Free Radical Polymerizations of Some Vinyl Monomers in Carbon Dioxide Fluid

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ABSTRACT: The effect of pressure ranging from ambient atmosphere to 28.5 MPa on the free radical polymerizations of methyl methacrylate (MMA) in carbon dioxide (CO_2) was investigated and discussed. The poly (methyl methacrylate) (PMMA) with high molecular weight was synthesized at quite high conversion of MMA in the polymerization at or below 9.2 MPa, as compared to those polymerized under 11.8–28.5 MPa. A phase transition behavior of MMA-CO_2 binary mixture from homogeneous state to vapor-liquid equilibrium (VLE) state was observed below 10.51 MPa. In such a VLE system, almost all MMA was found to exist in the liquid phase with higher concentration than that in homogenous system. Thus, the fast polymerization rate of MMA and high molecular weight of PMMA could be related to the VLE state of MMA/CO_2 under low pressure. Similar phenomena were also observed in the polymerization systems of styrene and vinyl acetate in CO_2, respectively. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 468–474, 2008

Key words: supercritical carbon dioxide; vinyl monomer; free radical polymerization; vapor-liquid equilibrium; diffusion

INTRODUCTION

As a natural solvent, supercritical carbon dioxide ($scCO_2$) is nonflammable, nontoxic, and inexpensive, making itself an environmental-friendly media for polymerizations of different monomers, which have been intensively studied during last decade.[1] Because most of the vinyl polymers are hardly soluble in $scCO_2$, thus heterogeneous polymerizations especially dispersion polymerization and precipitation polymerization were reported in literature.[2,3] In this case, high pressure from 12 to 36 MPa was extensively adopted in the precipitation polymerization in $scCO_2$, but the monomer conversion and the molecular weight (MW) of the vinyl polymer were relatively low. For example, polystyrene (PS) with low M_n = 8200 g/mol was synthesized by the precipitation polymerization of styrene at monomer conversion of 12% and 36 MPa [20%, weight/volume (w/v) styrene/1.2 × 10^{-2} M 2,2′-azobisisobutyronitrile (AIBN)/65°C/24 h],[4] and poly(methyl methacrylate) (PMMA) with M_n = 22,000 g/mol was synthesized by the precipitation polymerization of methyl methacrylate (MMA) at monomer conversion of 16% and 29 MPa (20%, w/v MMA/0.6 × 10^{-2} M AIBN/70°C/4 h).[5] In the presence of some amphiphilic fluorinated polymers or poly(dimethylsiloxane) (PDMS)-based polymers as stabilizers, the precipitation polymerization can be turned into the dispersion polymerization, resulting in high monomer conversion and high MW of vinyl polymer. For the dispersion polymerization of styrene, the monomer conversion and the M_n of PS increased to 90% and 30,000 g/mol, respectively, under the same conditions as the precipitation polymerization but with poly(styrene-*b*-dimethylsiloxane) as stabilizer,[4] and in the case of MMA system, the MMA conversion and the M_n of PMMA could be raised to 91% and 160,000 g/mol, respectively, in the presence of poly (methyl methacrylate-*b*-1H,1H,2H,2H-perfluorooctyl methacrylate) as stabilizer,[5] compared to those observed in the precipitation polymerizations. In the dispersion polymerization of vinyl acetate (VAc) with vinyl-terminated PDMS as stabilizer (20%, VAc/2.4 × 10^{-2} M AIBN/65°C/4 h) the VAc conversion from 50 to 70% at 35 MPa was observed, but the M_n of poly(vinyl acetate) (PVAc) synthesized was about the same as that produced in the precipitation polymerization.[6] Nevertheless, these stabilizers used in dispersion polymerization and involved in final products are usually difficult to be separated, so as to alter the performance of polymer

materials, especially the surface properties,[7] resulting in limitation of their application in industry. Furthermore, the high pressure, such as 20–46 MPa used to enhance the solubility of the stabilizer in scCO$_2$ is generally required for operating the dispersion polymerization.

Generally, the pressure for the polymerization of vinyl monomer in scCO$_2$ should be controlled as low as possible, if one considers performing it easily in industry. However, to the best of our knowledge, the precipitation polymerization of vinyl monomer in scCO$_2$ under pressure below 12 MPa has not been reported yet due to slow polymerization rate and quite low MW of polymer produced, as mentioned earlier. Therefore, it is necessary to further explore how to accelerate the polymerization in scCO$_2$ as well as to raise the MW of polymer in the absence of the stabilizer under low pressure, because it is significant not only in polymer chemistry, but in industry as well.

