should be cautious about drawing overly simple correlations between the percentage material extracted and the thermodynamic “solubility” of the samples. However, our previous studies using this method have shown results comparable with conventional cloud point measurements, good reproducibility, and the

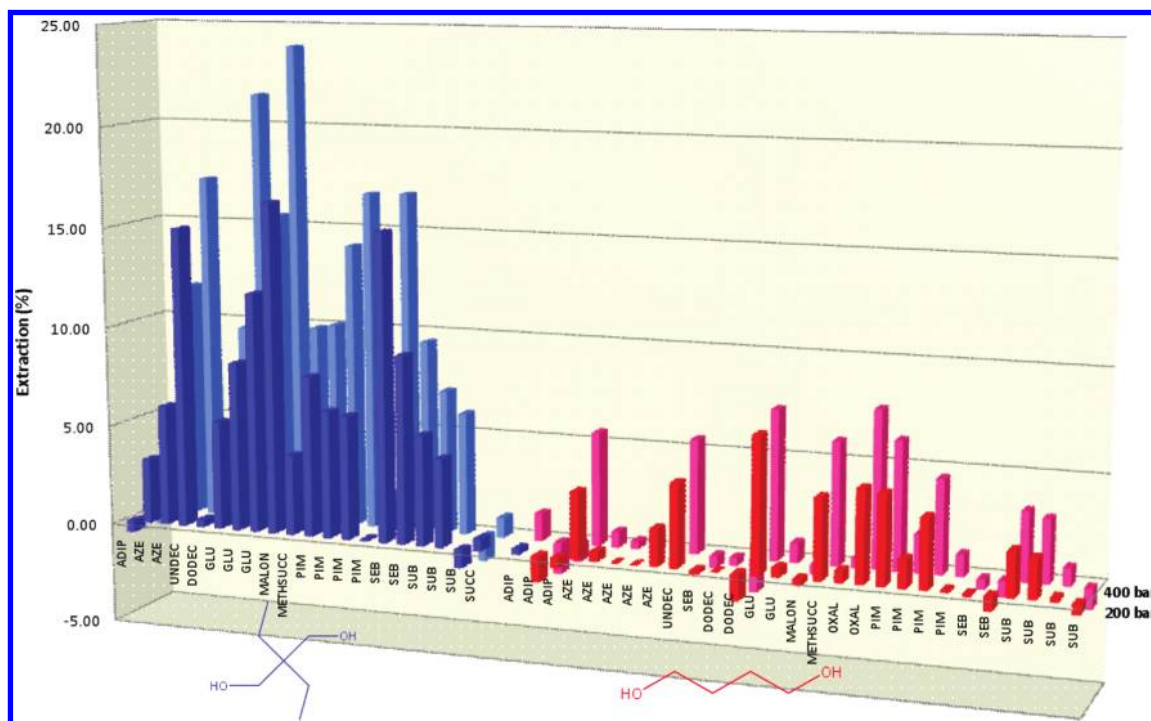


Figure 2. Effect of diol moiety on the extraction of polyesters in scCO_2 . Comparison of 2,2-diethyl-1,3-propanediol with 1,4-butanediol. Each sample represents a different polymer distinguished by diacid moiety and/or molecular weight. Polyesters with a branched diol moiety have an enhanced solubility.

ability to distinguish the solubilities among poorly soluble polymers.^{26,27}

Results and Discussion

1. Solubility of Linear Alkyl Polyesters. Linear alkyl polyesters are produced from the condensation of a diacid moiety with a diol moiety. Subtle variations of either moiety influence solubility in scCO_2 . Figure 1 shows the effect of the diol and diacid moieties on solubility in scCO_2 .

The overall trends show that extraction falls rapidly with increasing molecular weight.

Polyesters containing straight-chain diols such as 1,4-butanediol and 1,5-pentanediol show particularly poor extractability (Figure 2).

Typically, these produce polyesters which are crystalline solids at room temperature.³⁰ Those polyesters which have some branching in the diol moiety such as 2,2-diethyl-1,3-propanediol and 2-methyl-1,3-propanediol and in particular C8 acylated glycerol show higher levels of extractability, which reflects their greater free molar volume, reduced close packing of polymer chains, and their lower melting points.^{31–33} The presence of an ether link in the diol chain provides extra flexibility which increases extraction although the effect of the extra flexibility may be mitigated by a change in the electronegativity of the moiety (Supporting Information Figure S2). Table 1 shows the abbreviations used in this paper.

