Macromolecules

Volume 35, Number 17 August 13, 2002

Communications to the Editor

Impact of Fluorination and Side-Chain Length on Poly(methylpropenoxyalkylsiloxane) and Poly(alkyl methacrylate) Solubility in Supercritical Carbon Dioxide

Mark A. McHugh,*,† Alberto Garach-Domech,† Il-Hyun Park,‡ Dan Li,† Eugen Barbu,§ Paul Graham,‖ and John Tsibouklis‖

Department of Chemical Engineering, Virginia Commonwealth University, Richmond, Virginia 23284; Department of Polymer Science & Engineering, Kumoh National University of Technology, Kyungbuk, Korea; Chemistry Department, University of Ploiesti, Bd. Bucuresti 39, RO-2000, Ploiesti, Romania; and School of Pharmacy and Biomedical Sciences, University of Portsmouth, Portsmouth PO1 2DT, U.K.

Received December 14, 2001
Revised Manuscript Received June 24, 2002

Introduction. A great deal of interest has been generated within the past few decades on supercritical fluid technology applied to polymerization processes,[1] polymer purification and fractionation processes,[2] and solution coatings and powder formation processes.[3] A critical issue for each of these potential applications is the determination of polymer solubility in supercritical carbon dioxide, a highly preferred processing solvent. There exists a fair amount of experimental data on solubility of polymers and copolymers[4] in CO_2 from which it is possible to obtain insight into the properties of the polymer that control solubility. It is now well-known that fluorinating a polymer enhances its solubility in supercritical CO_2; however, it is also accepted that polymer polarity and backbone flexibility also have a strong influence on the temperatures and pressures needed to dissolve a polymer in supercritical CO_2.[5,6] In addition, it has been shown that fluorinating an alkyl side chain improves polymer solubility, and likewise, it has been shown that polymer solubility decreases significantly as the length of a nonfluorinated alkyl side chain is increased.[4,5,7−9]

In this paper, the impact of fluorination on polymer solubility in supercritical CO_2 is demonstrated by comparing the conditions needed to dissolve poly(methylpropenoxyalkyl siloxane) (PES_9), with a dodecyl alkyl chain, and two poly(methylpropenoxyperfluoroalkyl siloxanes) (PFE_5 and PFE_7, where the subscript is the number of CF_2 groups in the fluorinated alkyl side chain). Table 1 shows the structure and molecular weights for the PES_9 and the PFE_5 and PFE_7 synthesized for this study. Also presented here is information on the impact of alkyl side-chain length on CO_2 solubility of poly(hexyl methacrylate) (PHMA), poly(octyl methacrylate) (POMA), and poly(decyl methacrylate) (PDMA) and their fluorinated counterparts, poly(1*H*,1*H*,2*H*,2*H*-tetrahydroperfluorohexyl methacrylate) (PFHMA), poly(1*H*,1*H*,2*H*,2*H*-tetrahydroperfluorooctyl methacrylate) (PFOMA), and poly(1*H*,1*H*,2*H*,2*H*-tetrahydroperfluorodecyl methacrylate) (PFDMA). Table 1 presents characterization information on the poly(methacrylates) used in this study. It should be noted that as the alkyl side-chain length increases, the polarity per repeat group decreases since the dipole moment associated with the ester or ether linkage is distributed over larger and larger molar volumes.[10]

Materials. The synthesis of the poly(alkyl methacrylate)s and siloxane polymers used in this study has been discussed in detail elsewhere.[11,12] The molecular weights of these polymers are determined by GPC in tetrahydrofuran and are relative to polystyrene standards. Carbon dioxide was obtained from Roberts Oxygen (99.8% minimum purity) and was used as received.

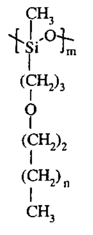
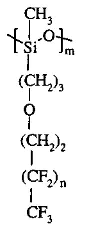
Experimental Section. Described elsewhere is the apparatus and techniques used to obtain CO_2-polymer cloud points.[13,14] The main component of the experimental apparatus is a high-pressure, variable-volume

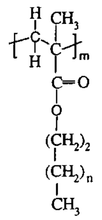
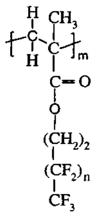
---

* Corresponding author.
† Virginia Commonwealth University.
‡ Kumoh National University of Technology.
§ University of Ploiesti.
‖ University of Portsmouth.

