1144 *J. Chem. Eng. Data* **2005,** *50,* 1144−1147

Methyl Methacrylate + Carbon Dioxide Phase Equilibria at High Pressures

Nimet I. Uzun, Mesut Akgün,* Nil Baran, Sennur Deniz, and Salih Dinçer*

Yildiz Technical University, Chemical Engineering Department, Davutpasa Campus,
No. 127, 34210 Esenler, Istanbul, Turkey

High-pressure vapor−liquid equilibria data for the binary system methyl methacrylate + carbon dioxide were measured using the static method. Experiments were carried out in the pressure range of (6 to 13) MPa and for temperatures of 323.15, 333.15, 343.15, and 353.15 K. Experimental results were correlated with the Peng−Robinson equation of state using conventional mixing rules with one interaction parameter.

Introduction

Methyl methacrylate (MMA) is an important raw material for polymer synthesis and is usually produced by acid-catalyzed methanolysis of acetone cyanohydrin and accompanying dehydration. Environmental concern over the emission of volatile organic solvents used in polymer synthesis has prompted researchers to look for less harmful alternatives.[1] Supercritical fluids show gaslike diffusivities while having liquidlike densities that allow for the solvation of many compounds. They exhibit a change in solvent density upon small variations in temperature or pressure without altering solvent composition.[2] When carbon dioxide is used as a supercritical solvent, additional advantages can be realized. CO_2 is naturally occurring and abundant and exists in natural reservoirs of high purity located throughout the world. CO_2 has a critical temperature of 31.2 °C, a modest critical pressure of 73.8 bar, and a critical density of 0.468 $g\cdot cm^{-3}$. These properties imply liquidlike densities at temperatures slightly above room temperature and solventlike characteristics.[3] These properties have led many researchers to use $scCO_2$ as an ideal medium for both homogeneous and heterogeneous radical polymerizations of methyl methacrylate.[4−10]

The design and development of MMA polymerization in $scCO_2$ medium depend on the knowledge of the phase behavior of MMA and CO_2. Lora and McHugh[11] have measured the phase behavior of MMA−CO_2 in the pressure range of (1 to 14) MPa for temperatures of (313, 353, and 379) K using a synthetic method.[12] Zwolak et al.[13] have recently reported VLE data for the CO_2 + MMA binary system at temperatures of 308, 313, 323, 333 K and pressures in the range of (1 to 8) MPa using the static method.[12] They assumed that the composition of the vapor phase was higher than 99% CO_2, because of the very small quantities of MMA collected in the solvent trap and the lack of reproducibility. However, no data in the literature have been reported on the phase behavior of MMA in CO_2 at high pressures, which consists of both liquid- and vapor-phase sampling.

In this work, vapor−liquid equilibria of the MMA + CO_2 binary were measured at (323.15 to 353.15) K and (6 to 13) MPa. The results were correlated with the Peng−Robinson equation of state (PR-EoS) using the van der Waals mixing rules with one interaction parameter.

Correlation

The general phase equilibrium relation for a liquid−gas mixture[14] is

$$\hat{f}_i^{\text{liq}}(T, P, x_i) = \hat{f}_i^{\text{vap}}(T, P, y_i) \tag{1}$$

or

$$\hat{\phi}_i^{\text{liq}} x_i = \hat{\phi}_i^{\text{vap}} y_i \tag{2}$$

where $\hat{\phi}_i^{\text{liq}}$ and $\hat{\phi}_i^{\text{vap}}$ are the fugacity coefficients for the liquid and vapor phases, respectively. In this work, these coefficients are calculated by the Peng−Robinson EoS described by[15]

$$P = \frac{RT}{V - b} - \frac{a(T)}{V(V + b) + b(V - b)} \tag{3}$$

where $a(T)$ and b are generalized functions of the critical temperature T_c, critical pressure P_c, and acentric factor ω of a pure component. For the mixture calculations, two-parameter mixing rules

$$a(T) = \sum_i \sum_j x_i x_j a_{ij} \tag{4}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{5}$$

are used, where

$$a_{ij} = (1 - k_{ij})\sqrt{a_i a_j} \tag{6}$$

$$b_{ij} = \frac{(b_{ii} + b_{jj})}{2}(1 - l_{ij}) \tag{7}$$

Here, k_{ij} and l_{ij} denote the adjustable binary parameters accounting for the interactions between *i* and *j* components. l_{ij} was assumed to be zero and was not taken into consideration during the calculations. k_{ij} was determined

---

* Corresponding authors. E-mail: dincer@yildiz.edu.tr, akgunm@yildiz.edu.tr. Fax: (90) 212 449 18 95. Tel: (90) 212 449 19 25.