Further examination of the library suggests that there are odd–even effects relating to the number of carbon atoms in the diacid moiety of the polyester. Odd–even effects in physical properties such as T_g , T_m , crystallinity, and chain packing arrangements in linear polyesters have been noted in the literature.^{34–40} Polyesters with an odd number of carbon atoms in the diacid moiety tend to exhibit more extractability than the even-numbered members of the library (Figure 3 and Supporting Information Figure S3). The effect seems

Table 1. Abbreviations Used for Diol and Diacid Moieties

| name | abbreviation |
|---------------------------------|---------------------|
| 1,3-propanediol | 1,3-PD |
| 1,4-butanediol | 1,4-BD |
| 1,5-pentanediol | 1,5-PD |
| 3-methyl-1,5-pentanediol | 3-M-1,5-PD |
| 2-methyl-1,3-propanediol | 2-M-1,3-PD |
| 1,3-cyclohexanediol | 1,3-CyclHex |
| 2,2-diethyl-1,3-propanediol | 2,2-dieth-1,3-PD |
| 2,2'-oxidiethanol | diethylene glycol |
| 1,3-propanediol-2-octonate | C8 glycerol |
| oxalic acid | oxalic C2 |
| malonic acid | malonic C3 |
| succinic acid | succinic C4 |
| glutaric acid | glutaric C5 |
| adipic acid | adipic C6 |
| pimelic acid | pimelic C7 |
| sebacic acid | sebacic C8 |
| undecanedioic acid | und C11 |
| dodecanedioic acid | dodec C12 |
| 2,2-oxidiacetic acid | diacetic |
| 2-methylsuccinic acid | 2-M-succinic |
| 2,3-dimethyl succinic acid | 2,3-M-succinic |
| 3,3-tetramethyleneglutaric acid | tetramethylglutaric |
| 3-methylglutaric acid | 3-M-glutaric |
| 3-methyladipic acid | 3-M-adipic |

to be observed most clearly with shorter chain diacids. In Figure 3 only one adipic acid polymer has a similar extractability to the glutaric acid polymers. This is a low molecular weight polymer where the diol is 1,3-cyclohexanediol, a particularly bulky diol. The difference may be associated with the way that the polymer chains pack and the influence this has on microcrystallinity, T_g , and chain flexibility.

The extractions were performed at two pressures: 200 and 400 bar. Where there is some extraction at 200 bar, the extraction is generally further increased at 400 bar. Where there is little extraction at 200 bar, there is very little increase at 400 bar

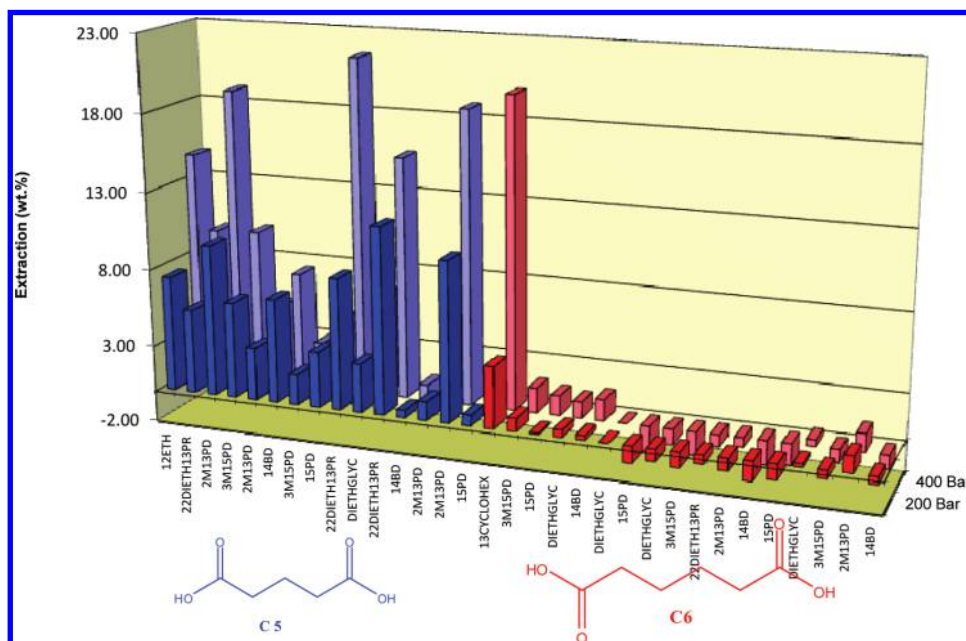


Figure 3. Odd–even effect of diacid on extractability of polyesters in scCO_2 . Glutaric (C5) and adipic (C6) diacid moieties. Each entry represents a different polymer sample distinguished by diol moiety and molecular weight.