In a previous article, we reported the dispersion polymerization of acrylonitrile in scCO$_2$ at 65°C.[8] It was found that when the polymerization was carried out around the critical pressure of CO$_2$ (7.7–7.8 MPa), the polyacrylonitrile with high MW was synthesized at high acrylonitrile conversion no matter whether the stabilizer was added. In this article, the free radical polymerizations of MMA in CO$_2$ under different pressures from ambient atmosphere to 28.5 MPa were reported. The experimental results showed that when the polymerization was carried out at or below 9.2 MPa, the PMMA with high MW was synthesized at high conversion of MMA, compared to that produced under 11.8–28.5 MPa. Meanwhile, the similar phenomena were also observed in the polymerization systems of styrene and VAc in CO$_2$, respectively.

EXPERIMENTAL

CO$_2$ (99.5%, Shanghai Wugang Co., Shanghai, China) was used as received. All other raw materials used in this research were standard laboratory reagents provided by Shanghai Chemical Reagent Plant (Shanghai, China). MMA, styrene, and VAc were purified by passing through a basic alumina column to remove the inhibitors. AIBN was recrystallized from hot methanol.

A 28-mL stainless steel high-pressure reactor equipped with a magnetic stir bar was charged with AIBN and monomer, and then the reactor was purged with a flow of CO$_2$ to remove the oxygen prior to the start of polymerization. After a desired amount of CO$_2$ was charged, the reactor was placed in a water bath heated to 65°C. Then additional CO$_2$ was charged to the system, if necessary, until the preset reaction condition was reached. Once the pre-

set temperature and pressure were reached, the reaction mixture was stirred for desired hours. At the end of the polymerization, the reactor was cooled and the CO$_2$ was slowly vented to recover the product. Finally, the reactor was rinsed with tetrahydrofuran (THF) to collect residue product for calculation of monomer conversion. The bulk polymerization of MMA was carried out at 65°C in the same reactor described above, in which the same amount of monomer and initiator was used as those polymerizations in CO$_2$.

A 35-mL visual high-pressure cell equipped with a magnetic stir bar and two sapphire windows permitting visual observation was used to observe the phase behavior of MMA-CO$_2$ system at 65°C. Twenty percent (w/v) of MMA was charged to the visual cell to attain the initial status of polymerization.

The average molecular weight and its distribution of polymers were tested on Waters 1515 gel permeation chromatography (GPC). THF was used as eluent at 40°C and PS with a narrow molecular weight distribution (Shodex SM-105) was used as a standard.

RESULTS AND DISCUSSION

Table I lists the experimental data of the polymerization of MMA in CO$_2$ under different pressures. In all systems, the pressures changed about to some extent during the polymerization process. Because of the low molar volume of the vinyl polymer produced compared to that of its parent monomer, the total volume of the reaction system should contract and its pressure was expected to decrease during polymerization. However, the final pressures were found to rise for all systems except for one carried out at 28.5 MPa, in which the final pressure decreased somewhat. Hsiao et al.[9] observed similar change of pressure during the dispersion polymerization of MMA in scCO$_2$ at 65°C, and found that there was an increase in pressure when the polymerization was initially started at or below 19.3 MPa and a decrease while the initial pressure was set up higher than 26.9 MPa. Bratton et al.[10] also observed that the final pressure rose by 300–500 psi (2.0–3.5 MPa) in the precipitation polymerization of ε-caprolactone in scCO$_2$ at 80°C. This unusual phenomenon of change in pressure was discussed by Lepilleur and Beckman[11] in a thermodynamic view in detail and was attributed to the nonideal mixing of fluid CO$_2$ and MMA under low pressure. In this case, we mainly discussed the initial pressure. For simplicity, it was called pressure.

Table I shows that as the pressure decreased from 28.5 to 11.8 MPa, both the MMA conversion and MW of PMMA decreased with the lowering of the pressure. In general, the rate of free radical polymerization of vinyl monomer and the molecular weight

TABLE I
Polymerization of Methyl Methacrylate in CO_2[a]