10.1021/je049639z CCC: $30.25

Table 1. Vapor−Liquid Equilibrium Data for the CO_2 + MMA System

323.15 K ($k_{ij} = 0.019$)					333.15 K ($k_{ij} = 0.039$)				
	CO_2 mole fraction					CO_2 mole fraction			
P/MPa	x^{exptl}	x^{calcd}	y^{exptl}	y^{calcd}	P/MPa	x^{exptl}	x^{calcd}	y^{exptl}	y^{calcd}
6.33	0.696	0.7057	0.999	0.9918	6.54	0.620	0.6149	0.996	0.9876
6.71	0.748	0.7398	0.997	0.9916	7.29	0.680	0.6762	0.995	0.9867
7.10	0.778	0.7742	0.996	0.9912	7.59	0.699	0.7005	0.994	0.9862
7.50	0.819	0.8087	0.995	0.9906	7.86	0.717	0.7223	0.993	0.9856
8.04	0.852	0.8543	0.995	0.9896	8.56	0.774	0.7790	0.991	0.9837
8.58	0.894	0.8989	0.993	0.9878	9.10	0.827	0.8229	0.982	0.9812
9.04	0.938	0.9366	0.979	0.9844	9.50	0.851	0.8563	0.979	0.9785
9.30	0.957		0.966		10.04	0.888	0.9032	0.961	0.9715
					10.54	0.926		0.934	

343.15 K ($k_{ij} = 0.039$)					353.15 K ($k_{ij} = 0.045$)				
	CO_2 mole fraction					CO_2 mole fraction			
P/MPa	x^{exptl}	x^{calcd}	y^{exptl}	y^{calcd}	P/MPa	x^{exptl}	x^{calcd}	y^{exptl}	y^{calcd}
6.36	0.540	0.5376	0.995	0.9834	6.23	0.476	0.4710	0.993	0.9780
6.58	0.559	0.5539	0.994	0.9833	6.76	0.496	0.5062	0.992	0.9775
7.02	0.583	0.5858	0.994	0.9828	7.68	0.567	0.5661	0.992	0.9763
7.50	0.612	0.6202	0.994	0.9821	8.02	0.588	0.5879	0.992	0.9757
7.81	0.638	0.6423	0.993	0.9815	8.68	0.624	0.6299	0.989	0.9740
8.40	0.686	0.6840	0.993	0.9801	9.44	0.683	0.6779	0.987	0.9713
8.90	0.716	0.7191	0.993	0.9785	10.03	0.714	0.7153	0.983	0.9683
9.25	0.756	0.7437	0.991	0.9771	10.69	0.757	0.7579	0.973	0.9637
9.90	0.802	0.7899	0.988	0.9735	11.21	0.795	0.7929	0.967	0.9584
10.44	0.821	0.8296	0.983	0.9687	11.70	0.820	0.8279	0.952	0.9506
10.77	0.839	0.8547	0.966	0.9642	12.23	0.878	0.8723	0.943	0.9320
11.02	0.870	0.8755	0.963	0.9591					
11.23	0.906	0.8947	0.957	0.9518					

Table 2. Thermophysical Properties of Methyl Methacrylate and CO_2

components	T_b/K	T_c/K	P_c/MPa	ω
methyl methacrylate[11]	373.0	564.0	3.68	0.317
carbon dioxide[14]	194.7	304.2	7.38	0.225

by minimizing the average absolute deviation (AAD) defined by[16]

$$\mathrm{AAD} = \frac{1}{N_x}\sum^{N_x}\left|\frac{x^{\mathrm{exptl}} - x^{\mathrm{calcd}}}{x^{\mathrm{exptl}}}\right| + \frac{1}{N_y}\sum^{N_y}\left|\frac{y^{\mathrm{exptl}} - y^{\mathrm{calcd}}}{y^{\mathrm{exptl}}}\right| \tag{8}$$

where N is the number of data points.

