

# POLYMERISATION OF METHYL METHACRYLATE EXPANDED WITH DENSE CARBON DIOXIDE

**F.P. Lucien**\*, G. Zwolak

School of Chemical Engineering & Industrial Chemistry, The University of New South Wales, UNSW Sydney, NSW 2052, Australia.

e-mail: [f.lucien@unsw.edu.au](mailto:f.lucien@unsw.edu.au), fax: +61-2-9385-5966

The catalytic chain transfer polymerisation of methyl methacrylate expanded with dense CO<sub>2</sub> is reported. Experimental values of the chain transfer constant ( $C_s$ ) are presented at 50°C and at pressures of 2 and 5 MPa, using a cobalt complex as the chain transfer catalyst. It is shown that the values of  $C_s$  for the catalyst in CO<sub>2</sub>-expanded methyl methacrylate are significantly higher than that in bulk monomer. This effect is mainly attributed to the enhancement of the chain transfer rate, arising from the reduction in the viscosity of the medium. These findings highlight the potential of CO<sub>2</sub>-expanded monomers for the synthesis of low molecular weight polymers via catalytic chain transfer polymerisation.

## INTRODUCTION

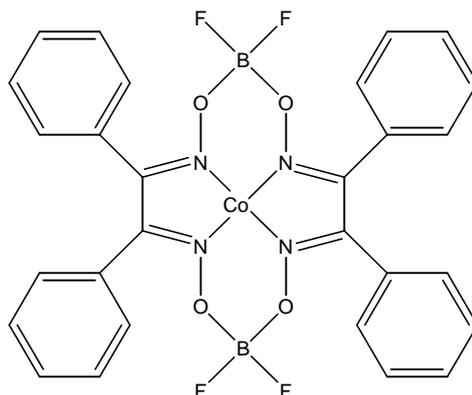
Dense CO<sub>2</sub> is increasingly finding application as a reaction solvent due to its tunable properties and its inertness towards many chemical species. Such reaction processes are most often carried out under supercritical conditions in which the CO<sub>2</sub>/reactant mixture forms a single homogeneous phase. Recent investigations have shown, however, that the advantages associated with the use of dense CO<sub>2</sub> as a reaction solvent can also be obtained by performing chemical synthesis in a liquid medium expanded with dense CO<sub>2</sub>. Furthermore, these advantages are realised at greatly reduced operating pressures.

Lui et al. [1,2] have employed CO<sub>2</sub>-expanded solvents in the polymerisation of styrene and methyl methacrylate (MMA). The solvents considered include tetrahydrofuran, cyclohexane, chloroform, ethyl acetate and iso-amyl acetate. Their work demonstrates that the properties of the polymers, such as the molecular weight and the polydispersity index, can be tuned by controlling the extent of volumetric expansion of the solvent. Wei et al. [3] have considered the application of CO<sub>2</sub>-expanded acetonitrile in homogeneous catalytic oxidations. They report oxidation rates that are 1 to 2 orders of magnitude greater than those obtained with either neat acetonitrile or supercritical CO<sub>2</sub> as the reaction medium. In these preceding examples, the advantages associated with CO<sub>2</sub>-expanded liquids have been obtained at pressures below 10 MPa.

Phiong et. al. [4] have recently reported a study on the catalytic hydrogenation of CO<sub>2</sub>-expanded  $\alpha$ -methylstyrene without the use of an additional solvent. It is shown that the rate of hydrogenation is enhanced significantly in the range of pressure from 7 to 13 MPa. This variation on the use of CO<sub>2</sub>-expanded liquids has yet to be explored in the area of polymer synthesis. The focus of the present study is the catalytic chain transfer (CCT) polymerisation of CO<sub>2</sub>-expanded MMA. Catalytic chain transfer polymerisation is a highly efficient method for producing low molecular weight polymers (oligomers) which are used as additives in detergents and coatings. The efficiency of the CCT method is expressed in terms of the chain transfer constant ( $C_s$ ). In this work, we present experimentally determined values of  $C_s$  for CO<sub>2</sub>-expanded MMA at 50°C and at pressures of 2 and 5 MPa.