Samples	Initial pressure (MPa)	Final pressure (MPa)	Monomer conversion (%)	M_n (kg/mol)	M_w (kg/mol)	PDI	Appearance
PMMA 1	28.5	27.5	54	55	212	3.85	Gel-like
PMMA 1R[b]	28.1	27.4	55	48	187	3.90	Gel-like
PMMA 2	19.7	22.4	52	43	119	3.49	Gel-like
PMMA 3	16.8	17.1	47	32	174	5.39	Gel-like
PMMA 4	11.8	13.1	44	30	72	2.40	Gel-like
PMMA 5	9.2	11.4	77	82	298	3.64	Gel-like
PMMA 6R[b]	8.7	11.3	79	82	300	3.64	Hard bulk
PMMA 6	8.4	10.8	79	105	314	2.98	Hard bulk
PMMA 7	7.5	9.4	100	131	332	2.54	Hard bulk
PMMA 8	6.0	7.2	96	91	250	2.75	Hard bulk
PMMA 9	5.0	6.3	95	88	227	2.58	Hard bulk
PMMA 10[c]	–	–	100	61	168	2.75	Hard bulk

[a] Reaction conditions: [M] = 20% (w/v), (total volume = 28 mL), [I] = 1.2×10^{-2} M, $T = 65°C$, and $t = 10$ h.
[b] Reproduced experimental data.
[c] Bulk Polymerization.

of its vinyl polymer mainly depends on three steps, i.e., initiation, propagation, and termination. In the case of this study, the initiation step may have no strong effect on the rate of polymerization and MW of polymer synthesized. Thus, the propagation and the termination steps in such a radical chain polymerization should be considered. Beuermann and Buback[12] reported that the chain propagation rate coefficients, k_p, in bulk polymerization at 30°C for some vinyl monomers, such as MMA, styrene, and VAc, under pressures in the range of atmosphere to 200 MPa decreased with pressure, but for the polymerization systems in $scCO_2$, it only reduced to a certain extent.[13] In this case, the termination process on the other hand may play an important role in decreasing the conversion of monomer and MW of PMMA with reducing the pressure, because the solubility of PMMA in $scCO_2$/MMA as well as the viscosity of the system decreased with the decrease of pressure and thus the diffusion-controlled termination rate increased. Carnelas et al.[4,6] found the MW of PS or PVAc synthesized by free radical polymerization in $scCO_2$ decreased with falling pressure due to the lowering of solvency between the $scCO_2$ and the growing chains of polymer. Thus, the experimental results of the free radical polymerizations performed under 28.5–11.8 MPa are consistent with those previous reported in the literature. However, as the pressure further went down to 9.2 MPa, the MMA conversion and the MW of PMMA increased appreciably and were much higher than those observed at 28.5 MPa. Furthermore, both the MMA conversion and MW of PMMA still rose obviously with the pressure decreasing from 9.2 to 7.5 MPa and the experimental data measured at 7.5 MPa were the highest over all other polymerization systems studied here. In comparison with the disper-

sion polymerization of MMA at 33 MPa in the presence of poly(perfluorooctylethylene methacrylate-co-propylene oxide) as stabilizer (30%, w/v MMA/1 wt % AIBN/65°C/12 h),[14] the monomer conversion at 7.5 MPa was high, although the MW of PMMA was somewhat low. When the pressure further decreased to 5.0 MPa, the MW of PMMA started to fall again (but still higher than that synthesized at 28.5 MPa), whereas the monomer conversion remained nearly the same. It is of interest to note that the MW of all the PMMA samples synthesized under 5.0–9.2 MPa is higher than that by bulk polymerization (see Table I). For checking the reproducibility of the experimental data, two experimental results of PMMA samples got under high and low pressure, respectively, were repeated, as listed in Table I. It shows that the reproducibility of the experiments is excellent.