Experimental Section

Chemicals. Methyl methacrylate (Acros) was used without further purification, and its purity was at least 99% as determined by gas chromatographic (GC) analysis. The main impurity is hydroquinone used as an inhibitor. CO_2 (purity 99.9%) was supplied by Habas, Istanbul.

Experimental Procedure. The vapor−liquid equilibrium data of the system MMA + CO_2 were taken as a function of pressure and temperature using the static method. The physical properties of MMA and CO_2 studied in this work are listed in Table 2.

The experiments were carried out at (323.15, 333.15, 343.15, and 353.15) K and pressures from (6 to 13) MPa.[17] The experimental apparatus used in this study[18,19] is shown in Figure 1. The equilibrium cell has an internal volume of 115 mL and is heated by a heating tape using a PID controller (±1 K). CO_2 was compressed to the system pressure by a syringe pump (ISCO model 260D) that could read pressure to within ±0.01 MPa. The equilibrium cell was loaded with MMA (30 mL) in each run and mixed by a tiny magnetic stirring bar. After the system was stirred for 30 min to reach equilibrium at the desired operating conditions, samples of the vapor phase and the liquid phase were collected in sample tubes. The sample size is 2 mL in the vapor phase and 0.5 mL in the liquid phase. The temperature was maintained constant all along the sample line by insulating the line. Whereas the MMA in the vapor and liquid samples was separately trapped in the collection bottle containing methanol, the amount of CO_2 in the samples was measured by a wet-test meter. After the experiment was terminated, the expansion valves were washed twice with methanol, and the concentration of MMA in each phase was determined by gas chromatographic (GC) analysis.

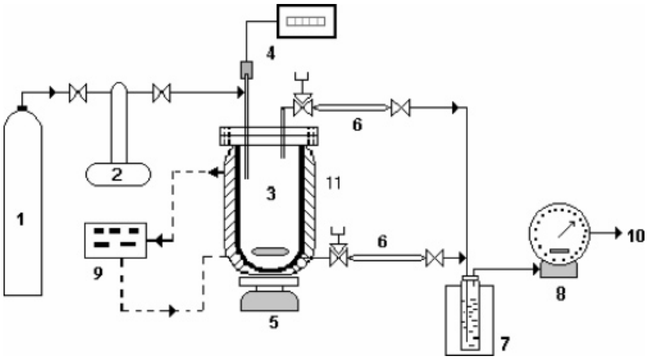

Figure 1. Experimental setup for VLE measurements: 1, CO_2 cylinder; 2, syringe pump; 3, equilibrium cell; 4, digital pressure display; 5, magnetic stirrer; 6, sample tube; 7, cold trap; 8, wet-test meter; 9, temperature controller with PID; 10, CO_2 vent; 11, heating tape.

Analytical Method. For the analysis, a Unicam model 610 GC with an FID detector was used. The separation was obtained by using a capillary column (ZB-WAX polyethylene glycol, 60 m × 0.32 mm i.d., film thickness 0.5 μm). Argon was used as the carrier gas. The GC was temperature programmed between 60 °C and 200 °C at 1 °C/min. The concentration of MMA was computed from GC peak areas using the calibration curve for the MMA + methanol mixture. Using the concentration of MMA and the amount of the MMA + methanol mixture in the collection bottle, the amount of MMA in CO_2 present in the sampling tubes was determined for each run.

Results and Discussion

The vapor−liquid equilibrium data were measured for the methyl methacrylate + CO_2 system at (323.15, 333.15, 343.15, and 353.15) K. The experimental data are given in Table 2, and the resulting plots as a function of pressure at each temperature are illustrated in Figure 2. The experiments were repeated several times with different loadings to get both vapor- and liquid-phase mole fractions. The reproducibility of both the liquid- and vapor-phase equilibrium compositions was calculated from the mean of the repeated experiments at the same conditions as the relative standard deviation (RSD), and the RSD is less than 1.2%.