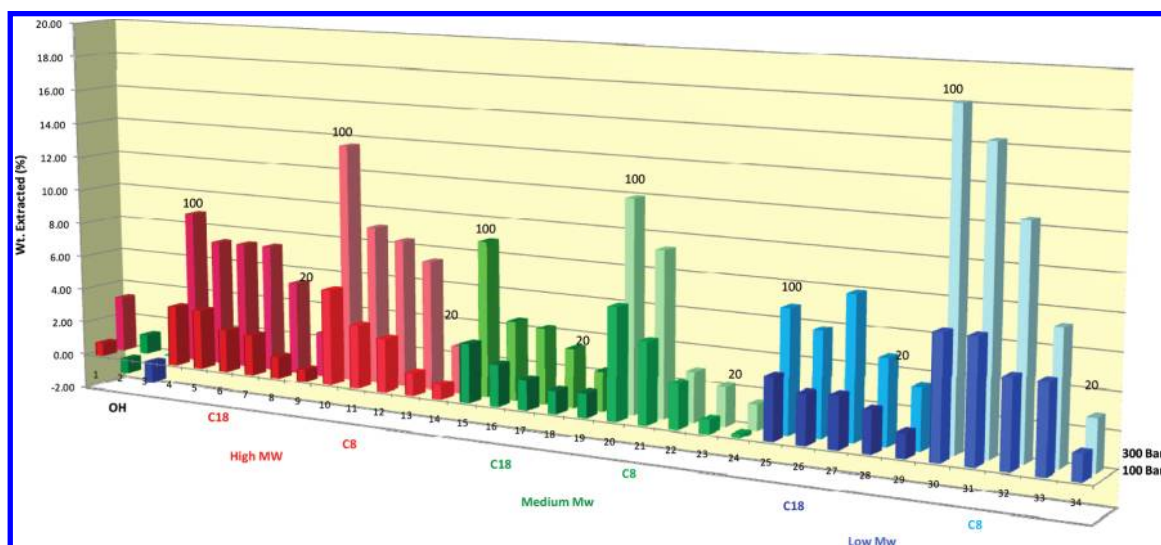


Figure 4. Solubility of 33 acylated poly(glycerol adipate)s, acylated with C18 or C8 chains from 100% acylation to 0% acylation. In each color group the degree of acylation decreases from 100 to 20% from left to right. The first three samples are the unacylated polymers of high, medium, and low molecular weight, respectively. C8 acylated polyesters show enhanced solubility over C18 acylated polyesters. Poly(glycerol adipate) without acylation is very poorly soluble, and solubility increases with the degree of acylation. Lower molecular weight acylated polymers exhibit the greatest solubility. Sample 9 is a control repeat of sample 1. The extractions are at 100 and 300 bar.

(Figure 3, right-hand side). There will always be some uncertainty though about predicting the differences in solubility between two pressures as precise differences in polydispersity of the polymers cannot be analyzed in libraries such as these.

2. Solubility of Acyl Branched Polyesters. Straight-chain alkyl polyesters exhibit poor CO_2 solubility, but poly(glycerol ester)s have the potential for further modification and the possibility for enhanced CO_2 solubility. There is a principle that weaker solvents magnify the effects of polymer architecture and properties on phase behavior.^{23,41}

i. Effect of Degree of Acylation on Solubility in scCO_2 . Acylating poly(glycerol adipate)s with linear aliphatic moieties has a dramatic effect upon extraction in scCO_2 (Figure 4). Poly(glycerol adipate)s with secondary hydroxyl groups show very little solubility. At 100 bar the lower molecular

weight starting backbone polymers absorb small amounts of CO_2 (samples 2 and 3) and so result in a weight gain during extraction.^{26,27} This reversal of the usual trend for greater extraction may be the result of enhanced influence of the polar end groups at lower M_w and the dominating influence of the hydroxyl groups on these unacylated polymer samples. The amount extracted at both 100 and 300 bar varies consistently with the degree of acylation. 100% acylation produces the greatest extraction.

ii. Effect of the Length of Acylation Chain and Molecular Weight. The length of the acylation chain has an influence on the degree of solubility. Solubility is greater with a C8 branch than it is with a C18 branch. There is greater extraction of acylated poly(glycerol adipate)s of lower molecular weight. Maximum extraction (18.1%) was obtained with extraction

at 300 bar—a C8 100% acylated low- M_w poly(glycerol adipate) (sample 30 in Figure 4). Comparison of the extractions at 100 and 300 bar shows that there is a significant increase in extraction at the higher pressure with those samples which show greater extraction at 100 bar, showing a proportionately greater increase at 300 bar. Increasing pressure increases the solvent density, thus improving the solvent effectiveness.

