How does magnetic field affect polymerization in supercritical fluids? Study of radical polymerization in supercritical CO_2

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The effect of magnetic field (MF) on the polymerization of methyl methacrylate and styrene initiated with benzoyl peroxide in supercritical (SC) CO_2 was studied. The polymerization yields and the molecular weight of poly(methyl methacrylate) increased when a MF was employed. However, the MF did not noticeably affect the polymerization in cyclohexane. This unusual phenomenon may result from the special swelling power of SC CO_2 for the polymers and the larger diffusivity of SC CO_2 than the liquid solvent.

Reactions in supercritical fluids (SCFs) have many unique properties,[1] such as tuneable solvent power. Recently, researchers have paid more and more attention to chemical reactions,[1] including polymerizations,[2,3] in SC CO_2, which is a promising reaction medium. In comparison to existing homogeneous and heterogeneous technologies for making polymers, CO_2 technology has several significant advantages, as it will allow for the elimination of (*a*) expensive polymer drying steps; (*b*) toxic and hazardous organic solvents; and (*c*) expensive waste-water treatment and disposal steps for removing monomers, surfactants and emulsifiers.[4]

It was well-known that a magnetic field (MF) can affect some chemical reactions occurring in solids, liquids, microemulsions, and in biological situations.[5] The magnetic field effect (MFE) on polymerization has been studied in bulk, emulsion, and solution polymerizations.[6–9] For example, the molecular weight of the polystyrene (PS) produced by photo-induced emulsion polymerization with an oil-soluble initiator increased by a factor of five with a relatively weak MF (1000 G).[8a] We think that the MF may affect some reactions in SCFs and may have some unique features, and MF may become a useful tool to control some reactions in SCFs. Therefore, to study the MFE on the chemical reactions in SCFs is of great importance to both pure and applied sciences.

In this work, we have studied the MFE on the radical polymerization of methyl methacrylate (MMA) and styrene (St) in SC CO_2 initiated with benzoyl peroxide (BPO). The MFE on the polymerization in cyclohexane was also studied for comparison.

Experimental

CO_2 with a purity of 99.95% was supplied by Beijing Analytical Instrument Factory. BPO, St, MMA, cyclohexane, and methanol were A. R. grade supplied by Beijing Chemical Factory. St and MMA was washed twice with 10% NaOH aqueous solution, and twice with water, dried over fused $CaCl_2$ for 24 h and distilled under reduced pressure. BPO was recrystallized twice from $CHCl_3$–MeOH.

The polymerization was conducted in a stainless steel reactor of 12.6 ml. Two permanent magnets were installed outside of the reactor. The strength of the measured MF in the reactor was 1000 G and 3000 G, respectively. In a typical experiment, the reactor was charged with a suitable amount of BPO and the degassed monomer. The air in the system was removed under vacuum at 0 °C. CO_2 was compressed into the reactor using a high-pressure syringe pump (model SCF 8000) to approximately 5 MPa at room temperature, and then the reactor was placed in a constant temperature water bath and more CO_2 was added to the system until the desired pressure was reached. After the desired reaction time, the reactor was cooled in cold water and the CO_2 was slowly vented. The product mixture was precipitated by a large excess of methanol, which was then collected by vacuum filtration over a Hirsch funnel. The product was dried under vacuum and the yield of the product was determined gravimetrically. The polymerization in cyclohexane was also conducted in the sealed stainless steel reactor. The concentrations of the monomer and initiator were the same as those in SC CO_2.

In order to determine the phase behaviour of the reaction system during the reaction, the polymerization experiments without MF were also performed in a high-pressure optical cell of 40 ml, which was used previously for phase behaviour studies.[10] Experiments showed that the reaction systems were initially homogeneous and that precipitation occurred during the polymerization process.

The molecular weight of PMMA were determined by gel permeation chromatography (PL-GPC210) using a differential refractometer as detector (eluent: THF; flow rate: 1 ml min^{-1}; injection volume: 10 uL; calibration: standard PS samples).

