Precipitation Polymerization of Methyl Methacrylate in Tetrahydrofuran with Compressed CO_2 as Antisolvent

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ABSTRACT: Precipitation polymerization of methyl methacrylate (MMA) in tetrahydrofuran (THF) with compressed CO_2 as an antisolvent was carried out at 335 K up to 8.5 MPa, and the decomposition rate of the initiator, 2,2′-azobisisobutyronitrile (AIBN), was studied with UV/vis. Gel permeation chromatography (GPC) and differential scanning calorimetry (DSC) were used to determine the average molecular weights and glass transition temperature (T_g), and scanning electron micrography (SEM) was used to observe the morphologies of the product. The results showed that the average molecular weights of the polymer vary considerably with the volume expansion of the solution induced by compressed CO_2. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 2427–2433, 2003

INTRODUCTION

Supercritical (SC) CO_2 has been widely used in chemical reactions,[1–10] including polymerization,[1–6] because it has a strong ability to dissolve many nonvolatile materials. At the same time, compressed CO_2 and some other gases are quite soluble in a number of organic solvents. Polymerizations of monomers in liquid solvents are common in industry, and the properties of the solvents affect the product properties considerably. When a compressed gas or SC fluid is highly soluble in liquid organic solvents, it can cause volume expansion of the liquid, thus reducing the solvent strength. As a result, precipitation of the dissolved solutes occurs under suitable conditions. This process is referred as the gas antisolvent process (GAS).[11,12] Recently, the GAS process has been used successfully in recrystallization and fine particle generation[13–19] and fractionation of natural products or mixtures.[20,21] One of the main advantages of the GAS process is that the properties of the solvents can be tuned continuously by simply changing the pressure, so the particle size, particle-size distribution, and morphology of the products can be controlled by the pressure. In addition, dry particles can be produced in a single processing step and solvents can be removed easily.

In a chemical reaction system, the composition of a gas–liquid solution will change with the pressure of the gas, that is, the properties of the reaction solvent can be tuned by pressure. In this work, methyl methacrylate (MMA) was polymerized in tetrahydrofuran (THF) with compressed CO_2 as the antisolvent. We aimed to study the effect of compressed CO_2 on the properties of the product.

EXPERIMENTAL

Materials

The purity of CO_2 was 99.995%, obtained from the Beijing Analytical Instrument Factory (Beijing, China). 2,2′-Azobisisobutyronitrile (AIBN) was supplied by the Beijing Chemical Factory (Beijing, China) and was recrystallized twice from methanol. MMA (>98%) was obtained from the Beijing YiLi Chemical Agent Co. (Beijing, China) and was deinhibited and purified by vacuum distillation. THF was A.R. grade produced by the Beijing Chemical Factory.

Apparatus for determining volume expansion

Although the reactor used in this work was optical, it could not be used to determine the volume expansion of the liquid accurately because the volume of the liquid in the reactor was not a linear function of the height of the liquid level. Thus, the dependence of the volume expansion of the liquid on the pressure at the experimental temperature was measured in a 33-mL optical stainless vessel in which the volume of the liquid was a linear function of the liquid level. The apparatus is shown in Figure 1. During the experi-
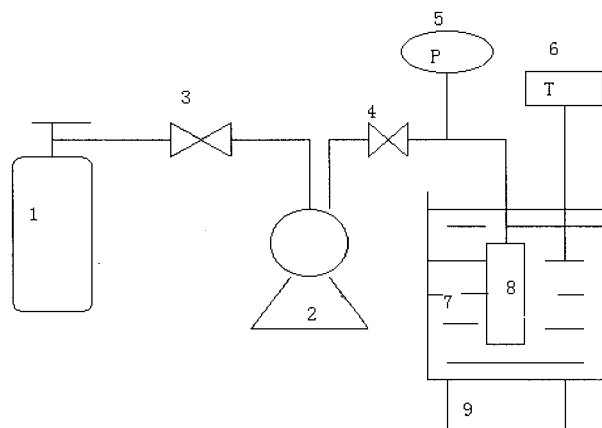
Figure 1 Schematic diagram of the polymerization apparatus: (1) gas cylinder; (3,4) valves; (2) high-pressure syringe pump; (5) pressure gauge; (6) temperature controller; (7) water bath; (8) optical cell; (9) magnetic stirrer.