The presence of secondary hydroxyl groups on a poly(glycerol adipate) polyester provides an environment that is very unfavorable to polymer solubility in CO_2 , so that the solubility is equivalent to that for most linear adipic acid polyesters. Kirby and McHugh²³ contend that hydrocarbon polymers must have some polarity to dissolve in CO_2 , but very polar polymers are not expected to dissolve in CO_2 . Achieving the necessary balance of polarity is difficult. The hydroxyl group on each repeat unit will confer considerable polarity to the overall polymer, ensuring poor solubility in scCO_2 . Fourie et al. found that changing the position of the hydroxyl group on C₈ alcohols affected solubility in supercritical CO_2 .⁴² Decreasing the polarity of the molecule by shifting the hydroxyl group nearer the center of the molecule resulted in enhanced solubility. Acylating the polyester with a C8 or C18 chain will have a number of effects. Acylation will reduce the overall polarity of the polymer. Acylation adds a chain branch to the polymer; this increases the free volume of the polymer which enhances solubility in a supercritical solvent.⁴³ Branching also reduces the intermolecular interactions between polymer segments that arise through short-range molecular orientation offered by a high content of linear segments without pendant groups.⁴¹ This should enhance solubility. Acylation adds a carbonyl group. These are electron-donating and have specific interactions with CO_2 . The carbon atom of the CO_2 acts as an electron acceptor, and the carbonyl oxygen acts as an electron donor.^{44,45} These interactions will tend to increase miscibility. Polyesters have a regular carbonyl group at each ester linkage along the chain, but this does not seem to increase solubility in scCO_2 . The placing of the carbonyl group in the acyl chain allows for some accessibility to carbon dioxide. As the branch chain length increases, the effective polarity decreases since dipole interactions scale inversely with the square root of molar volume.²⁵ This should result in an optimum length for a chain before polarity is reduced too much or before steric hindrance affects the accessibility of the carbonyl group. In this case it would appear that a C18 chain is beyond the optimum length. Han et al. found that cloud point pressures are *reduced* as the length of the branch increased from methyl to butyl in branched ethylene copolymers in sub- and supercritical propane.⁴⁶ This is, of course, a free volume effect rather than due to a change in polarity. For poly(alkyl acrylate)s cloud point pressures are *increased* as branch chain length increases.⁴⁷ But this effect may be the result of the poor accessibility of the carbonyl group in poly(alkyl acrylate)s which is exacerbated as the alkyl chain length increases. Increasing the percentage of acylation on the polymer not only decreases the polarity of the polymer background but also increases the total amount of branching. It has been observed by Krukons and co-workers with linear low-density polyethylene in supercritical ethane that increasing the degree of branches reduces cloud points.⁴¹ Chen et al. demonstrated the effect of ethyl branches on the cloud point pressure of hydrogenated polybutadiene in propane.⁴⁸ An increased number of branches enhanced miscibility. This was attributed to a lowering of the segment energy which made it closer to propane, thus enabling miscibility. Similarly, Spahl and Luft found with low-density polyethylene in ethylene that cloud point pressures reduced

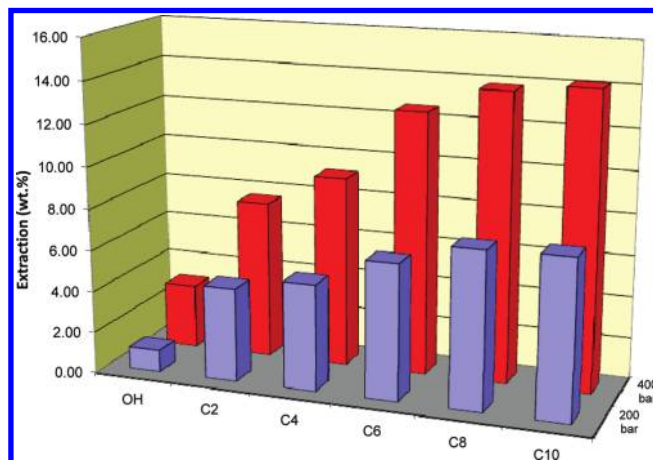


Figure 5. Extraction of 100% acylated poly(glycerol adipates) with chains varying from C2 to C10.

as the degree of branching increased.⁴⁹ This study confirms this trend by showing a similar effect with polyesters. The effect may well be twofold, that is, reduction in polarity as the hydroxyl group is replaced and reduction of segment energy as interactions are reduced.