10.1021/ma012169i CCC: $22.00

Table 1. Chemical Structure and Molecular Weight for the Poly(methylpropenoxyalkyl siloxane)s (PES_9), the Two poly(methylpropenoxyperfluoroalkyl siloxane)s (PFE_5 and PFE_7), the Three Poly(alkyl methacrylate)s (PMA_n) (PHMA, POMA, PDMA), and the Three Poly(tetrahydroperfluoroalkyl methacrylate)s ($PFMA_n$) (PFHMA, PFOMA, PFDMA) Used in This Study

Structure	Average Molar Mass	Structure	Average Molar Mass
 PES_n	11,700 for n = 9	 PFE_n	14,600 for n = 5 17,700 for n = 7

Structure	Average Molar Mass	Structure	Average Molar Mass
 PMA_n	230,000 for n = 3, PHMA 163,000 for n = 5, POMA 157,000 for n = 7, PDMA	 $PFMA_n$	200,000* for n = 3, PFHMA 292,000 for n = 5, PFOMA 196,000 for n = 7, PFDMA * estimated value[11]

cell (Nitronic 50, 7.0 cm OD × 1.6 cm ID, ~30 cm^3 working volume). The cell is first loaded with a measured amount of polymer to within ±0.002 g. The cell is then flushed very slowly with gaseous CO_2, at pressures less than 3 bar, to remove entrapped air. CO_2 is then transferred into the cell gravimetrically to within ±0.02 g using a high-pressure bomb. The mixture in the cell is viewed with a borescope (Olympus Corporation, model F100−024−000−55) placed against a sapphire window secured at one end of the cell. A stir bar activated by a magnet located below the cell mixes the contents of the cell. Fixed polymer concentrations of approximately 3−4 wt % are used for each cloud point since this concentration is expected to be close to the maximum in the pressure−composition isotherms.[14−17] The cloud-point pressure is defined as the point at which the solution becomes so opaque that it is no longer possible to see the stir bar in solution. These cloud points have been compared in our laboratories to those obtained using a laser light setup where the phase transition is the condition of 90% drop off in light transmitted through the solution. Both methods gave identical results within the reproducibility of the data. Cloud points are reproduced two to three times to within approximately ±4.0 bar, as measured with two Heise pressure gauges accurate to within ±0.7 bar for data to 700 bar and to within ±3.5 bar for data from 700 bar to 3000 bar, at each temperature held to within ±0.3 °C, as measured with a type K thermocouple.

Results. Figure 1 shows the impact of fluorination on the pressures and temperatures needed to dissolve PES in supercritical CO_2. Consider first the PES_9−CO_2 cloud-point curve. It takes at least 1200 bar of pressure at 200 °C to dissolve PES_9 in CO_2. As the temperature is lowered to 190 °C, the cloud-point pressure increases very rapidly indicating that polymer−polymer interactions that favor the formation of two phases dominate the solution interchange energy. Consider that the PES_9−CO_2 cloud-point curve exhibits the same shape

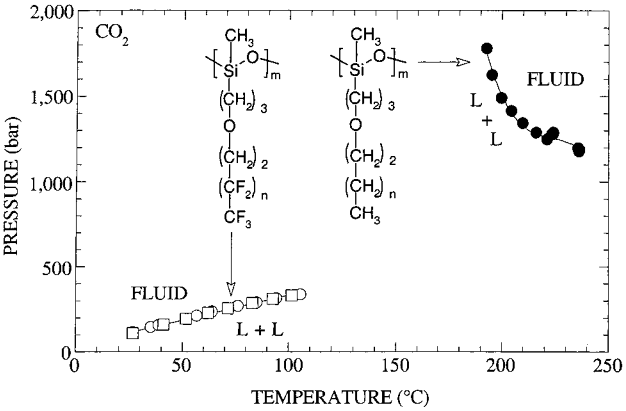


Figure 1. Impact of fluorination on the conditions needed to dissolve poly(methylpropenoxyalkyl siloxane)s in supercritical CO_2. Key: filled circles, poly(methylpropenoxyalkyl siloxane) (PES_9, $n = 9$); open squares and open circles, poly(methylpropenoxyperfluoroalkyl siloxane)s (PFE_5, $n = 5$, and PFE_7, $n = 7$, respectively). The siloxane concentrations are all ~3.5 wt % in CO_2. Fluid is a single-phase region and L + L is a two-phase, liquid plus liquid region.

