Macromolecular Research, Vol. 11, No. 4, pp 231-235 (2003)

Phase Behavior of Poly(ethylene-*co*-norbornene) in C_6 Hydrocarbon Solvents: Effect of Polymer Concentration and Solvent Structure

Hyuk-Sung Kwon and Sang-Ho Lee*

Department of Chemical Engineering, Dong-A University, Hadan 2-dong, Saha-gu, Busan 604-714, Korea

Received Aug. 24, 2002; Revised June 28, 2003

Abstract: Phase behavior information is necessary for accomplishing homogeneous copolymerization to obtain high yield of copolymers and prevent a fouling problem. Cloud-point data to 160 °C and 1,450 bar are presented for five C_6 hydrocarbon solvents, normal hexane, 2,2-dimethyl butane, 2,3-dimethyl butane, 2-methyl pentane, and 3-methyl pentane, with poly(ethylene-*co*-53 mol% norbornene) (PEN_{53}). The pressure-concentration isotherms measured for PEN_{53}/*n*-hexane have maximums that range between 5 and 12 wt% PEN_{53}. The cloud-point curves for PEN_{53} all have negative slopes that decrease in pressure with temperatures. The single-phase region of PEN_{53} in *n*-hexane is larger than the regions in 2,2-dimethyl butane, 2,3-dimethyl butane, 2-methyl pentane, and 3-methyl pentane. The cloud-point curve of PEN_{53} in 2,2-dimethyl butane is located at higher temperatures and pressures than the curve in 2,3-dimethyl butane due to the reduced dispersion interactions with and limited access of 2,2-dimethyl butane to the copolymer. Similar cloud-point behavior is observed for PEN_{53} in 2-methyl pentane and 3-methyl pentane.

Keywords: poly(ethylene-*co*-norbornene), phase behavior, high pressures.

Introduction

Poly(ethylene-*co*-norbornene) (PEN) is one of the major cyclo olefin copolymers (COC) that have tentatively been studied for commercializing since metallocene catalysts were introduced in synthesizing COC.[1-5] The most potential application of COC is optical plastic that is used to make substrates for optical storage devices such as high density compact disk (CD) and digital video disk (DVD). PEN also has the potential to be used in optical fiber, protecting sheets for displays, pick-up lenses for CD and DVD, and lenses for cameras and projection displays.

Polycarbonate (PC) and poly(methyl methacrylate) (PMMA) are currently the two most widely used optical plastics. PC has not only good mechanical properties and flow ability at high temperature but also good optical properties except birefringence.[2,6] However, the high birefringence of PC restricts its optical usage. PMMA has a low heat deflection temperature and easily uptakes moisture due to the methyl methacrylate repeat units in the backbone structure. PC and PMMA, both homopolymers have almost fixed glass transition temperatures so that their applications are constrained into limited temperature ranges. On the other hand, PEN has numerous desirable properties of PC and PMMA for optical application, such as low moisture absorption and permeability, heat stability and chemical resistance, low birefringence and high optical transparency, and good mechanical properties.[1,2,5,6] The advantageous properties of PEN result from incorporation of norbornene into polyethylene. As the content of norbornene in PEN backbone structure increases, PEN becomes amorphous and obtains excellent optical properties. The integration of norbornene also enhances the thermal stability and mechanical properties of the copolymer. Because of the wide variation in the copolymer properties, conditions of the copolymerization are changed. Therefore it is important to know the location of the phase boundaries for the copolymer-solvent mixtures in order to ensure homogeneous polymerization, which is essential to obtain a high yield of copolymers and prevent a possible fouling problem. The phase behavior information is also needed to efficiently separate product copolymers from unreacted monomers recycled to the reactor. Unfortunately, to the best of our knowledge, there are no phase behavior studies available in the literature for PEN hydrocarbon system. In this paper, we present the cloudpoint behavior of binary systems of poly(ethylene-*co*-53 mol% norbornene) (PEN_{53}) and C_6 hydrocarbon solvents to 160 °C and 1,450 bar. PEN_{53} contains 53 mol% of norbornene repeat unit in the backbone structure. The C_6 hydrocarbon solvents used in this study were *n*-hexane and four hexane isomers, methyl pentanes and dimethyl butanes that have one and

*e-mail : sangho@donga.ac.kr

two-branched methyl group, respectively. Especially, the effect of the subtle change of solvent structure on the phase behavior of PEN in hydrocarbon solvents is demonstrated. This phase behavior study provides useful experimental data to develop molecular simulation models. Also the fundamental thermodynamic data can be used to design and optimize PEN copolymerization process.