MMA is a liquid under the current experimental conditions, and the vapor−liquid equilibrium data can be taken and correlated at the pressures under the critical point of the mixture. Many equations of state give satisfactory results away from the critical point of the mixture. Various modeling procedures using an EoS have been proposed in the literature to predict the phase behavior of monomer + CO_2 systems. One of the modeling procedures is fitting the experimental equilibrium data with the PR-EoS using two adjustable parameters. Usually the second adjustable parameter, accounting for the size effect, is neglected because predictions using only one adjustable parameter

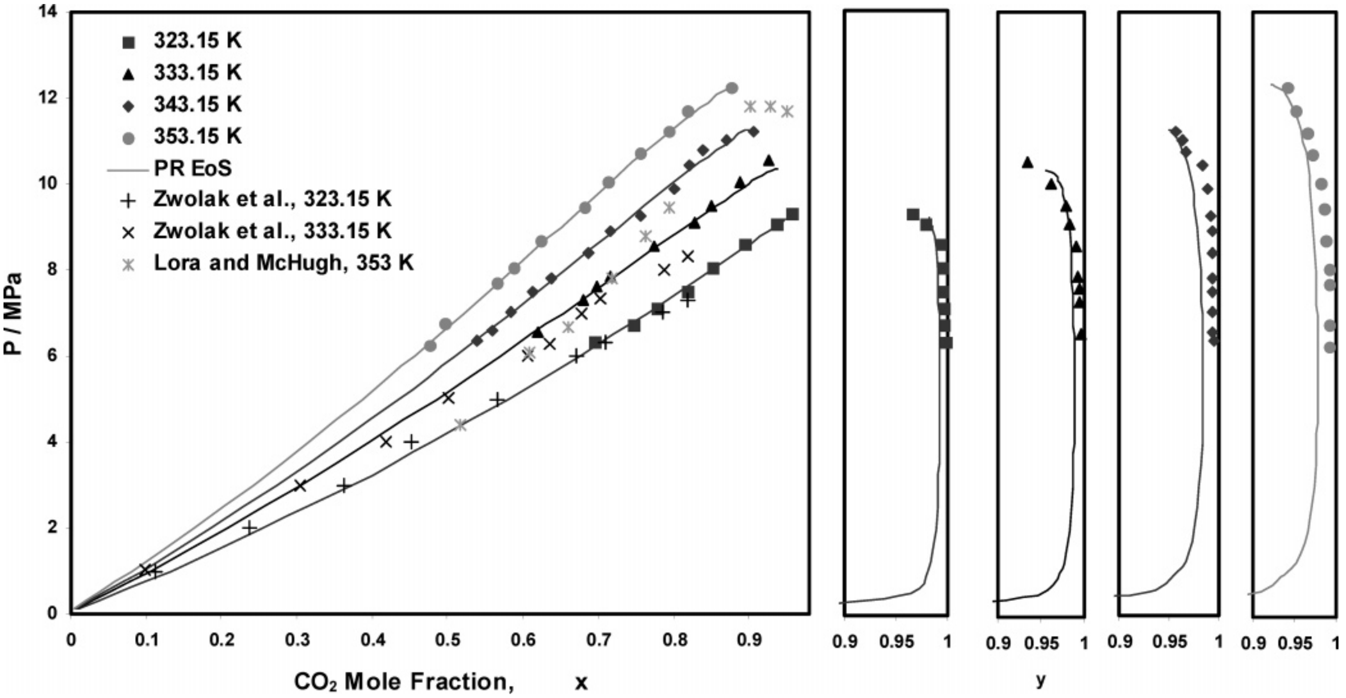

Figure 2. Vapor−liquid equilibrium data for the CO$_2$−methyl methacrylate system: $k_{ij} = 0.019$ at 323.15 K, $k_{ij} = 0.039$ at 333.15 K, $k_{ij} = 0.039$ at 343.15 K, and $k_{ij} = 0.045$ at 353.15 K using the PR-EoS.

Table 3. Values of AAD and k_{ij} at Different Temperatures

	T/K					
	323.15		333.15		343.15	353.15
$k_{ij}{}^a$	0.019^c	0.0331^b	0.039^c	0.0293^b	0.039^c	0.045^c
AAD	0.038^c	0.041^b	0.044^c	0.047^b	0.080^c	0.073^c

[a] Lora and McHugh[11] report a constant value of −0.073 for k_{ij} in the temperature range of (313 to 379) K. [b] Data are from ref 13. [c] Data are from this work.

k_{ij} yield, in general, satisfactory results. All of the data obtained in this work were well correlated by the PR-EoS using one parameter, k_{ij}, and the calculated results are shown in Figure 2 together with the experimental data. Table 3 compares AAD values at different temperatures for different k_{ij} values. It can be concluded that the correlation of the experimental data of this work by the PR-EoS with one adjustable parameter is quite acceptable. A comparison between the model prediction $(\hat{\phi}^{\mathrm{liq}}_{\mathrm{CO_2}}/\hat{\phi}^{\mathrm{vap}}_{\mathrm{CO_2}})$ and the experimental data $(y_{\mathrm{CO_2}}/x_{\mathrm{CO_2}})$ on the basis of eq 2 from (323.15 to 353.15) K is shown in the plot of Figure 3. The plot indicates that the predictions are slightly lower than the experimental values but are still within the reported accuracy of the experimental data.