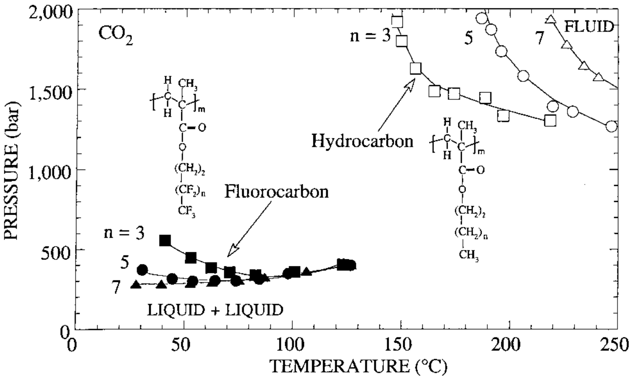


Figure 2. Impact of fluorination on the conditions needed to dissolve poly(alkyl methacrylate)s in supercritical CO_2. Key: open squares, poly(hexyl methacrylate) (PHMA, $n = 3$); open circles, poly(octyl methacrylate) (POMA, $n = 5$); open triangles, poly(decyl methacrylate) (PDMA); filled squares, poly(tetrahydroperfluorohexyl methacrylate) (PFHMA, $n = 3$); filled circles, poly(tetrahydroperfluorooctyl methacrylate) (PFOMA, $n = 5$); filled triangles, poly(tetrahydroperfluorodecyl methacrylate) (PFDMA). The polymer concentrations are all ~4.0 wt % in CO_2.

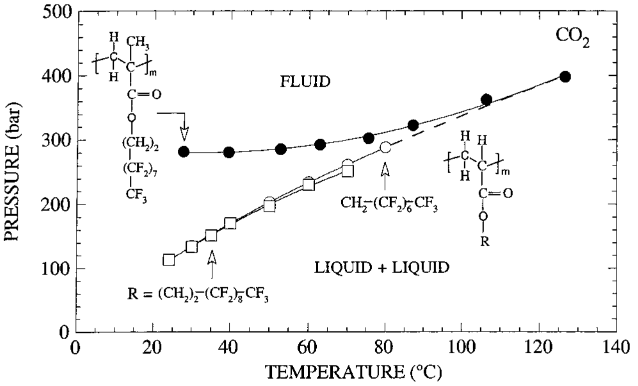


Figure 3. Comparison of the phase behavior of poly(1*H*,1*H*,2*H*,2*H*-tetrahydroperfluorodecyl methacrylate) (filled circles) obtained in this study with that of poly(1*H*,1*H*,2*H*,2*H*-tetrahydroperfluorodecyl acrylate) (open squares)[7] and poly(1*H*,1*H*-dihydroperfluorooctyl acrylate) (open circles)[9] (PFOA) in supercritical CO_2. The polymer concentrations are ~4.0 wt % in each case. The dashed line is a linear extrapolation of the PFOA data.

and it appears in approximately the same pressure–temperature space as the cloud-point curves in CO_2 for poly(ethylhexyl acrylate) and poly(octadecyl acrylate),[5] which are poly(acrylates) with long alkyl side chains. The PES_9 data reinforce the observation that CO_2 does not easily dissolve slightly polar polymers.[4] In contrast to the PES_9–CO_2 solubility behavior, it is possible to dissolve poly(dimethylsiloxane) in CO_2 at temperatures as low as ~40 °C and pressures as low as 300 bar.[18–23] The PES_9–CO_2 phase behavior is likely fixed by the long alkyl tail of the side chain since very high temperatures and pressures are needed to dissolve this siloxane. Even though the propenoxy group in the side chain contributes some polar character to this siloxane, the magnitude per volume of side chain is very low. The propenoxy segment also enhances the flexibility of the side chain, which reduces the entropy penalty for dissolving this polymer in CO_2, however, the increased flexibility cannot overcome the unfavorable energetics of methyl–CO_2 interactions.

Figure 1 also shows the cloud-point curves for PFE_5 and PFE_7 in CO_2. Here it is apparent that fluorinating the alkyl tail of the side chain on the siloxane significantly reduces the pressures and temperatures needed to dissolve this polymer in CO_2. On the basis of earlier studies, it is not surprising that fluorinating a side chain improves polymer solubility;[4,6] however, in this instance the side-by-side comparison of similar siloxanes provides a dramatic example of the impact of fluorination. The differences in the phase behavior between fluorinated and nonfluorinated PES cannot be rationalized based on the small differences in the average molar mass of these three polymers. It is also interesting to note that the cloud-point curves for PFE_5 and PFE_7 in CO_2 are indistinguishable. Unfortunately, other PFE_x polymers were not available to determine the effect of side chain length on CO_2 solubility for this class of polymer.