Experimental

Materials. PEN_{53} was obtained from Ticona AG. Table I shows the properties of PEN_{53} used in this study. Normal hexane, 2,2-dimethyl butane, 2,3-dimethyl butane, 2-methyl pentane, and 3-methyl pentane were obtained from Aldrich Chemical Company. All hydrocarbon solvents have a minimum purity of 99.5% and were used as received. Table II lists properties of C_6 hydrocarbon solvents.[7-9]

Apparatus and Measurements. Figure 1 shows the schematic diagram of the experimental apparatus used for determining cloud-point behavior. Cloud-points are obtained with a high-pressure, variable-volume cell that has a 1.59 cm I.D., 7.0 cm O.D., and a working volume of ~28 cm^3. A 1.9 cm thick sapphire window is fitted in the front part of the cell for observation of the phases. Typically 0.350± 0.002 g of copolymer are loaded into the cell, which is subsequently purged several times at room temperature with nitrogen to remove any entrapped air. Generally, five-to-seven ±0.002 g of the solvent of interest are transferred into the cell with the

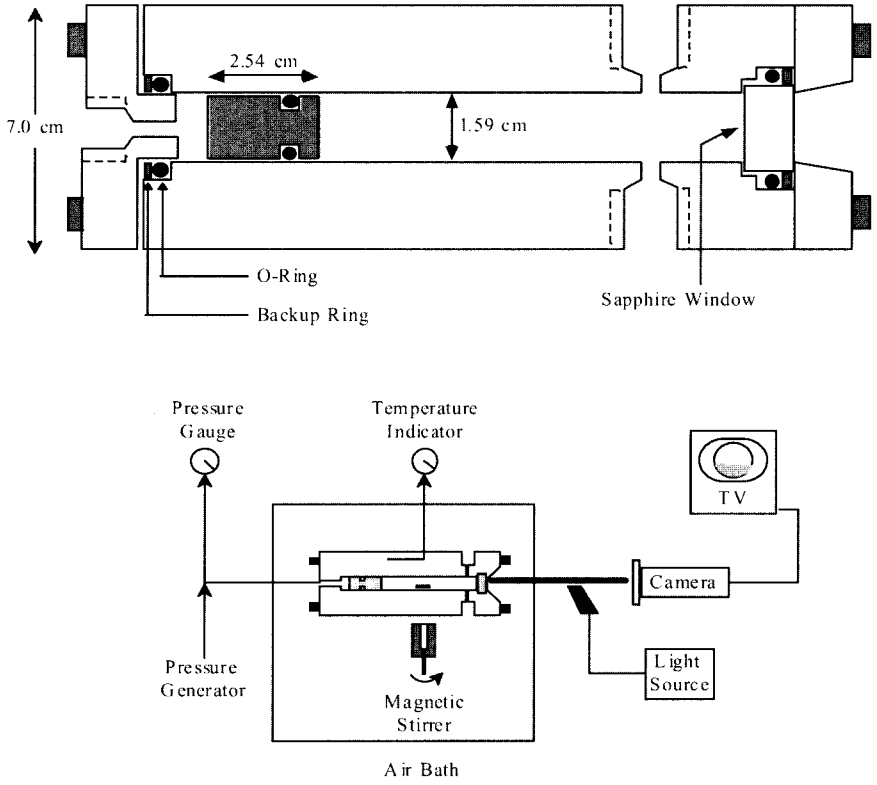

Figure 1. Schematic diagram of the experimental apparatus used.