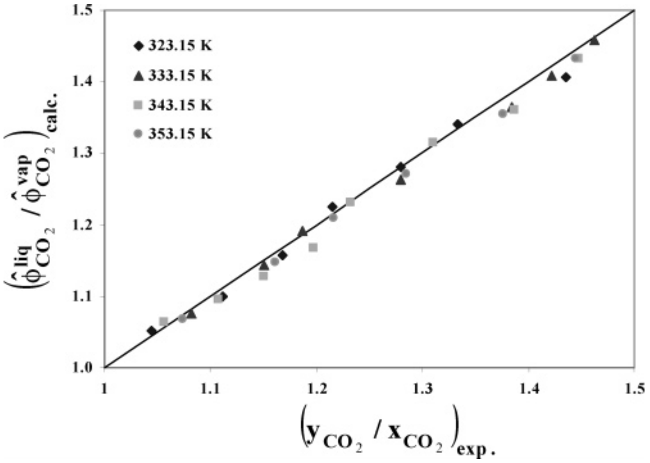

Figure 3. Comparison between the model prediction $(\hat{\phi}^{\mathrm{liq}}_{\mathrm{CO_2}}/\hat{\phi}^{\mathrm{vap}}_{\mathrm{CO_2}})$ and the experimental data $(y_{\mathrm{CO_2}}/x_{\mathrm{CO_2}})$ from (323.15 to 353.15) K.

Lora and McHugh[11] and recently Zwolak et al.[13] have reported VLE data for the CO$_2$ + MMA binary system at temperatures of (308 to 379) K. A comparison between our data and the previously published data at 323 K,[13] 333 K,[13] and 353 K[11] is also included in Figure 2. Significant discrepancies exist between our data and Lora and McHugh's data. For example, at 9.4 MPa and 11.7 MPa the solubilities of CO$_2$ in the liquid phase, as measured by Lora and McHugh, are both around 16% higher than measured in this work. Their data deviate from their model by about the same amount as their data deviate from our data. Although their data at 313 K match their model well, their data at 353 K and 379 K are lower than their model. In addition, they report a constant (−) value for k_{ij} when the second adjustable parameter is set equal to zero, which indicates specific interactions between MMA and CO$_2$. They refer to the work of Kazarian et al.,[20] who found strong specific interactions between PMMA and CO$_2$ from spectroscopic studies. However, an extension of their study to the MMA−CO$_2$ system needs further critical study. Zwolak et al.[13] also reported significant discrepancies between their data and the data of Lora and McHugh.[11] Although Zwolak et al. have not taken into consideration the vapor-phase data because of the very small quantities of MMA collected in the solvent trap and lack of reproducibility, there is better agreement between their liquid-phase data and the data of this study (Figure 2). In addition, they have not measured the liquid-phase composition in the vicinity of the mixture critical point for each temperature because the solubility of CO$_2$ becomes more sensitive to pressure. They have correlated their data using both one and two adjustable parameter PR-EoS's. Their k_{ij} values are shown in Table 3 together with the k_{ij} values of this study, using the one adjustable parameter PR-EoS.

Literature Cited

(1) Jessop, P. G.; Leitner, W. *Chemical Synthesis Using Supercritical Fluids*; Wiley-VCH: Weinheim, Germany, 1999.

(2) McHugh, M. A.; Krukonis, V. J. J. *Supercritical Fluid Extraction: Principles and Practice*, 2nd ed.; Butterworth-Heinemann: Boston, 1993.

(3) Baser, S. J.; Stern, K. M. In *Catalytic Activation of Carbon Dioxide*; Ayers, W. M., Ed.; American Chemical Society: Washington, DC, 1998.

(4) Hsiao, Y. L.; Maury, E. E.; DeSimone, J. M. Dispersion Polymerization of Methyl Methacrylate Stabilized with Poly(1,1-dihydroperfluorooctyl acrylate) in Supercritical Carbon Dioxide. *Macromolecules* **1995**, *28*, 8159−8166.