Results and discussion

The polymerization of St

The polymerization of St was conducted in SC CO_2 at 70.0 °C and at pressures of 13.0 and 16.0 MPa. The density of CO_2 is 0.404 g cm^{-3} at 13 MPa and 0.550 g cm^{-3} at 16 MPa at this temperature; these values were calculated from an accurate equation for CO_2.[11] The initial concentration of the monomer was 1.0 mol l^{-1} and the concentration of initiator was 0.02 mol l^{-1}.

The reproducibility of the experiments is crucial in this work. Thus, we first tested the reproducibility of the yields at

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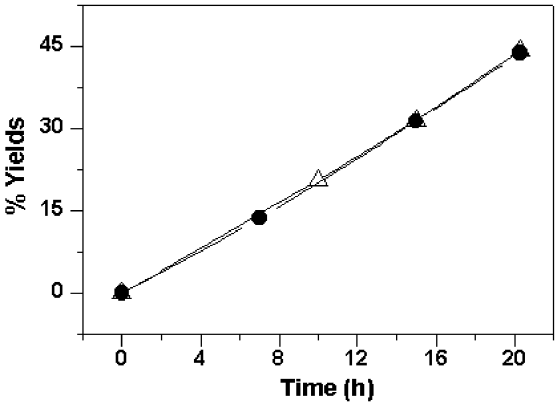

Fig. 1 The yields of two series of independent experiments at 70.0 °C and 16.0 MPa in the absence of magnetic field.

70.0 °C and 13.0 MPa with a reaction time of 10 h by repeating the experiments four times. The results indicated that the reproducibility was better than 0.5%. We also tested the reproducibility by comparing the dependence of the yields on reaction time of two independent series of experiments at 16.0 MPa without MF, and the results are shown in Fig. 1. The two curves of the independent series of experiments are nearly overlapped, which further indicates good reproducibility.

Fig. 2 shows the dependence of the yields of PS on reaction time at 13.0 and 16.0 MPa with and without external MF (1000 G). The results in the figure show that the yields in the presence of MF are higher at both pressures. In other words, the external MF accelerates the polymerization. In order to express the effect of MF quantitatively, we define the relative change *R*(*H*) of the yields as: $R(H) = 100 \times (Y_{\mathrm{MF}} - Y_0)/Y_0$, where Y_{MF} and Y_0 stand for the yields with and without MF, respectively. The average *R*(*H*) is 4.6% at 13.0 MPa, and 5.0% at 16 MPa. To investigate the effect of the strength of the MF on yields, the polymerization at 16 MPa was also conducted with a 3000 G external MF. The results are shown in Fig. 3 and the average *R*(*H*) is 10.2%, which is twice as large as that at the 1000 G MF.

For comparison with the polymerization in a conventional solvent, the MFE on the polymerization in cyclohexane was also studied with a 3000 G MF. The yields are also shown in Fig. 3. With the application of MF, the yields do not change noticeably. The average *R*(*H*) is only 0.8% which is nearly within the experimental error.

Our experiments indicate that the effect of MF on the molecular weight of PS polymerized in both SC CO_2 and cyclohexane is not considerable. The main reason may be that the effect of MF on the reaction rate is not significant.

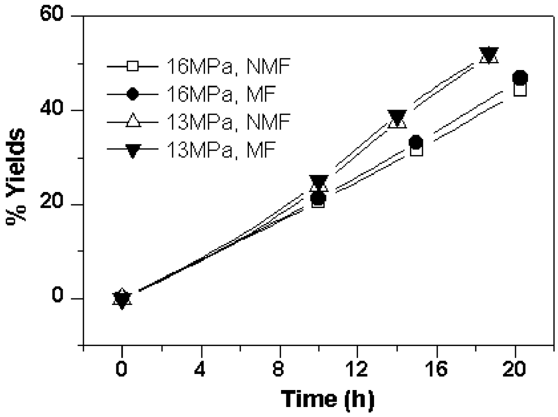

Fig. 2 The MFE on the yield of PS polymerized at different pressures of SC CO_2 with (MF) and without (NMF) a 1000 G external magnetic field.