Table I. Properties of Poly(ethylene-*co*-53 mol% norbornene) Used

T_g (°C)	M_n	M_w	Polydispersity (M_n/M_w)	Norbornene Content (mol%)
156.3	45,800	111,300	2.4	53

Table II. Properties of C_6 Hydrocarbon Solvents Used[7-9]

Property	*n*-Hexane	2-Methyl pentane	3-Methyl pentane	2,2-Dimethyl butane	2,3-Dimethyl butane
T_c (°C)	234.5	224.6	231.5	215.9	226.9
P_c (bar)	30.3	30.4	31.2	31.0	31.5
ρ_c (g/cm^3)	0.234	0.234	0.234	0.241	0.239

using a syringe. The solution is compressed to the desired pressure with an internal piston that is moved using water displaced by a high-pressure generator. The pressure of the mixture is measured with a Heise gauge (Dresser Ind., model CM128639, 0 to 2,068 bar, accurate to within ± 2.0 bar) above 350 bar and with a Konics pressure transducer (model PT-3300, 0 to 50 bar, accuracy ± 0.3%) below 50 bar. Because the measurement is made on the water side of the piston, a small correction (~ 1 bar) is added to account for the pressure required to move the piston. The temperature of the cell is measured using a platinum-resistance thermometer (Thermometrics Corp., Class A) connected to a digital multimeter (Konics Co., Model KN-2300-5, accuracy ±0.2%). The system temperature is typically maintained to within ±0.2 °C. The mixture inside the cell is viewed on a video monitor using a camera coupled to a borescope (Olympus Corp., model R08002400050) placed against the outside of the sapphire window. Light is transmitted into the cell with a fiber optic cable connected at one end to a high-density illuminator (DolanJenner Industries, Inc., model 180) and at the other end to a borescope. The solution in the cell is well mixed using a magnetic stir bar activated by an external magnet beneath the cell.

Figure 2(A) shows the typical change of opaqueness in the system caused by decreasing the pressure in the vicinity of the cloud point at a fixed copolymer concentration. The copolymer solution in the cell is compressed to a single-phase at a fixed temperature. The solution is maintained in the one-phase region at the desired temperature for at least 20 min so that the cell can be in thermal equilibrium. The pressure is then slowly decreased until the solution becomes cloudy. 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 the solution. The cell is then repressurized to a single phase, at least 150 bar above the cloud-point pressure, and maintained for at least 10 min. The cloud points are repeated at least twice at each temperature, and are typically reproducible to within ± 3 bar at the highest temperatures. In the pressure-temperature (P-T) region where the cloud-point pressure increases very rapidly for a small change in temperature, the cloud points are reproducible to within ± 6 bar. Using the data of several P-T curves, it is possible to construct pressure-concentration (P-x) isotherms. Figure 2(B) shows the schematic P-x diagram at fixed temperature. Cloud-point pressures of copolymer solutions typically have maxima at concentrations lower than 15 wt% polymer.[10-13]

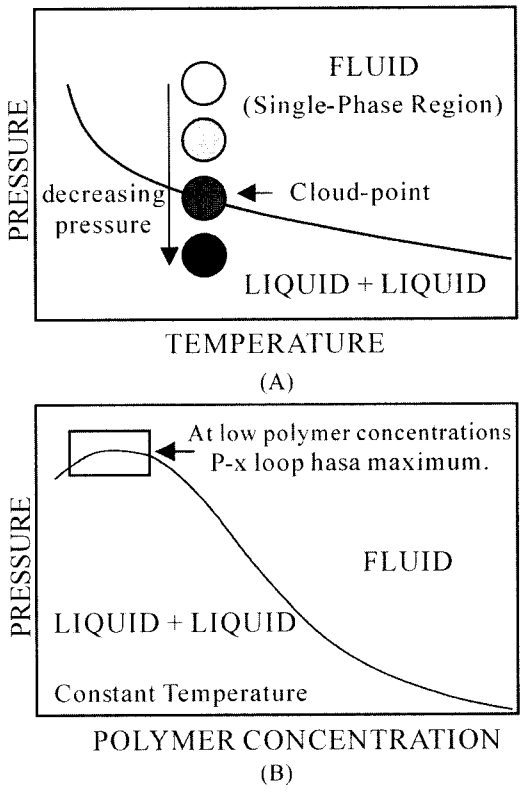

Figure 2. (A) Typical change of opaqueness in polymer solution caused by decreasing the pressure in the vicinity of the cloud point at fixed copolymer concentration. (B) Schematic pressure - polymer concentration (P-x) diagram at fixed temperature.

