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A Kinetic Investigation of the *In Situ* Polymerization of Methyl Methacrylate Under Supercritical Fluid CO₂ Conditions Using High-Pressure DSC

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ABSTRACT: The polymerization kinetics of methyl methacrylate (MMA) under supercritical fluid CO₂ was studied by using high-pressure DSC. The results indicate that CO₂ can significantly reduce the cage effect and improve the chain propagation reactions, with the observed solvent-like effects being enhanced by increased CO₂ pressures. The polymerization of MMA under isothermal conditions and 56 atm of CO₂ was characterized by a first-order

kinetic rate expression over the conversion range 20–80%. The apparent activation energy for the reaction was found to be 51.6 kJ/mol, which is less than the value reported under ambient conditions (68.2 kJ/mol). The polymerization kinetics were also evaluated under nonisothermal conditions. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1236–1239, 2004

Key words: polymerization; CO₂; DSC; reaction kinetics

INTRODUCTION

Over the last decade, several researchers have explored the use of supercritical carbon dioxide (Sc-CO₂) as an environmentally friendly solvent for a number of chemical technologies.¹ Sc-CO₂ offers a wide range of opportunities as a benign media for chemical reactions and a replacement for more toxic solvents that have the potential to be responsible for undesirable vapor emissions.² For example, in the area of polymer synthesis, the use of Sc-CO₂ has received much attention as a replacement for volatile organic solvents such as chlorofluorohydrocarbons, and high molecular weight fluoropolymers were successfully synthesized by using free-radical initiators in Sc-CO₂. From the synthesis and processing points of view, these fluoropolymers are difficult to process because of their low solubility in most organic solvents. Fluoropolymers, however, are exceedingly soluble in Sc-CO₂, thus making this an ideal environmental alternative to chlorofluorocarbons. Other monomers such as *p*-perfluoroethyleneoxymethylstyrene (STF) were also polymerized with excellent results by using Sc-CO₂ as the solvent.^{1–4} Sc-CO₂ is now well established as a solvent for use in a wide variety of chemical technologies including extraction, dry cleaning, and paint spraying. The reasons are principally associated with the prop-

erties of this fluid, such as being nontoxic, nonflammable, inexpensive, and easy to recycle and dispose of, making it ideal as a sustainable green solvent.^{5–7}

Although the use of liquid Sc-CO₂ as a green, environmentally friendly solvent for polymerization has become a widespread, growing reality, little or no information is available on real-time reaction kinetics. For Sc-CO₂ to function as a solvent, the reaction must be carried out in a sealed environment with CO₂ in the highly compressed state. Thus, to obtain real-time kinetic data, special and unique equipment are required. High-pressure reaction vessels⁸ and a high-pressure extruder⁹ are two typical types of instruments that were used to perform these measurements. Consequently, conventional analytical techniques, such as FTIR spectroscopy and conventional DSC, alone are not well suited for the study of polymerization reactions involving Sc-CO₂. Previous work in our laboratory has involved the use of high-pressure DSC to measure CO₂-induced plasticization,¹⁰ crystallization,^{11,12} and melting¹³ of polymers. These studies have allowed us to establish effective *in situ* techniques for the characterization of polymer–gas systems. In this current work, we have used these established methods to study the polymerization kinetics of methyl methacrylate (MMA) under high-pressure CO₂.

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EXPERIMENTAL

MMA monomer was purchased from Aldrich. The free-radical initiator, benzoyl peroxide (BPO), was ob-

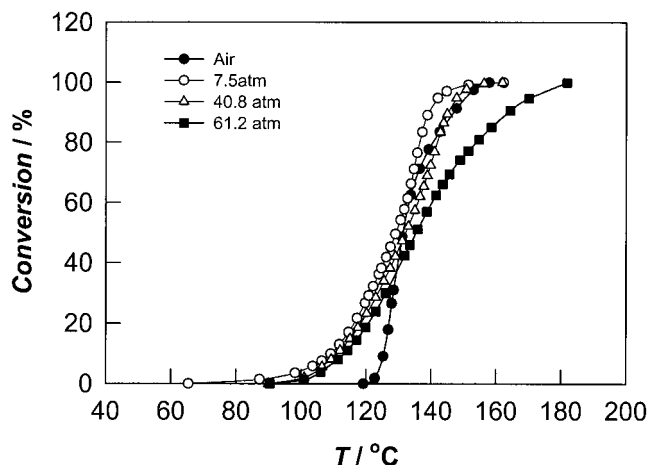


Figure 1 MMA conversions at different CO₂ pressures. Nonisothermal reaction at conditions of 5°C/min from 25 to 220°C (Initiator, 0.5% BPO).

tained from Fisher Scientific. Bone-dry CO₂ was a product of Matheson, with a purity of 99%.