Figure 2 shows the PHMA, POMA, and PDMA–CO_2 cloud-point curves obtained in this study. As the alkyl tail increases in length these methacrylate polymers become less polar and polymer solubility decreases. It is interesting that PDMA, the least soluble methacrylate polymer, also has the lowest molecular weight. Hence, the differences in the phase behavior shown in this figure cannot be rationalized on the differences in polymer molecular weight. The trend in the phase behavior shown in Figure 2 is also consistent with the observation that CO_2 cannot dissolve nonpolar polyolefins or polydienes.[5,24–26] The phase behavior data shown in Figure 2 are not unexpected since acrylate polymers also exhibit the same trends in supercritical CO_2. It is worthwhile to note that it takes approximately 1200 bar of pressure to dissolve these methacrylate polymers in CO_2 at moderate-to-high temperatures where mainly dispersion interactions should be operative. Very high pressures are needed to increase the density of CO_2 to magnify the weak, nonpolar dispersion interactions of CO_2 that scale with solvent density.[10]

Figure 2 also shows the cloud-point curve for PFHMA, PFOMA, and PFDMA in CO_2. Once again it is apparent that fluorinating the alkyl tail of the side chain on the methacrylate significantly reduces the pressures and temperatures needed to dissolve this class of polymer in CO_2. The density of CO_2 cannot be the only factor controlling solubility otherwise the three fluoromethacrylate curves would superpose. Note that, at the lowest temperature studied, the cloud-point pressure increases by approximately 350 bar as the alkyl tail length decreases and, thus, as the methacrylate polymer becomes more polar since the dipole moment of the ester group is distributed over a smaller molar volume.[10] Hence, the shape of the PFHMA–CO_2 curve at temperatures less than 50 °C is likely a consequence of enhanced FHMA–FHMA polar interactions as compared to FHMA–CO_2 interactions, which favor solubility.

Figure 3 provides a comparison of the PFDMA–CO_2 cloud-point curve with those for poly(1*H*,1*H*,2*H*,2*H*-tetrahydroperfluorodecyl acrylate) (poly(TAN)[7] and poly(1*H*,1*H*-dihydroperfluorooctyl acrylate) (PFOA)[9] in CO_2. These acrylate and methacrylate cloud-point curves do not superpose even though the types and strengths of polymer–CO_2 intermolecular interactions should be very similar since the length of the alkyl side chain and the number of fluorinated methyl groups of PFDMA are intermediate to those of PFOA and poly(TAN). However, CO_2 has easier access to the ester group on the poly(acrylate)s compared to PFDMA since the methyl group on a methacrylate α-carbon more effectively repels CO_2 due to both steric hindrance and repulsive interactions than does the hydrogen on an acrylate α-carbon. The carbonyl oxygen of the ester is an electron donor that interacts specifically with the electron-accepting carbon of CO_2, resulting in a CO_2−ester complex with an interaction strength near 1 kcal/mol.[27] Although the strength of this complex is only slightly greater than the strength of dispersion interactions, the impact of the complex is magnified because the solution density is very high. In fact, Rindfleisch et al. showed that, at room temperature, poly(methyl acrylate) (PMA) dissolves in CO_2 at a pressure that is more than 1700 bar greater than that needed to dissolve poly(vinyl acetate) (PVAc) due to the easier access CO_2 has to the ester group in PVAc compared to PMA.[5] At temperatures greater than ∼100 °C, where CO_2−ester complex formation is not favored, the fluoroacrylate and the PFDMA cloud-point curves now superpose, suggesting that the phase behavior is governed primarily by nonspecific dispersion interactions. The phase behavior shown in Figure 3 reinforces the notion that CO_2 is such a weak quality solvent that any increase in the strength or type of intermolecular interactions has an impact much larger than that found with high quality liquid solvents.