Figure 2 Volumetric expansion of the liquid phase with compressed CO_2 as a function of pressure at 335 K.

ments, the vessel was immersed in a constant temperature water bath, which was controlled to 335 K with a HAAKE F3 controller. The pressure in the system was measured using a pressure gauge consisting of a transducer (IC Sensors Co. Model 93) and an indicator, which can be accurate to ±0.05 MPa in the pressure range from 0 to 20 MPa. A magnetic stirrer was used to mix the materials in the reactor.

Reactor

High-pressure reactions were carried out in a 10-mL stainless-steel reactor equipped with two quartz windows for observation of the phase behavior. Liquid CO_2 was delivered to the reactor with an SFC 8000 pump. The pressure in the reactor was measured by the same pressure gauge as used in the volume expansion. A magnetic stirrer was used to mix the materials in the reactor.

Polymerization

In a typical reaction, the reactor was purged with a flow of CO_2 for about 15 min. Then, the reactor was charged with the initiator AIBN (0.020 g) and a 2-mL
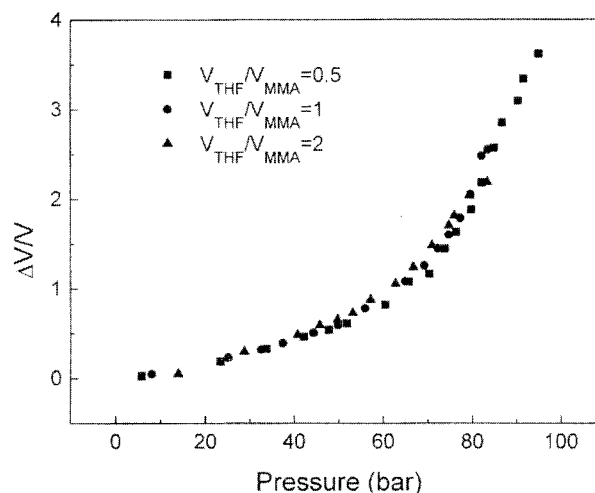
MMA and THF mixture. The temperature was then gradually increased to the desired reaction temperature of 335 K. The stirrer was started and carbon dioxide was charged into the reactor until the desired pressure was reached. Reactions were allowed to proceed for 24 h. At the end of the reactions, CO_2 was released slowly from the vessel. We found that all the THF was carried out by the released CO_2 and the product was collected as a white coagulum.

Characterization

An IR (PE 683) study confirmed that the products were poly(methyl methacrylate) (PMMA). The molecular weights of the polymers were determined by using a Maxium 80 gel permeation chromatograph (GPC) with Styragel columns of 10^3-, 10^4-, and 10^5-μ porosities. THF (25°C and 1.0 mol/min flow rate) was used as an eluent against polystyrene standards. A scanning electron micrograph (SEM) (Hitachi, Model S-530) was used to observe the polymer morphologies and a differential scanning calorimeter (DSC; PE 7 series) was used to obtain the glass transition temperature (T_g).

TABLE I
Effect of Monomer Concentration on the Precipitation Polymerization of MMA with Compressed CO_2 as Antisolvent

Sample	V_{THF}/V_{MMA} [a]	$\Delta V/V_0$ [b]	C_m (%)[c]	M_n (kg/mol)	M_w/M_n	T_g (K)
1	0.5	0.5	44.6	30.76	3.16	340.5
2	1.0	0.5	33.3	30.59	3.94	338.4
3	2.0	0.5	26.7	29.33	6.49	344.5

Reaction conditions: [AIBN] = 4.0×10^{-2} M (after expansion with CO_2); 24 h reaction time; T = 335 K.
[a] The whole volume of THF and MMA is 2 mL.
[b] Volumetric expansion of liquid phase.
[c] C_m is the initial monomer concentration in volume percentage after expansion.