Acylating poly(glycerol adipate) with short chains enhances the solubility in scCO_2 dramatically. It is likely that the effect is due to a number of factors:

Altering the overall polarity of the polyester—the stepwise increase in solubility with increased degree of acylation suggests this. The effect of a branch which increases the free molar volume will also enhance solubility. The presence of an accessible carbonyl group in a short chain provides a component to the polymer which has a particular affinity to CO_2 as is the case with PVAc.^{44,50–53} Reducing the intersegmental energy creates a closer match with scCO_2 .

The confirmation of the significance of branching in a linear polymer in both degree and length suggests that further libraries with varying degrees of branching and varying lengths and polarities would be a fruitful exercise in the search for CO_2 -soluble polymers.

3. Solubility of C2–C10 Acylated Poly(glycerol adipates).

This part of the study examines the effect of altering the length of the acylation chain from C2 to C10. Figure 5 summarizes the results of the extraction of six poly(glycerol adipate)s with acyl chains with lengths from C2 to C10. The results show a steady increase in extractability in CO_2 at both 200 and 400 bar as the acyl chains increase in length from C2 to C10.

The increase in extractability as the branch increases from C2 to C10 suggests that the continuing decrease in polarity and increase in free molar volume enhances extractability. As the branch increases in length, the effective charge on the carbonyl group is lessened, altering the polarity of the polymer. At some point (before C18) there will be a falloff of extractability as increasing branch chain length limits accessibility of CO_2 to the carbonyl group. The location of the carbonyl group and its accessibility are significant. The great difference in solubility between the isomers poly(vinyl acetate) (PVAc) and poly(methyl acrylate) (PMA) suggests that it is critical.^{44,54} The slightly higher T_g of PVAc is a reflection of stronger polar interactions between vinyl acetate groups as compared to methyl acrylate groups when these are tethered to a polymer chain. CO_2 can more easily access the carbonyl group in PVAc than in PMA, which makes PVAc more soluble in CO_2 with decreasing temperature.²³

Comparison of the C2–C10 acylated poly(glycerol adipate)s with some of the C8 polymers in the first investigation