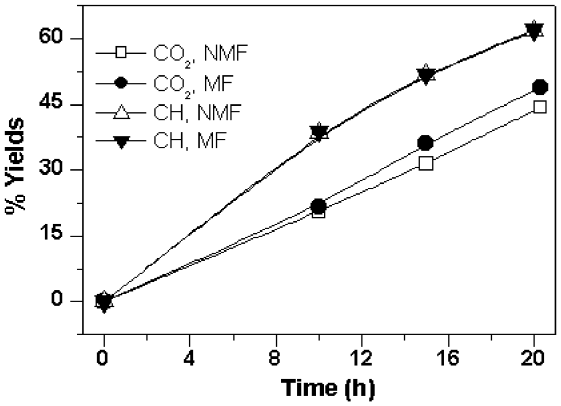

Fig. 3 The MFE on the yield of PS polymerized in SC CO_2 and cyclohexane (CH) with (MF) and without (NMF) a 3000 G external magnetic field.

The polymerization of MMA

The polymerization of MMA was conducted in SC CO_2 at 60.0 °C and 13.0 MPa with different reaction times. A 3000 G external MF was applied to test the MFE on the polymerization. The reaction temperature is lower because the reactivity of MMA is higher than St, as can be seen from a comparison of Figs. 3 and 4. The yields and weight average molecular weights (MW) of the PMMA are shown in Figs. 4 and 5, respectively. These two quantities are much higher in the presence of MF than in the absence of MF. The *R*(*H*) are 147%, 199%, and 7.9% for 2, 3, and 4 h, respectively. When the reaction time is 3 h, the yield of PMMA with MF is almost three times as large as that without MF. Owning to the very high conversion reached when the reaction time is 4 h, the difference in yields with and without MF is small.

The polymerization of MMA in cyclohexane at the same temperature, initial monomer concentration, and reaction time was also carried out. The results are shown in Figs. 4 and 5. It can be seen that the effect of MF on the yields and MW of PMMA polymerized in cyclohexane is very limited.

Mechanism of the MFE

It was reported that MF (43 000 G) influenced the singlet-sensitized photolysis of BPO in toluene owing to the Δg mechanism.[12] However, the MFE on BPO decomposition in our experiment may be negligible because of the low MF strength.

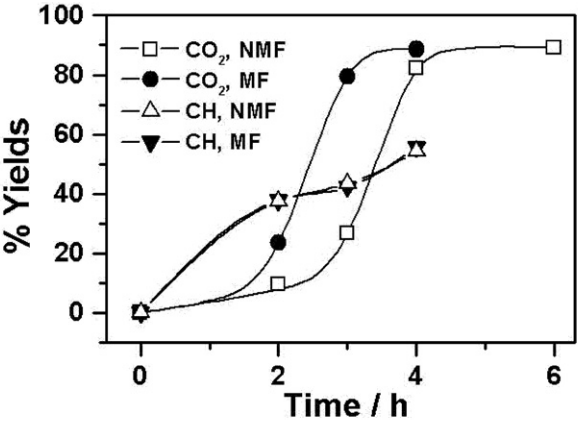

Fig. 4 The yield of PMMA at different reaction times in SC CO_2 and cyclohexane with and without MF.

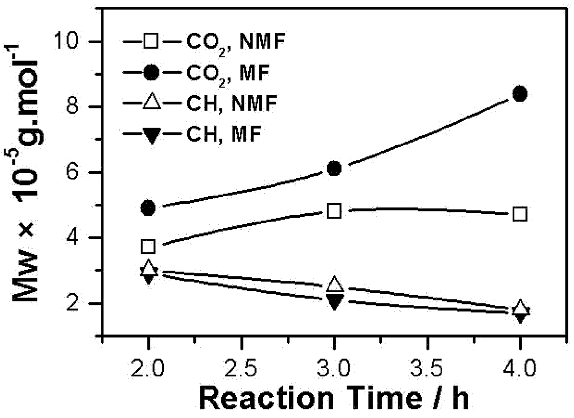

Fig. 5 The weight average molecular weight of PMMA at different reaction times in SC CO_2 and cyclohexane with and without MF.