The polymerization kinetics were studied with a Setaram DSC-121, described in detail elsewhere.¹⁰ The DSC unit, consisting of two symmetrical high-pressure cells (about 0.15 cm³ in volume), was connected to a gas reservoir and a gas-handling manifold. Samples (30–60 mg) of MMA containing various concentrations of dissolved BPO were loaded into the sample cell and sealed with an aluminum O-ring. Both the reference and the sample cells were then pressurized with CO₂ to the desired level and held for a few minutes at 25°C. The sample was then scanned from 25 to 225°C at the controlled heating rates of 5, 10, and 15°C/min. The high-pressure cells were constantly purged with N₂ gas at a flow rate of 70 cm³/min. Reactions were also studied under isothermal conditions at 80, 90, 100, and 110°C, respectively. During the isothermal studies, both the sample and the reference cells were rapidly heated to the selected temperature, which was then held constant while the associated heat of reaction was recorded. Molecular weights and polydispersity of the resultant polymers were determined by gel permeation chromatography (GPC) by using tetrahydrofuran (THF) as solvent by means of a Waters 515 HPLC pump, coupled with a Waters 410 differential refractometer detector and a Waters 996 array detector, operating at a wavelength of 260 nm. A set of Microstyragel columns (10³, 10⁴, and 10⁵) were used and calibrated with polystyrene standards in THF.

The measured exothermic DSC curves were used to evaluate the kinetics of the polymerization reaction by using the standard *t* slice integration methodology.¹⁴ It was assumed that the total integrated area corresponded to 100% conversion of the monomer to the polymer. The kinetics were analyzed by using the rate equation for an *n*th order reaction expressed as^{15,16}

$$\frac{d\alpha}{dt} = k(1 - \alpha)^n \quad (1)$$

$$k = A \exp\left(\frac{-E_a}{RT}\right) \quad (2)$$

where, in eq. (1), $d\alpha/dt$ is the reaction rate (s⁻¹), α is the fractional conversion, k is the specific rate constant, and n is the reaction order. In eq. (2), A is the pre-exponential factor, E_a is the apparent activation energy, R is the universal gas constant, and T is the reaction temperature (K).

RESULTS AND DISCUSSION

The nonisothermal conversion of MMA under various pressures of CO₂ is shown in Figure 1 along with the conversion obtained in air at ambient pressure. From these graphs, it can be seen that the polymerization is rapid in air because of the well-known auto-acceleration effect.¹⁵ However, the introduction of CO₂ results in a retardation of the reaction whose rate decreases with increasing CO₂ pressure. These effects can be quantified by the reaction half-time temperature and the slope of the conversion-temperature curve (Table I). GPC analysis of the poly(methyl methacrylate) (PMMA) sample prepared in air gave values of $M_n = 19,700$ and $M_w/M_n = 2.2$, while the sample prepared under 56 atm of pressurized CO₂ gave values of $M_n = 26,500$ and $M_w/M_n = 2.2$. The fact that higher molecular weight polymers are obtained in the presence of CO₂ clearly indicates that CO₂ is acting as a solvent during the polymerization, thereby reducing the cage effect and preventing the associated localized overheating. This conclusion is supported by the fact that CO₂ is highly soluble in PMMA^{16,17} (e.g., 8 wt % of CO₂ would dissolve in PMMA at 80°C and 56 atm¹⁷ due to the strong interactions between PMMA molecules and CO₂).¹⁶ In addition, the CO₂ can have a plasticization effect on PMMA,^{16,17} allowing the polymer chains to be highly mobile. This clearly favors reaction between the polymerizing chain and the monomers (i.e., chain propagation reaction), promoting the formation of polymers with higher molecular weight.