TABLE II
Effect of Monomer Concentration on the Precipitation Polymerization of MMA with Compressed CO_2 as Antisolvent

Sample	V_{THF}/V_{MMA} [a]	$\Delta V/V_0$ [b]	C_m (%)[c]	M_n (kg/mol)	M_w/M_n	T_g (K)
1	0.5	1.0	33.5	19.11	2.79	347.4
2	1.0	1.0	25.0	17.47	3.08	343.3
3	2.0	1.0	20.0	13.89	3.98	349.4

Reaction conditions: [AIBN] = 3.0×10^{-2} M (after expansion with CO_2); 24 h reaction time; T = 335 K.
[a] The whole volume of THF and MMA is 2 mL.
[b] Volumetric expansion of liquid phase.
[c] C_m is the initial monomer concentration in volume percentage after expansion.

RESULTS AND DISCUSSION

Volume expansion of liquid phase with different monomer concentration

A measure of the liquid solvent solubility is given by the volumetric expansion of the liquid phase in the presence of the compressed CO_2 at a given value of temperature and pressure. Mathematically, the relative volume expansion ΔV is defined as

$$\Delta V = [V(P,T) - V_0]/V_0 \qquad (1)$$

where $V(P,T)$ is the volume of the liquid phase loaded with the compressed CO_2 and V_0 is the volume of the pure liquid phase at atmospheric pressure conditions.

Since we were interested in operating the precipitation polymerization of MMA with different properties of the solvent, the availability of the liquid expansion data of different concentrations of the monomer and at different pressures was necessary. Here, the change of the ratio of THF to the monomer is under the condition that the whole volume of THF and the monomer is fixed. Figure 2 shows the volume expansion of three different systems at the temperature of 335 K. It reveals that the different compositions of the liquid loaded with THF and the MMA monomer have little effect on the solubility of the CO_2. From the dependence of the expansion coefficient on the pressure in Figure 2, the precipitation polymerization with different solvent properties can be realized by changing the CO_2 pressure.

Precipitation polymerization

The precipitation polymerizations were conducted at 335 K in the pressure range of 4.0–8.5 MPa, which was adjusted to a fixed expansion coefficient for different polymerization systems. Before polymerization, two phases existed: the gas phase at the top and the liquid phase at the bottom which contained THF, CO_2, the MMA monomer, and the initiator AIBN. According to the literature, the dispersion polymerization of MMA stabilized with a stabilizer provided an efficient system to produce a polymer with high yield, high molecular weights, and particle products. In the absence of the stabilizer, the polymerization of MMA yielded a coagulum with a relatively low molecular weight. Also, the polymerization time in our system is long compared with the reports of dispersion polymerization in the literature.[22,23] After 24 h, after venting the carbon dioxide, the products were collected as a white coagulum. After washing with ethanol, yields were determined gravimetrically and about 50% conversion could be achieved. The molecular weight and glass transition temperatures (T_g's) of the products with different compositions in the liquid phase and different volume expansions are listed in Table I–III.

Effect of monomer concentration on molecular weight

During this experiment, the changing of the volume ratio of THF to the monomer was on the basis of a

TABLE III
Effect of Monomer Concentration on the Precipitation Polymerization of MMA with Compressed CO_2 as Antisolvent

Sample	V_{THF}/V_{MMA} [a]	$\Delta V/V_0$ [b]	C_m (%)[c]	M_n (kg/mol)	M_w/M_n	T_g (K)
1	0.5	2.0	22.3	22.47	3.82	349.5
2	1.0	2.0	16.7	20.11	5.42	344.1
3	2.0	2.0	13.3	19.17	8.13	350.0

Reaction conditions: [AIBN] = 2.0×10^{-2} M (after expansion with CO_2); 24 h reaction time; T = 335 K.
[a] The whole volume of THF and MMA is 2 mL.
[b] Volumetric expansion of liquid phase.
[c] C_m is the initial monomer concentration in volume percentage after expansion.