Results and Discussion

The effect of PEN_{53} concentration on the location of the cloud-point curve was determined for normal hexane. Figure 3 shows the effect of PEN_{53} concentration on the cloud point behavior of PEN_{53}/*n*-hexane system in P-T space. UCST-type phase behavior was observed for the binary mixture of PEN_{53} and *n*-hexane. The cloud point curve for 5 wt% PEN_{53} locates at higher pressures than other curves. While the differences in the cloud point pressures for PEN_{53} concentration between 2 and 12 wt% are approximately identical, the differences in the cloud point pressures at 1, 20, and 28 wt% PEN_{53} progressively enlarge with decreasing temperature. Using the data in Figure 3, it is possible to construct P-x

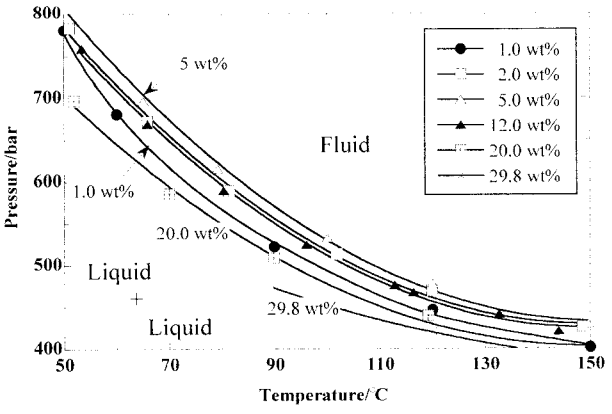

Figure 3. The effect of PEN_{53} (53 mol% norbornene) concentration on the cloud-point curves of PEN_{53}/*n*-hexane mixture.

isotherms of PEN_{53} in *n*-hexane at various temperatures. Figure 4 shows P-x isotherms for the PEN_{53}/*n*-hexane at 60, 90 and 120 °C. The P-x curves obviously reveal that the isotherms have a maximum at the concentrations around 5 wt% PEN_{53}, suggesting that at these polymer concentrations, the cloud-point pressures are reasonably close to the true mixture-critical point.[10-13] It should be noted that at 90 and 120 °C the P-x isotherms of PEN_{53}/*n*-hexane system are approximately flat between copolymer concentrations of 5 to 12 wt%. Therefore, cloud-point pressures are measured at fixed copolymer concentrations 5~12 wt% in this study. From the phase behavior shown in Figures 3 and 4, it is supposed that PEN_{53}/*n*-hexane system has type IV polymer-solvent phase behavior, which the schematic P-T diagram is shown in Figure 5.[14]

Figure 6 shows the cloud-point behavior of PEN_{53} in *n*-hexane, 2,2-dimethyl butane and 2,3-dimethyl butane. 2,2-dimethyl butane and 2,3-dimethyl butane are isomers of *n*-hexane. Both isomers have two substituted methyl groups at the internal carbon of the butane. However, 2,2-dimethyl butane has two methyl groups branched at the second carbon of the butane whereas 2,3-dimethyl butane does one methyl group at the second carbon and the other at third carbon of the butane. In P-T space, a single-phase region of PEN_{53} shrank in 2,2- and 2,3-dimethyl butane compared to the region in *n*-hexane. Since PEN_{53}, *n*-hexane, 2,2-dimethyl butane, and 2,3-dimethyl butane all are non-polar, it is expected that dispersion forces between PEN_{53} and the three solvents governed the phase behavior. 2,2- and 2,3-dimethyl butane have more contracted conformations than *n*-hexane. Therefore, the dispersion interactions between PEN_{53} and dimethyl butanes are less than the interactions between PEN_{53} and *n*-hexane due to the molecular structure of the dimethyl butanes.

It is predictable that the one-phase region of PEN_{53}/*n*-hexane mixture is greater than the region of PEN_{53}/2,3-dimethyl butane because *n*-hexane has larger surface area than 2,3-dimethyl butane and interacts as much via dispersions with PEN_{53}. Similarly, the one-phase region of PEN_{53}/2,3-dimethyl butane mixture is supposed greater than the region of PEN_{53}/2,2-dimethyl butane since the surface area of 2,3-dimethyl butane is larger than that of 2,2-dimethyl butane. However, in P-T space the difference in cloud-point pressures between the dimethyl butane curves is so large. Whereas the cloud-point pressures of PEN_{53}/2,3-dimethyl butane mixture are 30~50 bar higher than the pressure of PEN_{53}/*n*-hexane mixture at temperatures between 50 and 165 °C, the cloud-point pressures of PEN_{53}/2,2-dimethyl butane mixture are higher than the pressure of PEN_{53}/2,3-dimethyl butane mixture up to 400 bar. The decreasing solubility in 2,2-dimethyl butane is too large to ascribe only to the reduced dispersion interactions between PEN_{53} and 2,2-dimethyl butane, resulting from decreasing surface area of 2,2-dimethyl butane. The large decrease of PEN_{53} solubility in 2,2-dimethyl butane is likely the consequence of limited accessibility of 2,2-dimethyl butane to PEN_{53} that contains 53 mol% norbornene repeat