To further study these interesting phenomena, we observed the state of MMA-CO_2 mixture through the visual windows of the high-pressure cell at $T = 65°C$. The concentration of MMA was kept the same as that at the beginning of the polymerization. Figure 1 shows the digital photographs of the MMA-CO_2 mixture under different pressures. The MMA-CO_2 mixture was found homogeneous at 10.81 MPa and started up a vapor-liquid equilibrium (VLE) state at 10.51 MPa or below. Three phase equilibrium state (vapor-liquid-liquid) was not observed, indicating an excellent solubility between MMA and CO_2. Recently, Zwolak et al.[15] have investigated the VLE of MMA-CO_2 binary mixture in the range of 1–8 MPa and 25–60°C in detail, in which CO_2 was shown highly soluble in MMA (70–80 mol % at 60°C and 7–8 MPa) and only less than 2 mol % of MMA existed in gas phase. Thus, the experimental results in Figure 1 are well consistent with those reported
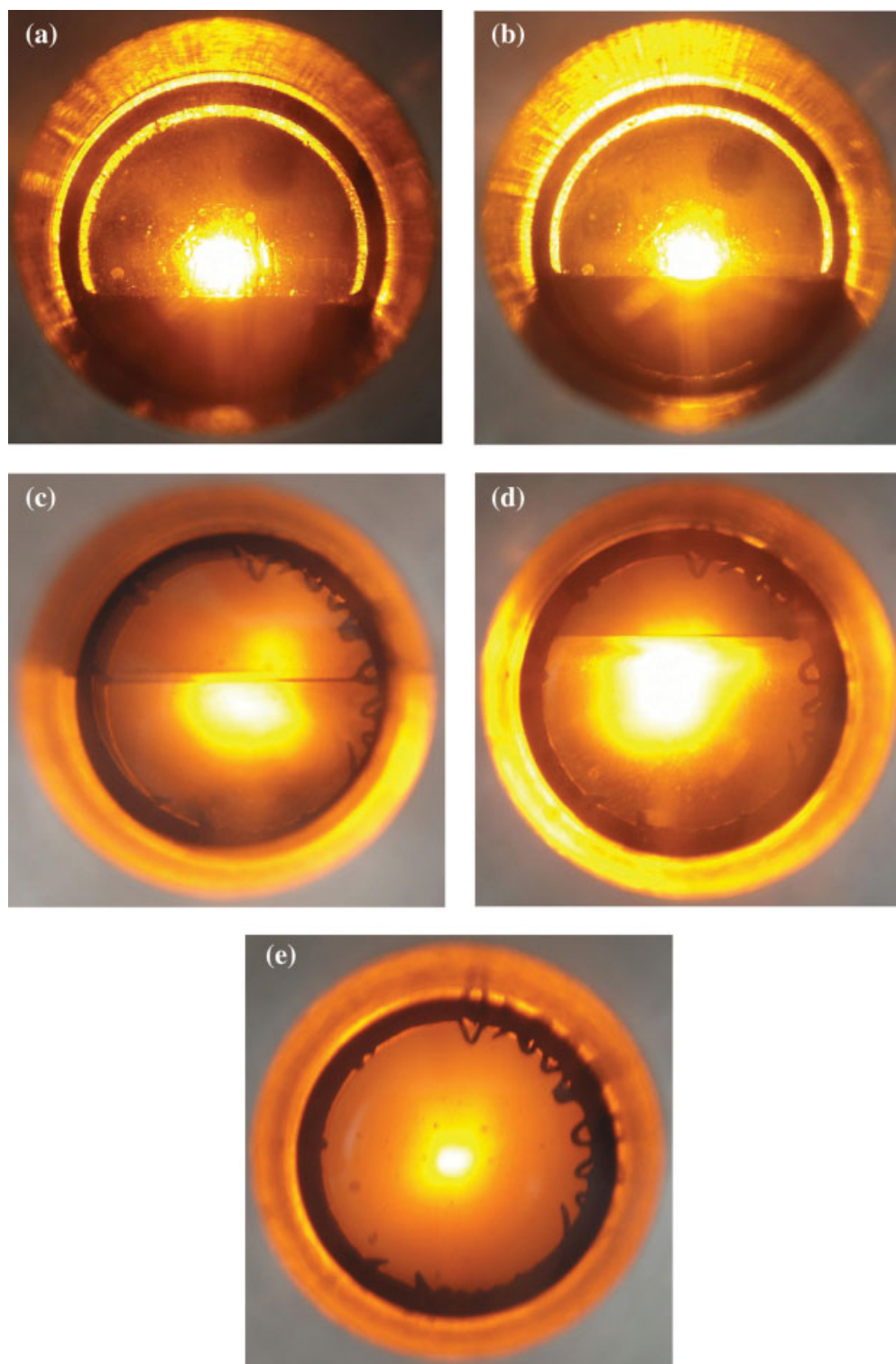
Figure 1 Digital Photos of MMA-CO$_2$ system at different pressures. (a) 8.50 MPa; (b) 9.30 MPa; (c) 10.41 MPa; (d) 10.51 MPa; (e) 10.81 MPa. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

by Zwolak et al.,[15] and could be considered to explain the enhancement in both polymerization rate and MW of PMMA listed in Table I.