TABLE I
Effect of CO₂ Pressure on the Nonisothermal Polymerization of MMA (Initiator 0.5% BPO)

	$T_{1/2}$ (°C)	$t_{1/2}$ (min)	$d\alpha/dT$ (°C ⁻¹) ^a
1 atm air	131.1	18.70	0.0534
7.5 atm CO ₂	129.0	20.05	0.0289
40.8 atm CO ₂	132.0	20.60	0.0264
61.2 atm CO ₂	135.9	19.43	0.0208

^a Determined within the conversion range of 20 to 80%.

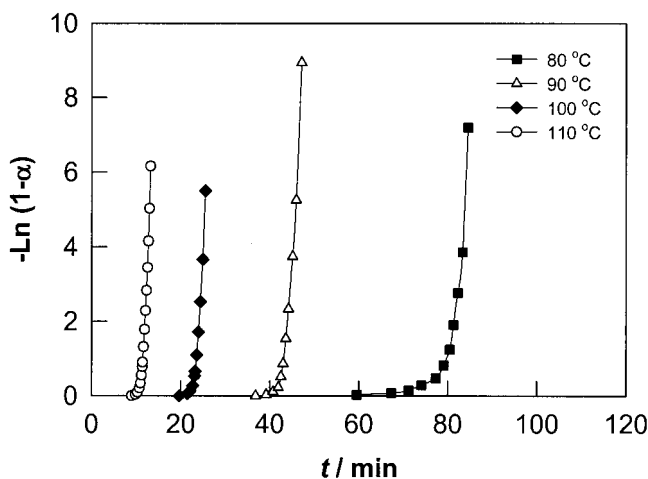


Figure 2 First-order plot of MMA under CO₂ in isothermal condition (BPO = 0.5%, CO₂ pressure was 56 atm).

These findings are similar to those observed by Davidson and DeSimone,^{1,18} who studied the kinetics of the free-radical polymerization of 1,1-dihydroperfluorooctyl acrylate with azobis-isobutyronitrile (AIBN) as an initiator in Sc-CO₂. In their study, which involved monitoring the reaction by using high-pressure UV spectroscopy, it was concluded that, for CO₂ to be an effective solvent for the free-radical polymerization, it must act as an inert agent, even in the presence of the highly electrophilic hydrocarbon radicals. Additionally, it was observed that the initiator efficiency was much greater in CO₂, which is in good agreement with the results that we obtained for the MMA polymerization in this work. As shown in Figure 1, it can be clearly seen that the reaction commences earlier under CO₂ when compared to the reaction under air.

A more detailed study of the polymerization kinetics of MMA under CO₂ was performed under isothermal conditions. Figure 2 shows the first-order plot of MMA conversion under 56 atm of CO₂. It will be noted that a linear relationship between $\ln(1 - \alpha)$ and t was obtained in the conversion range 20–80%, in agreement with literature reports.^{15,19} Consequently, eq. (1) can be simplified such that

$$-\ln(1 - \alpha) = kt \quad (3)$$

By using this equation and data from Figure 2, the reaction rate constant k of MMA under 56 atm of pressurized CO₂ was determined and used in the Arrhenius-type relationship [eq. (2)] to determine E_a . Figure 3 depicts the Arrhenius plot of $\ln(k)$ versus $1/T$, from which an apparent activation energy of $E_a = 51.6$ kJ was calculated.

Generally, the kinetic parameters for MMA polymerization in air are used to monitor the rates of

radical formation. In the free-radical polymerization of MMA, the bimolecular termination of the radicals proceeds simultaneously by combination and disproportionation reactions, with both rates being highly temperature dependent. Reports indicate that the disproportionation rate has a higher activation energy than the combination reaction.²⁰ Furthermore, physical factors such as the viscosity of the reaction medium can greatly influence the rates of polymerization. In highly viscous media, the rate of termination is reduced in both bulk and solution polymerization processes,²¹ with the rate dependent upon the reaction temperature and initial monomer concentration. The polymerization kinetics of MMA in air is, therefore, reproducibly determined by the ratio of the propagation and termination rate constants. The activation energy can, therefore, be determined by using the relationship²⁰

$$\text{Rate} = A \exp \left[\frac{-(2E_p - E_t)}{RT} \right] \quad (4)$$

where E_p and E_t are the activation energies for the propagation and termination reactions, respectively. According to the literature, the activation energy for MMA polymerization is 68.2 kJ/mol in air, using BPO as the initiator and benzene as the solvent.^{20,21} This compares with an activation of 51.6 kJ/mol under CO₂. This is an overall value due to the fact that it is very difficult to determine the individual activation energies (propagation and termination) by using the high-pressure DSC method. Although this value is similar to the activation energy obtained in air, it does, however, represent a reduction because the use of CO₂ lowers the viscosity and favors the interaction of this gas with PMMA, resulting in a more rapid reaction (Fig. 1).