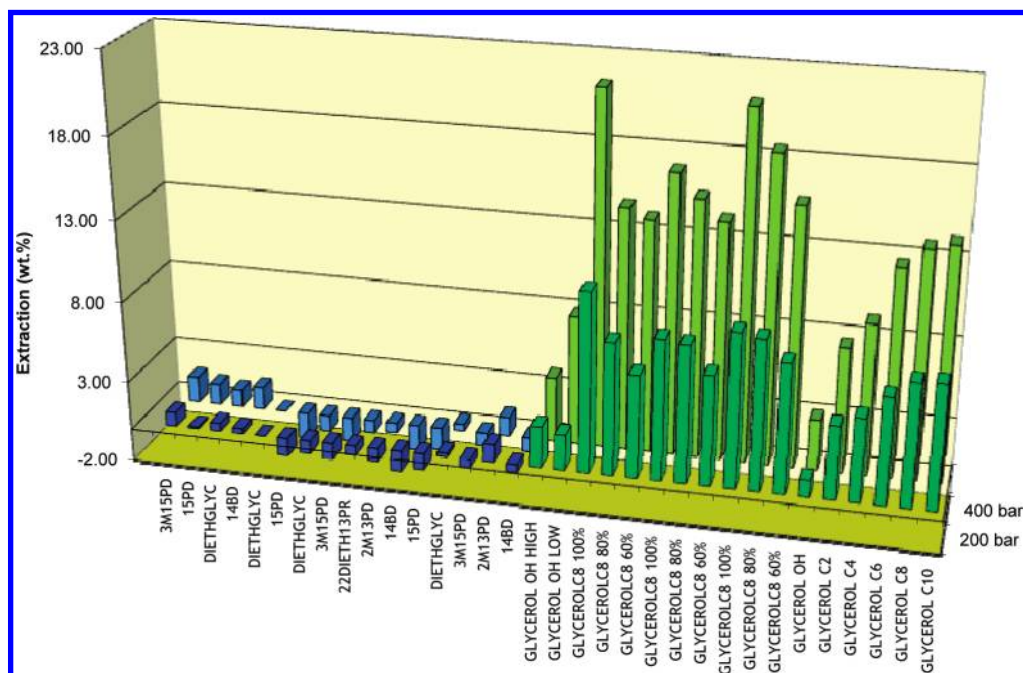


Figure 6. Comparison the solubility of C2–C10 acylated poly(glycerol adipates) with other adipate polyesters. Green bars = acylated adipic polyesters; blue bars = adipic acid polyesters with a variety of diol moieties.

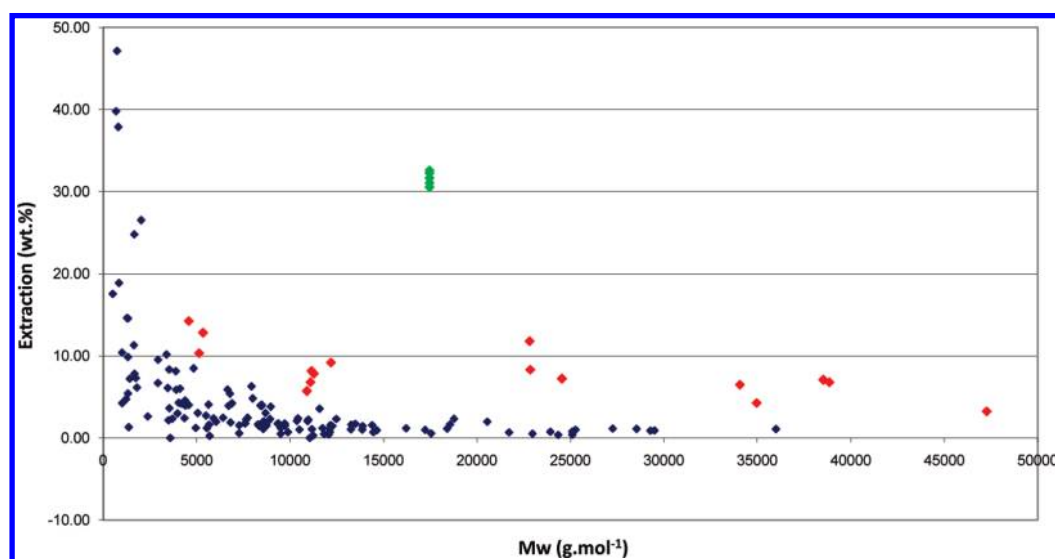


Figure 7. Extraction in scCO_2 of a polyester library vs M_w . The diagram shows the extraction at 400 bar after previous extraction at 200 bar. The PVAc internal standards (green, 10 values) show good reproducibility between runs. Acylated poly(glycerol adipate)s (red) show enhanced solubility compared with linear alkyl polyesters (blue) of comparable molecular weight.

(Figure 6, right-hand side) shows that there is slightly less extraction, but the earlier polymers were all of a lower M_w . Further comparison with adipate polymers polymerized with a range of other diols shows how the acylation of the adipic polymer enhances solubility by at least 20 times (Figure 6).

Summary and Conclusions

Linear alkyl polyesters have very little solubility in scCO_2 . Nevertheless, variations in solubility resulting from small structural changes can be discerned. Branching in either the diacid moiety or diol moiety imparts a significant increase in solubility, and in particular, branching with acyl chains enhances solubility by as much as 20 times. The length of the acyl chain is significant with the solubility of the polymer increasing as the acyl chain

length increases to 10 carbon atoms. There is an odd–even effect observed with the diacid moiety. Those polyesters with an odd number of carbon atoms between ester groups exhibit enhanced solubility. The possibility of designing alkyl polyesters with increased frequency of acyl branching of varying lengths is likely to result in solubilities which match or exceed that of PVAc which should increase the number of uses for CO_2 as a solvent.

Figure 7 shows that acylated alkyl polyesters have a significantly increased solubility compared to linear alkyl polyesters. But for these polymers to be useful in applications such as surfactants, phase transfer catalysts, or ligands in scCO_2 , their level of solubility would need to match or exceed that of PVAc. At present, even the acylated polyesters fall short of that standard although further refinement is possible. PVAc and related copolymers remain the gold standard for alkyl polymer solubility in scCO_2 (Figure 7), but the findings in this study could be applied to

the modification of those polymers and their solubility and range of applications could be extended.