Several observations concerning polymer solubility in supercritical CO_2 can be gleaned from the phase behavior shown in Figures 1−3. Enhanced polymer solubility is observed if the polymer has some polar character and if it is at least partially fluorinated. However, the conditions needed to dissolve a polymer cannot be rationalized solely as a result of CO_2 density especially when temperature-sensitive interactions are possible, such as complex formation. Large changes in polymer solubility can result from modest changes in polymer architecture since CO_2 and most supercritical fluid solvents are very weak quality solvents even when compressed to liquidlike densities.[28] The phase behavior data shown here offer valuable insight for the design of CO_2-soluble polymers.

Acknowledgment. The authors thank Dr. Zhihao Shen for performing GPC analysis of the fluoromethacrylate polymers used in this study. The authors also thank Dr. Suresh Shenoy for helpful technical discussions on the interpretation of the data in this manuscript.

References and Notes

(1) Kendall, J. L.; Canelas, D. A.; Young, J. L.; DeSimone, J. M. *Chem. Rev.* **1999**, *99*, 543.

(2) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction, Principles and Practice*, 2nd ed.; Butterworth-Heinemann: Boston, MA, 1994.

(3) Mandel, F. S.; Green, C. D.; Scheibelhoffer, A. S. United States 5,399,597, 1995.

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

(5) Rindfleisch, F.; DiNoia, T. P.; McHugh, M. A. *J. Phys. Chem.* **1996**, *100*, 15581.

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

(7) Mawson, S.; Johnston, K. P.; Combes, J. R.; DeSimone, J. M. *Macromolecules* **1995**, *28*, 3182.

(8) Hsiao, Y.-L.; Maury, E. E.; DeSimone, J. M.; Mawson, S.; Johnston, K. P. *Macromolecules* **1995**, *28*, 8159.

(9) Luna-Barcenas, G.; Mawson, S.; Takishima, S.; DeSimone, J. M.; Sanchez, I. C.; Johnston, K. P. *Fluid Phase Equilib.* **1998**, *146*, 325.

(10) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid-Phase Equilibria*, 2nd ed.; Prentice Hall: Englewood Cliffs, NJ, 1986.

(11) Tsibouklis, J.; Graham, P.; Eaton, P. J.; Smith, J. R.; Nevell, T. G.; Smart, J. D.; Ewen, R. J. *Macromolecules* **2000**, *33*, 8460.

(12) Tsibouklis, J.; Stone, M.; Thorpe, A. A.; Graham, P.; Nevell, T. G.; Ewen, R. J. *Langmuir* **1999**, *15*, 7076.

(13) Meilchen, M. A.; Hasch, B. M.; McHugh, M. A. *Macromolecules* **1991**, *24*, 4874.

(14) Mertdogan, C. A.; Byun, H.-S.; McHugh, M. A.; Tuminello, W. H. *Macromolecules* **1996**, *29*, 6548.

(15) Allen, G.; Baker, C. H. *Polymer* **1965**, *6*, 181.

(16) Irani, C. A.; Cozewith, C. J. *Appl. Polym. Sci.* **1986**, *31*, 1879.

(17) Lee, S. H.; LoStracco, M. A.; Hasch, B. M.; McHugh, M. A. *J. Phys. Chem.* **1994**, *98*, 4055.

(18) Yilgor, I.; McGrath, J. E.; Krukonis, V. J. *Polym. Bull.* **1984**, *12*, 499.

(19) Krukonis, V. J. *Polym. News* **1985**, *11*, 7.

(20) Hoefling, T. A.; Enick, R. M.; Beckman, E. J. *J. Phys. Chem.* **1991**, *95*, 7127.

(21) Hoefling, T. A.; Stofesky, D.; Reid, M.; Beckman, E. J.; Enick, R. M. *J. Supercrit. Fluids* **1992**, *5*, 237.

(22) Xiang, Y.; Kiran, E. *Polymer* **1995**, *36*, 4817.

(23) Zhao, X.; Watkins, R.; Barton, S. W. *J. Appl. Polym. Sci.* **1996**, *55*, 773.

(24) Gregg, C. J.; Stein, F. P.; Radosz, M. *Macromolecules* **1994**, *27*, 4981.

(25) Gregg, C. J.; Stein, F. P.; Radosz, M. *Macromolecules* **1994**, *27*, 4972.

(26) McHugh, M. A.; Park, I.-H.; Reisinger, J. J.; Ren, Y.; Lodge, T. P.; Hillmyer, M. A. *Macromolecules* **2002**, in press.

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

(28) DiNoia, T. P.; Kirby, C. F.; van Zanten, J. H.; McHugh, M. A. *Macromolecules* **2000**, *33*, 6321.

MA012169I