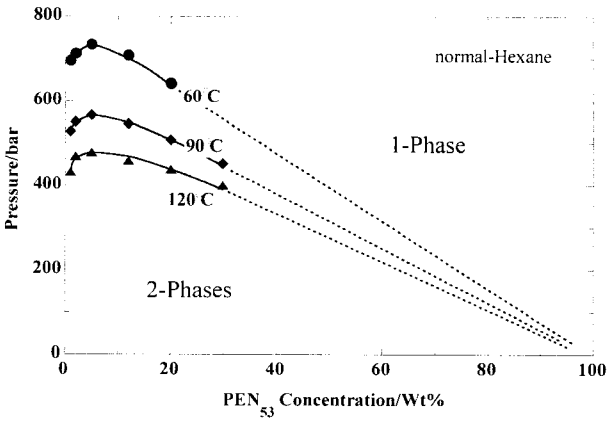

Figure 4. Pressure-composition plot for the PEN_{53} (53 mol% norbornene)/*n*-hexane system at 60, 90, and 120 °C.

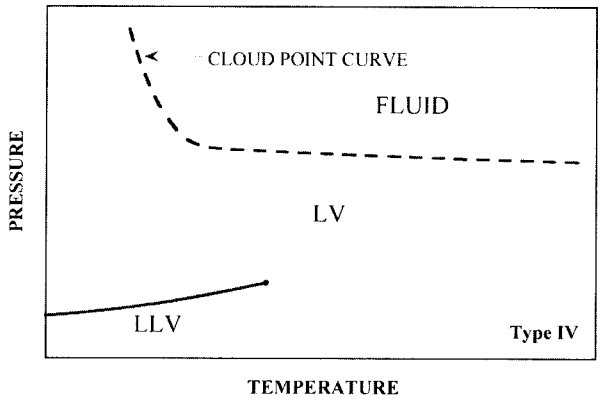

Figure 5. Schematic, pressure-temperature diagram (Type IV) for a mixture consisting of polymer and a low molecular weight solvent.[14]

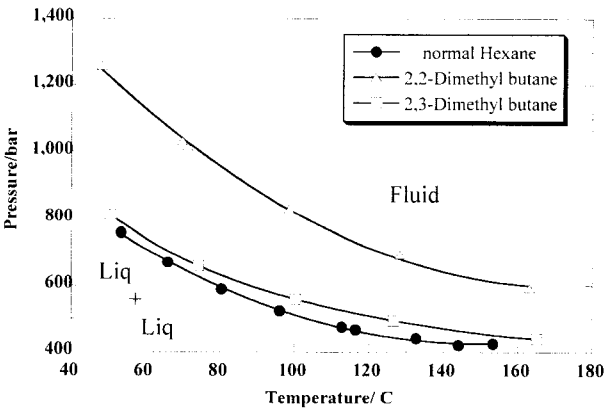

Figure 6. The cloud-point curves for PEN_{53} in *n*-hexane, 2,2-dimethyl butane, and 2,3-dimethyl butane. The PEN_{53} concentration in each solvent is 12 wt%.

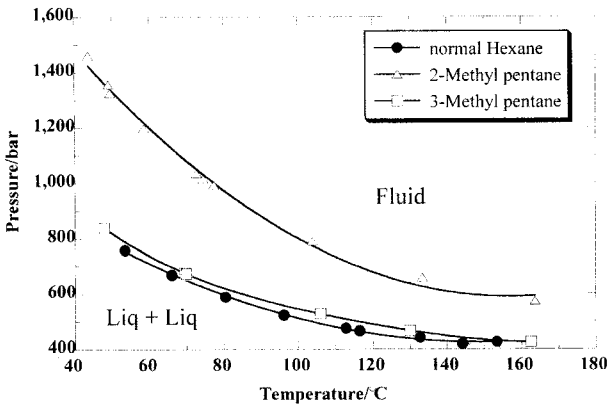

Figure 7. The cloud-point curves for PEN_{53} in *n*-hexane, 2-methyl pentane, and 3-methyl pentane. The PEN_{53} concentration in each solvent is 12 wt%.

unit in the backbone structure. 2,2-dimethyl butane, having 2 methyl groups on the second carbon of the butane, is so bulky that 2,2-dimethyl butane is hindered to approach to ethylene repeat unit of PEN_{53}. The limitation of access to PEN_{53} and the reduced surface area of 2,2-dimethyl butane, both are unfavorable to dissolve the copolymer and greatly decrease the solubility of PEN_{53} in 2,2-dimethyl butane.