(5) Van Herk, A. M.; Canelas, D.; DeSimone, J. M. Propagation Rate Coefficients of Styrene and Methyl Methacrylate in Supercritical Carbon Dioxide. *Macromolecules* **1997**, *30*, 4780−4782.

(6) Hsiao, Y. L.; DeSimone, J. M. Dispersion Polymerizations of Methyl Methacrylate in Supercritical Carbon Dioxide: The Influence of Helium Concentration on Particle Size and Particle Size Distribution. *J. Polym. Sci.* **1997**, *35*, 2009−2013.

(7) Quadir, M. A.; DeSimone, J. M.; van Herk, A. M.; German, A. L. Pulsed-Laser Polymerization of Methyl Methacrylate in Liquid and Supercritical Carbon Dioxide. *Macromolecules* **1998**, *31*, 6481−6485.

(8) Okubo, M.; Fujii, S.; Maenaka, H.; Minami, H. Production of Submicron-sized Poly(methyl methacrylate) Particles by Dispersion Polymerization with a Poly(dimethylsiloxane)-based Azoinitiator in Supercritical Carbon Dioxide. *Colloid Polym. Sci.* **2002**, *280*, 183−187.

(9) Lepilleur, C.; Beckman, E. J. Dispersion Polymerization of Methyl Methacrylate in Supercritical CO_2. *Macromolecules* **1997**, *30*, 745−756.

(10) Giles, M. R.; Hay, J. N.; Howdle, S. M. The Copolymerization of Methyl and Ethyl Methacrylate in Supercritical Carbon Dioxide. *Macromol. Rapid Commun.* **2000**, *21*, 1019−1023.

(11) Lora, M.; McHugh, M. A. Phase Behavior and Modeling of the Poly(methyl methacrylate)-CO_2-Methyl Methacrylate System. *Fluid Phase Equilib.* **1999**, *157*, 285−297.

(12) Christov, M.; Dohrn, R. High-pressure Fluid Phase Equilibria Experimental Methods and Systems Investigated (1994−1999). *Fluid Phase Equilib.* **2002**, *202*, 153−218.

(13) Zwolak, G.; Lioe, L.; Lucien, F. P. Vapor−Liquid Equilibria of Carbon Dioxide + Methyl Methacrylate at 308, 313, 323, and 333 K. *Ind. Eng. Chem. Res.* **2005**, *44,* 1021−1026.

(14) Sandler, S. I. *Chemical and Engineering Thermodynamics*, 2nd ed.; John Wiley & Sons: New York, 1989.

(15) Peng, D. Y.; Robinson, D. B. A New Two-Constant Equation of State. *Ind. Eng. Chem. Fundam.* **1976**, *15*, 59−64.

(16) Sheng, Y. J.; Chen, P. C.; Chen, Y. P.; Wong, D. S. H. Calculations of Solubilities of Aromatic Compounds in Supercritical Carbon Dioxide. *Ind. Eng. Chem. Res.* **1992**, *31*, 967−973.

(17) Uzun, N. I. Phase Behavior of CO_2+Methyl Methacrylate Binary System at High Pressures. M.S. Thesis, Yildiz Technical University, Istanbul, Turkey, 2005.

(18) Akgün, M.; Akgün, N.; Dinçer, S. Phase Behaviour of Essential Oil Components in Supercritical Carbon Dioxide. *J. Supercrit. Fluids* **1999**, *15*, 117−125.

(19) Akgün, M.; Emel, D.; Baran, N.; Akgün, N. A.; Deniz, S.; Dinçer, S. Styrene-Carbon Dioxide Phase Equilibria at High Pressures. *J. Supercrit. Fluids* **2004**, *31*, 27−32.

(20) Kazarian, S. G.; Vincent, M. F.; Bright, F. V.; Liotta, C. L.; Eckert, C. A. Specific Intermolecular Interaction of Carbon Dioxide with Polymers. *J. Am. Chem. Soc.* **1996**, *118*, 1729−1736.

Received for review October 13, 2004. Accepted April 25, 2005. This work was supported by DPT (Turkish State Planning Organization, project no. 22-DPT-07-01-01) and YTU-BAPK (Yildiz Technical University, Organization of Scientific Research Project, project no. 22-07-01-04).

JE049639Z