The use of a HTGE method for CO₂ solubility opens up the possibility for rapid solubility measurements of large polymer libraries. The synthesis of polymer libraries with low polydispersity and precise chemical composition should enable quantitative structure–property relationships to be studied. It should be possible to predict the structures of highly soluble polymers and enhance the theoretical understanding of polymer solubility in scCO₂.

Acknowledgment. We thank EPSRC for supporting this research (GR/S16744/01) and the Royal Society for a Research Fellowship to A.I.C.

Supporting Information Available: Characterization data, monomer structures, and additional supporting diagrams. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Cooper, A. I. *J. Mater. Chem.* **2000**, *10*, 207–234.
- (2) Pitter, S.; Dinjus, E.; Ionescu, C.; Maniut, C.; Makarczyk, P.; Patcas, F. *Top. Organomet. Chem.* **2008**, *23*, 109–147.
- (3) Cooper, A. I.; L., J. D.; Wignall, G.; McClain, J. B.; Samulski, E. T.; Lin, J. S.; Dobrynin, A.; Rubinstein, M.; Burke, A. L. C.; Fréchet, J. M. J.; DeSimone, J. M. *Nature* **1997**, *389*, 368–371.
- (4) McCluskey, G. E.; Lee, J.-K.; Sha, J.; Ober, C. K.; Watkins, S. E.; Holmes, A. B. *MRS Bull.* **2009**, *34* (2), 108–115.
- (5) Rayner, C. M. *Org. Process Res. Dev.* **2007**, *11* (1), 121–132.
- (6) Kendall, J. L.; Canelas, D. A.; Young, J. L.; De Simone, J. M. *Chem. Rev.* **1999**, *99*, 543–563.
- (7) Kazarian, S. G. *Polym. Sci., Ser. C* **2000**, *42* (1), 78–101.
- (8) Baiker, A. *Chem. Rev.* **1999**, *99*, 453–474.
- (9) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1999**, *99*, 475–493.
- (10) Mesiano, A. J.; Beckman, E. J.; Russell, A. J. *Chem. Rev.* **1999**, *99*, 623–634.
- (11) Beckman, E. J. *Chem. Commun.* **2004**, *17*, 1885–1888.
- (12) Lee, J.-Y.; Tan, B.; Cooper, A. I. *Macromolecules* **2007**, *40* (6), 1955–1961.
- (13) Kilic, S.; Michalik, S.; Wang, Y.; Johnson, J. K.; Enick, R. M.; Beckman, E. J. *Macromolecules* **2007**, *40*, 1332–1341.
- (14) Gregory, A. M. T.; K. J.; Howdle, S. M. *Macromolecules* **2008**, *41*, 1215–1222.
- (15) Drohmann, C.; Beckman, E. J. *J. Supercrit. Fluids* **2002**, *22* (2), 103–110.
- (16) Tapriyal, D.; Wang, Y.; Enick, R. M.; Johnson, J. K.; Crosthwaite, J.; Thies, M. C.; Paik, I. H.; Hamilton, A. D. *J. Supercrit. Fluids* **2008**, *46* (3), 252–257.
- (17) Hong, L.; Tapriyal, D.; Enick, R. M. *J. Chem. Eng. Data* **2008**, *53*, 1342–1345.
- (18) Tan, B.; Cooper, A. I. *J. Am. Chem. Soc.* **2005**, *127*, 8938–8939.
- (19) Tan, B.; Lee, J.-Y.; Cooper, A. I. *Macromolecules* **2007**, *40*, 1945–1954.
- (20) Kilic, S.; Wang, Y.; Johnson, J. K.; Beckman, E. J.; Enick, R. M. *Polymer* **2009**, *50* (11), 2436–2444.
- (21) Lee, H.; Terry, E.; Zong, M.; Arrowsmith, N.; Perrier, S.; Thurecht, K. J.; Howdle, S. M. *J. Am. Chem. Soc.* **2008**, *130* (37), 12242–12243.
- (22) Lee, H.; Pack, J. W.; Wang, W.; Thurecht, K. J.; Howdle, S. M. *Macromolecules* **2010**, *43* (5), 2276–2282.