The cloud-point behaviors of PEN_{53} in 2-methyl and 3-methyl pentane are shown in Figure **7**. The shape of the cloud-point curves of PEN_{53}/methyl pentane mixtures is almost identical to the PEN_{53}/dimethyl butane curves. Again, the small change of location of a methyl group in methyl pentane, from the third to the second carbon of pentane, abruptly shifts the cloud-point curve of PEN_{53}/methyl pentane mixture to high pressure region. Compared to the mixture of PEN_{53} and 3-methyl pentane, it is reasonable to attribute the large decrease in solubility of PEN_{53} in 2-methyl pentane is the consequence of limited accessibility of 2-methyl pentane to PEN_{53}. More work with heptane isomers is in progress to resolve the effect of solvent molecular structure.

Conclusions

The P-x loops of PEN_{53}/*n*-hexane mixture have a maximum at polymer concentrations between 5~12 wt% at temperatures between 60 to 120°C. When C_6 hydrocarbon solvent is switched from *n*-hexane to dimethyl butane and methyl pentane, solubility of PEN_{53} decreases in the branched hydrocarbons due to the reduced dispersion interactions between PEN_{53} and the branched hydrocarbons. As the location of substituted methyl group shifted from the third to the second carbon of dimethyl butane and methyl pentane, the single-phase region of PEN_{53} in the solvents shrinks up to 400 bar at 70°C. The large decrease in the solubility of PEN_{53} is likely the consequence of limited access of 2,2-dimethyl butane and 2-methyl pentane to PEN_{53}, which the bulky norbornene content in the backbone of the copolymer is 53 mol%. Further work is in progress with heptane isomers to verify that the decreasing solubility of PEN_{53} results from the difference of molecular packing between PEN_{53} and branched hydrocarbon solvents.

Acknowledgements. The authors acknowledge the Center for Advanced Net Shape Manufacturing and Clean Processes (CANSMC) for financial support of this study under Grant R12-2002-004-01-003.

References

(1) G. Khanarian, *Opt. Eng.*, **40**, 1024 (2001).
(2) R. R. Lamonte and D. McNalley, *Plastics Engineering*, **56**, 51 (2000).
(3) G. Khanarian, *Polym. Eng. Sci.*, **40**, 2590 (2000).
(4) C.-K. Y. Thomas, H.-Y. T. Stanley, S.-F. Wang, and C.-C. Juan, *Composition Sci. and Technol.*, **62**, 655 (2002).
(5) Cyclic Olefin Copolymers, 94/95S5, Chem. Systems Inc., New York, 1996, Chapter IV.
(6) T. Weller, D. Schulz, and D. McNally, *Plastics Technology*, **43**, 58 (1997).
(7) R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill, New York, U.S.A., 1987, pp 656.
(8) J. A. Abara, D. W. Jennings, W. B. Kay, and A. S. Teja, *J. Chem. Eng. Data*, **33**, 242 (1988).
(9) T. E. Daubert, *J. Chem. Eng. Data*, **41**, 365 (1996).
(10) S.-H. Lee, M. A. LoStracco, B. M. Hasch, and M. A. McHugh, *J. Phys. Chem.*, **98**, 4055 (1994).
(11) C. A. Irani and C. Cozewith, *J. Appl. Polym. Sci.*, **31**, 1879 (1986).
(12) M. T. Rätzsch, P. Wagner, C. Wohlfarth, and D. Heise, *Acta Polymerica*, **33**, 463 (1982).
(13) M. T. Rätzsch, P. Wagner, C. Wohlfarth, and S. Gleditzsch, *Acta Polymerica*, **34**, 340 (1983).
(14) M. A. McHugh and V. J. Krukonis, *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed., Butterworths, Stoneham, MA, U.S.A., 1994, pp 64.