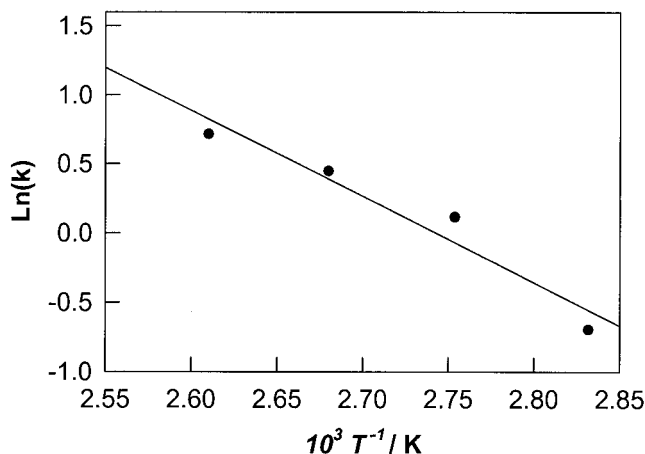


Figure 3 Arrhenius plot for the polymerization of MMA under CO₂ and isothermal conditions (Initiator, BPO = 0.5%, CO₂ pressure was 56 atm).

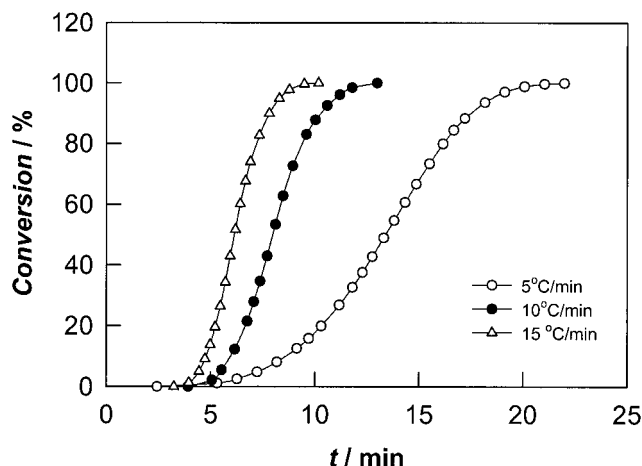


Figure 4 Polymerization of MMA under CO_2 and nonisothermal condition (Initiator BPO = 0.5%, CO_2 pressure was 56 atm).

The nonisothermal polymerization of MMA under CO_2 (56 atm) was also investigated and the results are presented in Figure 4. From this data, it can be seen that high heating rates favor more rapid reaction. This observation is consistent with eq. (2) because the faster the heating rate, the shorter is the time needed to reach the higher reaction temperatures. However, it should be noted that the faster heating rate did not aid in the completion of the polymerization reaction as measured by monomer conversion within a fixed temperature range (i.e., 25–225°C). For example, it was noted that, for reactions conducted at a heating rate of 15°C/min, the total measured heat was 122.3 J/g, while when the reaction was conducted at 5°C/min, it was 365.0 J/g. The reason is that, under higher heating rate conditions, there is sufficient time to allow the monomer to diffuse and complete the chain propagations. Consequently, lower molecular weight polymers are expected from the reactions conducted under higher heating rates.

CONCLUSION

By using the established high-pressure DSC technique, it was found that CO_2 at supercritical condi-

tions is an effective solvent in the formation of PMMA during a free-radical polymerization reaction. During this study, higher molecular weight PMMA was obtained, which indicated a reduction in the cage effect when CO_2 is used as the solvent. Furthermore, the apparent activation energy of 51.6 kJ/mol obtained from the first-order kinetic data is lower than the energy for this reaction under air, indicating the strong interaction of this gas with PMMA, favoring chain propagation.

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