- (23) Kirby, C. F.; McHugh, M. A. *Chem. Rev.* **1999**, *99*, 565–602.
- (24) Kauffman, J. F. *J. Phys. Chem. A* **2001**, *105* (14), 3433–3442.
- (25) Prausnitz, J. M.; Lichtenthaler, R. N.; Azevedo, E. G. *Molecular Thermodynamics of Fluid Phase Equilibria*; Prentice Hall: Englewood Cliffs, NJ, 1986.
- (26) Bray, C. L.; Tan, B.; Wood, C. D.; Cooper, A. I. *J. Mater. Chem.* **2005**, *15* (3), 456–459.
- (27) Tan, B.; Bray, C. L.; Cooper, A. I. *Macromolecules* **2009**, *42*, 7945–7952.
- (28) Kallinteri, P. H.; S.; Hutcheon, G. A.; St-Ourcin, C. B.; Garnett, M. C. *Biomacromolecules* **2005**, *6* (4), 1885–1894.
- (29) Kline, B. J.; Beckman, E. J.; Russell, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 9475–9480.
- (30) Bunn, C. W. *J. Polym. Sci.* **1955**, *16* (82), 323–343.
- (31) Bikales, N. M. *Polyesters*; Interscience: New York, 1969; Vol. *11*, pp 62–128.
- (32) Goodman, I. *Angew. Chem., Int. Ed. Engl.* **1962**, *74* (16), 606–612.
- (33) Goodman, I.; Rhys, J. A. *Polyesters*; Iliffe Books, Ltd., for The Plastics Institute: London, 1965; Vol. *1*.
- (34) Goodman, I. *Angew. Chem., Int. Ed. Engl.* **1962**, *74* (16), 606–612.
- (35) Bikales, N. M. *Polyesters*; Interscience: New York, 1969; Vol. *11*, pp 62–128.
- (36) Bunn, C. W. *J. Polym. Sci., Part A* **1955**, *16*, 323–343.
- (37) Goodman, I.; Rhys, J. A. *Polyesters*; Iliffe Books, Ltd., for The Plastics Institute: London, 1965; Vol. *1*.
- (38) Conix, A.; Vankerpel, R. *J. Polym. Sci.* **1959**, *40* (137), 521–532.
- (39) Fuller, C. S.; Frosch, C. J.; Pape, N. R. *J. Am. Chem. Soc.* **1942**, *64*, 154–160.
- (40) Nishimura, A. A. *Polymer* **1967**, *8*, 446–448.
- (41) Hasch, B. M.; Lee, S.-H.; McHugh, M. A.; Watkins, J. J.; Krukonis, V. J. *Polymer* **1993**, *34*, 2554.
- (42) Fourie, F. C. v. N.; Schwarz, C. E.; Knoetze, J. H. *J. Supercrit. Fluids* **2008**, *47*, 161–167.
- (43) Charlet, G.; Ducasee, R.; Delmas, G. *Polymer* **1981**, *22*, 1190–1198.
- (44) Kazarian, S. G.; Vincent, M. F.; Bright, F. V.; Liotta, C. L.; Eckert, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 1729–1736.
- (45) O'Shea, K. E.; Kirmse, K. M.; Fox, M. A.; Johnston, K. P. *J. Phys. Chem.* **1991**, *95*, 7863–7867.
- (46) Han, S. J.; Lohse, D. J.; Radosz, M.; Sperling, L. H. *Macromolecules* **1998**, *31*, 2533–2538.
- (47) Rindfleisch, F.; DiNoia, T. P.; McHugh, M. A. *J. Phys. Chem.* **1996**, *100*, 15581–15587.
- (48) Chen, S.-J.; Banaszak, M.; Radosz, M. *Macromolecules* **1995**, *28*, 1812–1817.
- (49) Spahl, R. L. G. *Ber. Bunsen-Ges. Phys. Chem. Chem. Phys.* **1982**, *86*, 621–625.
- (50) Raveendran, P.; Wallen, S. L. *J. Am. Chem. Soc.* **2002**, *124*, 7274.
- (51) Raveendran, P.; Ikushima, Y.; Wallen, S. L. *Acc. Chem. Res.* **2005**, *38* (6), 478–485.
- (52) Sarbu, T.; Styrane, T. J.; Beckman, E. J. *Nature* **2000**, *405*, 165–168.
- (53) Nelson, M. R.; Borkman, R. F. *J. Phys. Chem. A* **1998**, *102*, 7860–7863.
- (54) 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.