Lora and McHugh[16] calculated the VLE of MMA-CO$_2$ system at temperatures of 40, 80, and 105.5°C

by Peng-Robinson equation of state and fitted this model well to the experimental data. The same calculation procedure was employed here to estimate the composition in gas (Y_{CO_2} and Y_{MMA}) and liquid (X_{CO_2} and X_{MMA}) phase for the MMA-CO$_2$ VLE

TABLE II
Calculated VLE Data and Diffusion Coefficient of MMA-CO₂

Samples	Initial pressure (MPa)	Final pressure (MPa)	X_{CO_2} (mol%)	X_{MMA} (mol%)	Y_{CO_2} (mol%)	Y_{MMA} (mol%)	ρ^a (mol/m³)	c_{MMA} (mol/L)	D_{AB} (10^{-4} cm²/s)
PMMA 5	9.2	11.4	72.1	27.9	96.2	3.8	13,926	3.88	2.58
PMMA 6	8.4	10.8	67.0	33.0	97.0	3.0	13,421	4.43	2.46
PMMA 7	7.5	9.4	62.9	37.1	97.8	2.2	12,990	4.82	2.37
PMMA 8	6.0	7.2	53.5	46.5	98.2	1.8	12,071	5.61	2.06
PMMA 9	5.0	6.3	47.0	53.0	98.3	1.7	11,479	6.08	2.06
PMMA 10	–	–	–	–	–	–	–	–	0.425

ª Density of the liquid phase.

system at 65°C, in which AIBN was neglected due to low quantity as a first approximation. The binary interaction parameter k_{ij} was set to −0.073 according to the fitted model in Lora and McHugh's research. The calculated data are listed in Table II. It shows that the molar fractions of MMA in the gas phase are one magnitude lower than those in the liquid phase in all systems under 5.0–9.2 MPa, indicating the liquid phase being the main loci of polymerization. Furthermore, the high molar fraction of CO_2 found in the liquid phase, increased from 47.0 to 72.1 mol % as the pressure rose from 5.0 to 9.2 MPa, was consistent with the high solubility of CO_2 in MMA reported by Zwolak et al.[15]

The monomer concentration c_{MMA} at the beginning of the polymerization was then calculated according to the density and the composition of the liquid phase, as also listed in Table II. Although the pressure decreased from 9.2 to 5.0 MPa, c_{MMA} climbed up from 3.88 to 6.02 mol/L, which is much higher than that of the homogeneous system under higher pressures than 10.81 MPa. High monomer concentration in VLE systems could be considered as one of the factors leading to high MMA conversion and high MW of PMMA. Tables I and II, show that however, despite the value of c_{MMA} decreased with pressure rising from atmosphere pressure to 9.2 MPa, the MW of PMMA reached a maximum value at 7.5 MPa. On the other hand, the MMA conversion remained nearly unchanged while the pressure was lower than 7.5 MPa, but decreased under higher pressures than 8.4 MPa. These experimental results could not be well related to the change in c_{MMA} alone, thus the effect of diffusion and the

phase separation in liquid phase due to polymer phase formed in these polymerizations may need to be taken into account.

The diffusion coefficient of the solute on infinite dilution in the liquid phase can be calculated by Wilke-Chang equation[17]:

$$D^0_{AB} = \frac{7.4 \times 10^{-8}(\phi M_B)^{1/2}T}{\eta_B V_A^{0.6}} \tag{1}$$

where D^0_{AB} is the diffusion coefficient of solute A on infinite dilution in solvent B in cm²/s, M_B is the MW of solvent B in g/mol, T is the temperature in Kelvin, η_B is the viscosity of solvent B in cP, V_A is the molar volume of solute A at normal boiling temperature in cm³/mol, and ϕ is the association factor of solvent B. Once two diffusion coefficients on infinite dilution of MMA (A) or CO_2 (B) are calculated according to (1), the diffusion coefficient of A in a given concentration can be estimated by the geometric average of A and B respected to their molar fractions[18]:

$$D_{AB} = (D^0_{AB})^{X_B}(D^0_{BA})^{X_A} \tag{2}$$

where X_A and X_B stand for the molar fraction of the component A and B, respectively. The calculated results are listed in Table II. It is noted that the diffusion coefficients of MMA in VLE systems are much higher than that in bulk polymerization, thus the polymerization rate of MMA increases. Therefore, the MWs of all PMMA samples produced in such VLE systems were higher than that produced in bulk polymerization. In spite that the monomer concentration decreased as the pressure rose from

TABLE III
Polymerization of Styrene in CO_2^a

Samples	Initial pressure (MPa)	Final pressure (MPa)	Monomer conversion (%)	M_n (kg/mol)	M_w (kg/mol)	PDI	Appearance
PS 1	15.4	13.9	26	6.5	8.5	1.31	Oil-like
PS 2	9.2	9.6	55	36	107	2.97	Gel-like
PS 3	7.5	8.5	98	50	99	1.98	Hard bulk
PS 4	5.0	6.4	98	30	50	1.67	Hard bulk

ª Reaction conditions: [M] = 20% (w/v) (total volume = 28 mL), [I] = 1.2×10^{-2} M, T = 65°C, and t = 18 h.