TABLE IV
Effect of Volume Expansion of Liquid Phase on the Precipitation Polymerization of MMA
with Compressed CO_2 as Antisolvent

Sample	V_{THF}/V_{MMA} [a]	$\Delta V/V_0$ [b]	C_m (%)[c]	M_n (kg/mol)	M_w/M_n	T_g (K)
1	0.5	0.5	44.6	30.76	3.16	340.5
2	0.5	1.0	33.5	19.11	2.79	347.4
3	0.5	2.0	22.3	22.47	3.82	349.5

Reaction conditions: [AIBN] = 5.0×10^{-2} M (before expansion with CO_2); 24 h reaction time; T = 335 K.
[a] The whole volume of THF and MMA is 2 mL.
[b] Volumetric expansion of liquid phase.
[c] C_m is the initial monomer concentration in volume percentage after expansion.

fixed whole volume of V_{THF} and V_{MMA}. Figure 2 shows that the three graphs nearly coincide with each other. Therefore, it is demonstrated that, for the systems of different compositions, the solubility of CO_2 in them was near to stable, and the volume ratio of THF to MMA at a fixed volume expansion can reflect the concentration of MMA in the solution phase. Tables I–III present the experimental results and it can be seen that the average molecular weight decreases with the concentration of the monomer. This can be explained by the equations below[24]:

$$R_p = -d[M]/dt = K_p[M \cdot][M] \qquad (2)$$

$$R_t = -d[M \cdot]/dt = 2K_t[M \cdot]^2 \qquad (3)$$

$$V = R_p/R_t = K_p[M]/2K_t[M \cdot]$$
$$= K_p[M]/(2f K_d K_t[I])^{1/2} \qquad (4)$$

where R_p, R_t, and V are the propagation rate, termination rate, and chain length, respectively. $[M \cdot]$ $[M]$, and $[I]$ stand for, respectively, the radical, monomer, and initiator concentration. K_p and K_t are the propagation and termination rate constant. f denotes the initiator efficiency. It is known from eq. (4) that decreasing the concentration of the monomer $[M]$ is expected to decrease the molecular weight for radical polymerization.

Effect of volume expansion on polymerization product

The primary objective of our experiment, to carry out precipitation polymerization of MMA, lies in the idea to utilize compressed CO_2 to adjust the properties of the solvent and to change the molecular weight of the products. As we know, THF is a solvent of MMA and PMMA and compressed CO_2 is the antisolvent to PMMA. So, the molecular weights of the products change with addition of different amounts of CO_2. The experimental results in Table IV–VI demonstrate this. Usually, molecular weights first decreased with the volume expansion and then increased when the volume expansion coefficient increased to 2.

The mechanism of how the change of the solvent property affected the polymerization is discussed in detail: First, with addition of compressed CO_2 and with the volume expansion of the liquid phase, the concentration of the monomer in the liquid phase decreased; so, from the equation below,

$$V = R_p/R_t = K_p[M]/2K_t[M \cdot] \qquad (5)$$

it is deduced that the molecular weight would decrease. Second, as CO_2 mixes with the liquid phase, it not only acts as a diluent, but also decreases the cohesive energy density (solvent strength) substantially. So, it is concluded that with increase of the volume

TABLE V
Effect of Volume Expansion of Liquid Phase on the Precipitation Polymerization of MMA
with Compressed CO_2 as Antisolvent

Sample	V_{THF}/V_{MMA} [a]	$\Delta V/V_0$ [b]	C_m (%)[c]	M_n (kg/mol)	M_w/M_n	T_g (K)
1	1.0	0.5	33.3	30.59	3.94	338.4
2	1.0	1.0	25.0	17.07	3.08	343.3
3	1.0	2.0	16.7	20.11	5.42	344.1

Reaction conditions: [AIBN] = 5.0×10^{-2} M (before expansion with CO_2); 24 h reaction time; T = 335 K.
[a] The whole volume of THF and MMA is 2 mL.
[b] Volumetric expansion of liquid phase.
[c] C_m is the initial monomer concentration in volume percentage after expansion.