The MFE on the yields of the polymerization in this work may be explained with the hyperfine mechanism on random radical pairs. MFEs for random radical pairs have been observed in micelles.[13] When two radicals experience a random encounter, the formed radical pair has a 25% chance of having a singlet (S) multiplicity and a 75% chance of being triplet (T). At zero field, the three sublevels of the triplet, T_0 and $T_{\pm}$, are energy degenerate, and they all can transform to the singlet through intersystem crossing. Owning to the Zeemann effect, the $T_{\pm}$ sublevels will split from T_0 in an external MF. As a result, in the presence of the MF triplet-singlet crossing from $T_{\pm}(T_{\pm} \rightarrow S)$ will be slowed down or completely shut off. Therefore, the MF can affect the distribution between the triplet and singlet states of radical pairs. Generally, the singlet radical pairs tend to recombine readily while triplet radical pairs tend to separate by diffusion. As a result, the MF affects the competition between recombination and separation of radical pairs.

In radical polymerization, the termination process involves the random encounter of two radicals. When the formed radical pair is singlet, it has a large probability to recombine, thus terminating the propagating chain. When the pair is a triplet, they can not terminate except by first evolving to the singlet. When a MF is applied, the $T_{\pm} \rightarrow S$ crossings are slowed down or shut off. As a result, the termination rate of the polymerization process decreases and the yield of the polymer increases under the MF. However, it is not true that in all cases the termination will be affected by the MF. When the solvent "cage" is very weak, such as in low viscosity solutions, the lifetime of a radical pair is so short that no intersystem crossing occurs. So the reaction of the radical pair will not affected by the MF. Therefore, the MFE should be more significant when the solvent cage effect is large, such as in viscous solution and in micelles.[5a,13,14]

It is surprising that the MFE on the polymerization in SC CO_2 is much more obvious than in cyclohexane while the viscosity of SC CO_2 is much lower than that of cyclohexane. This unusual phenomenon may result from the strong ability of CO_2 to swell and plasticize the polymer. It was reported that the glass transition temperature of PMMA decreases with an increase in CO_2 pressure.[15] Under our experimental conditions the reaction temperature is above the glass transition temperature of the highly plasticized PMMA precipitate. All these will facilitate the diffusion of the monomer and initiator into the precipitate phase such that the polymerization can proceed inside the precipitation phase. The viscosity of the precipitate is very high. The translational movement and rotation of the oligomer radicals are restricted inside the precipitate. Thus, the viscous precipitate supplies a strong "cage" for the randomly encountered radical pairs. The termination rate of the polymerization in the precipitate is reduced in the presence of MF owing to the influence of MF on the intersystem crossing process, as stated above. Consequently, the yield increases in comparison with that in the absence of MF.

The above explanation is further supported by the difference of the magnitude of the MFE on PMMA and PS. Our experiments showed that the PMMA were porous and foamy after the venting of CO_2, while the PS is not porous. PMMA was swelled by CO_2 to a larger extent, and thus a larger percentage of the reaction takes place in the precipitate phase. MF mainly accelerates the reaction in the precipitate phase. Thus, the MFE on the polymerization of MMA is more significant than on that of St.

In the case of polymerization of MMA in cyclohexane precipitation also occurred during the reaction process. However, polymerization in the precipitate is negligible as the diffusion of the monomers and initiator into the precipitate is much slower. Therefore, the MFE is not significant.

Conclusion

In summary, the effect of external MF on the polymerization of MMA and St in SC CO_2 was investigated. It was observed that MF affects the yield and molecular weight of PMMA significantly, but the effect of the MF on the polymerization of St is much smaller. The polymerization of the two monomers in cyclohexane was not affected by the MF under the same conditions.

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