TABLE IV
Polymerization of Vinyl Acetate in CO_2[a]

Samples	Initial pressure (MPa)	Final pressure (MPa)	Monomer conversion (%)	M_n (kg/mol)	M_w (kg/mol)	PDI	Appearance
PVAc 1	15.6	16.8	50	18	49	2.74	Gel-like
PVAc 2	9.2	10.7	54	34	84	2.44	Gel-like
PVAc 3	8.0	9.2	82	79	165	2.08	Gel-like
PVAc 4	5.0	6.1	93	44	112	2.52	Soft bulk

[a] Reaction conditions: [M] = 20% (w/v) (total volume = 28 mL), [I] = 2.4×10^{-2} M, $T = 65°C$, and $t = 4$ h.

5.0 to 7.5 MPa, the MW of PMMA increased further. The polymer phase should form even in the early stage of polymerization because of the antisolvent effect of CO_2. Because of the fast interphase diffusion enhanced by CO_2, the polymerization could undergo in both the continuous phase and the polymer phase.[19,20] Therefore, we believe that the high molar fraction of CO_2 in liquid phase under elevated pressures resulted in increasing the diffusion coefficient of MMA thus PMMA with high MW. While the pressure was further increased to 8.4 MPa, however, both the monomer conversion and the MW of PMMA started to fall and they even decreased more seriously at 9.2 MPa. As aforementioned, these two systems should exist in VLE at the beginning of the polymerization, but their final pressures were higher than 10.81 MPa (see Table I). Therefore it is reasonable to consider that a phase transition of MMA-CO_2 mixture from VLE system to homogeneous one took place during the polymerization so as to decrease the monomer concentration and hence the rate of polymerization. As a result, the monomer conversion and the MW of PMMA decreased.

The free radical polymerization of styrene and VAc in CO_2 was also examined, as listed in Tables III and IV. Table III shows that the monomer conversion and the MW of PS were relatively low in the polymerization of styrene under 15.4 MPa, but they both increased with the decrease of pressure from 9.2 to 7.5 MPa, and the MW of PS decreased somewhat as the pressure went down further to 5.0 MPa in spite of the high monomer conversion. Furthermore, the MW of PS was somewhat low, when compared with PMMA. Beuermann and Buback[12] collected the k_p values for styrene and MMA determined by PLP-SEC, in which $k_{p,MMA}$ was found 2–3 times higher than $k_{p,styrene}$ in bulk polymerization, due to the lower activation energy of MMA system than styrene (22.4 vs. 32.5 kJ/mol). Kazarian et al.[21] revealed that the carbon atom of CO_2 acted as an electron acceptor could complex with the carbonyl oxygen in PMMA resulting in its high solubility in CO_2. In this case, the higher MW of PMMA synthesized than that of PS could be explained.

Table IV shows that in the polymerization of VAc, the monomer conversion and the MW of PVAc syn-

thesized at 15.6 MPa were also low in the polymerization under 15.6 MPa. Although the MW of PVAc reached the highest value at 8.0 MPa among the experiments studied, the VAc conversion increased monotonously as the pressure going down. It is clear that the polymerization of styrene exhibits a same trend as in the MMA system, but the VAc is different from the aforementioned two. The reasons of these experimental results are not clear, but they might be attributed to the quite low glass transition temperature of PVAc (30°C)[22] and the relatively high polymerization rate of VAc,[12] which should be further investigated.

CONCLUSIONS

The effect of pressure from ambient atmosphere pressure to 28.5 MPa on the free radical polymerization of MMA in CO_2 fluid was investigated. It was found that, when the polymerization of MMA was performed under 28.5–11.8 MPa, the MMA conversion and the MW of PMMA were relatively low and MMA-CO_2 mixture was in a homogeneous phase. However, while the polymerization was carried out at or below 9.2 MPa, in which the MMA-CO_2 mixture was at VLE, the PMMA with high MW was synthesized at quite high MMA conversion. These experimental results could be related to the phase transition behavior of polymerization system from homogeneous state to VLE state. The similar phenomena were observed in styrene and VAc polymerization systems.

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