TABLE VI
Effect of Volume Expansion of Liquid Phase on the Precipitation Polymerization of MMA with Compressed CO_2 as Antisolvent

Sample	V_{THF}/V_{MMA} [a]	$\Delta V/V_0$ [b]	C_m (%)[c]	M_n (kg/mol)	M_w/M_n	T_g (K)
1	2.0	0.5	26.7	29.33	6.49	344.5
2	2.0	1.0	20.0	13.89	3.98	349.4
3	2.0	2.0	13.3	19.17	9.13	350.0

Reaction conditions: [AIBN] = 5.0×10^{-2} M (before expansion with CO_2); 24 h reaction time; T = 335 K.
[a] The whole volume of THF and MMA is 2 mL.
[b] Volumetric expansion of liquid phase.
[c] C_m is the initial monomer concentration in volume percentage after expansion.

expansion the oligomeric radicals precipitated from the solution decreased and the locus of the polymerization shifted from the solution phase to the polymer phase. Usually, when polymerization proceeds in the particle phase, R_t will decrease due to the high viscosity of the particle phase.[25] According to eq. (5), the molecular weight of the product is inversely proportional to the termination rate constant K_t. So, the molecular weight will increase with increase of the volume expansion. Apart from the two factors discussed above, other factors were explored. Usually, in bulk polymerization, the propagation rate of K_p has been shown to be almost constant, unaffected by change in the polymerizing medium, until the conversion is very high. So, in our polymerization, the effect of the propagation rate constant was not considered. But how does the radical concentration change with increase of the volume expansion? This is the third aspect that is discussed.

A UV/vis spectroscopic method was used to examine the initiation rate.[26] In considering that the monomer will polymerize during the process of initiator decomposition, ethyl acetate (EA) was used to replace the monomer MMA to initiate the polymerization system. The experimental results are listed in Table VII, which reveals that the initiator efficiency (f) increased with the volume expansion and R_d increased. So, the concentration of the monomer radical $[M \cdot]$ increased with the volume expansion. On the basis of eq. (5), the molecular weight is inversely proportional to $[M \cdot]$. The higher the radical concentration, the lower are the molecular weights. Hence, it is concluded that the

TABLE VII
Decomposition Rates of AIBN in CO_2—EA–THF Mixtures at 335 K

Sample	V_{THF}/V_{EA} [a]	$\Delta V/V_0$ [b]	R_d (S^{-1})
1	1.0	0.5	4.47×10^{-6}
2	1.0	1.0	4.94×10^{-6}
3	1.0	2.0	6.24×10^{-6}

[a] The whole volume of THF and EA is 2 mL.
[b] Volumetric expansion of liquid phase.

molecular weight decreased with the volume expansion of the liquid phase.

When compressed CO_2 was added to the polymerization system, there were three factors that influenced the molecular weights of the products: First, the diluents decreased the monomer concentration in the liquid phase. Second, the change of the solvent property makes the polymerization transfer from the solution phase to the particle phase, where it decreases K_t. Third, the change of the solvent property is attributed to the increase of R_d and so $[M \cdot]$ increased. Also, the first and the third factors contribute to the decrease of the molecular weight. The second factor contributes to the increase of the molecular weight. When the volume expansion is comparatively low, the first factor of the diluents and the third factor of increasing $[M \cdot]$ are decisive, that is, the molecular weights decrease with the volume expansion of the liquid. When the volume expansion is up to 2, the second factor of decreasing R_t is more decisive and molecular weights began to increase again. At the same time, the molecular weight distribution also increased.

Effect of volume expansion on the glass transition temperature and morphology

The results in Tables I–III demonstrate that the glass transition temperatures do not change regularly with the molecular weight of the products as usually happens in organic solvents. In this work, bulk polymerization without CO_2 was also carried out at the same polymerization condition and T_g was 388.2 K, which is much higher than those of the products obtained in the presence of CO_2. Hsiao et al.[22] reported that the compressed CO_2 and SC CO_2 could highly plasticize PMMA. The plasticization of the products may be one of the main reasons for the reduction of the glass transition temperature.

The SEM was used to observe the polymer morphologies. The results of the products polymerized at $V_{THF}/V_{MMA} = 1$ with different $\Delta V/V_0$ are shown in
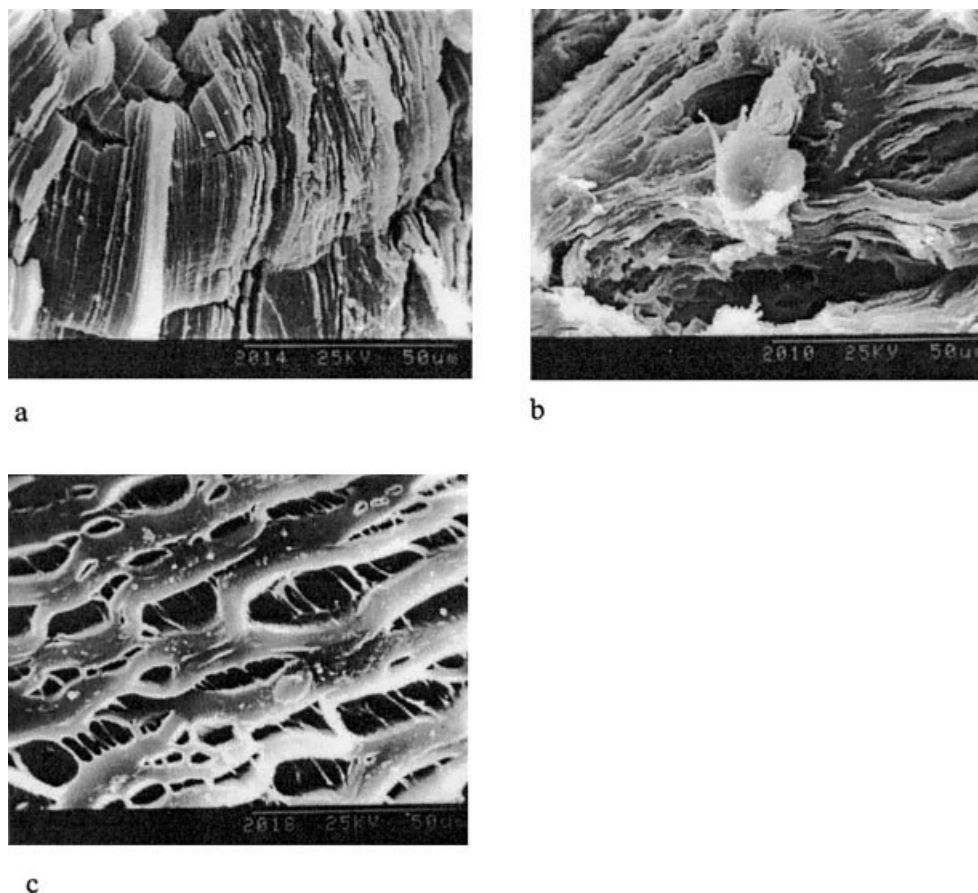
Figure 3 Scanning electron micrographs of PMMA prepared by precipitation polymerization in THF with compressed CO_2 as the antisolvent at 335 K ($V_{THF}/V_{MMA} = 1.0$; [AIBN] $= 5.0 \times 10^{-2}$ M, before expansion with CO_2): (a) $\Delta V/V_0 = 0.5$; (b) $\Delta V/V_0 = 1.0$; (c) $\Delta V/V_0 = 2.0$.

Figure 3. The products become porous at $\Delta V/V_0 = 2.0$ for the reason that the higher was $\Delta V/V_0$ the more compressed CO_2 the product contained and it was charged into bubbles during the releasing process and left holes in the products. So, the swelling of compressed CO_2 in the polymerization product can be reflected by the surface morphologies.

CONCLUSIONS

The precipitation polymerization of MMA in THF with compressed CO_2 as the antisolvent was carried out at 335 K. Compressed CO_2 can be used to adjust the properties of the solution so as to adjust the molecular weight of the product. Due to the effect of plasticization, the glass transition temperature decreased sharply.

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