## MATERIALS AND METHODS

**Materials.** Methyl methacrylate (99%) was passed through a column of activated basic alumina to remove the polymerisation inhibitor (4-methoxyphenol). Carbon dioxide with a purity of 99.995% was used in the polymerisation experiments. 2,2'-azobis(isobutyronitrile) (AIBN) was used as the initiator while bis[(difluoroboryl)diphenylglyoximato]cobalt(II) (COPhBF) was used as the chain transfer catalyst (see Figure 1). The reader is referred to elsewhere for the method of preparing COPhBF [5]. High-purity nitrogen (99.99%) was used for purging oxygen from solutions of MMA and catalyst.



**Figure 1.** Chemical structure of COPhBF.

**Apparatus and Procedure.** The CCT polymerisation of CO<sub>2</sub>-expanded MMA was carried out in a 300 mL stirred autoclave reactor. A detailed description of the actual reactor set-up has been reported in a previous study on catalytic hydrogenation in supercritical CO<sub>2</sub> [4]. As a control experiment, CCT polymerisation of bulk MMA was also carried out in the presence of high purity nitrogen at 0.1 MPa and in the same reactor. The reactor was cooled to 5°C prior to the addition of any materials. An amount of 100 mg of AIBN was added to the reactor followed by the addition of a known mass of monomer. The reactor was sealed and stirring was initiated to mix the AIBN and MMA. The reactor contents were purged with high-purity nitrogen (0.1 MPa) to remove oxygen. A known volume of a catalyst stock solution (MMA + COPhBF) was added to the reactor followed by purging with nitrogen. The reactor contents were further purged with CO<sub>2</sub> (0.1 MPa), to remove traces of nitrogen, followed by pressurisation with CO<sub>2</sub> to an intermediate level of pressure.

The system was then heated to 50°C with continuous stirring in order to maintain equilibrium between the liquid and vapour phases. Stirring was ceased once the desired operating temperature and pressure had been reached (~ 20 minutes). In preliminary work, it was established that negligible polymerisation of the monomer occurred during this heating stage. The actual polymerisation was carried out for a period of around 2 hours. This was followed by cooling of the reactor to ambient temperature in order to terminate the polymerisation. A sample of the partially polymerised monomer was collected and evaporated to isolate the polymer. The molecular weight distribution of the polymer was determined with size exclusion chromatography.

The efficiency of CCT for molecular weight reduction is expressed in terms of the chain transfer constant ( $C_s$ ) which is defined as the ratio of the rate coefficients for chain transfer ( $k_s$ ) and propagation ( $k_p$ ). The standard method for evaluating chain transfer constants is via the Mayo equation [6]. A simplified form of this equation is as follows:

$$\frac{1}{DP_n} = \frac{1}{DP_{n,0}} + C_s \frac{[S]}{[M]} \quad (1)$$

where  $DP_n$  is the number-average degree of polymerisation,  $DP_{n,0}$  is the number-average degree of polymerisation produced in the absence of the chain transfer catalyst,  $[S]$  is the concentration of chain transfer catalyst and  $[M]$  is the monomer concentration. To obtain  $C_s$ , the experimentally determined values of  $1/DP_n$  are plotted as a function of  $[S]/[M]$  to yield a straight line with an intercept of  $1/DP_{n,0}$  and a slope of  $C_s$ . Provided that the conversion of the monomer is low (<5%), the value of  $[S]/[M]$  can be calculated from the initial concentrations of the chain transfer catalyst and the monomer.

## RESULTS AND DISCUSSION

**Phase Behaviour.** Prior to the polymerisation experiments, the volumetric expansion behaviour of MMA with dense  $CO_2$  was examined. The expansion data were measured in a high pressure sight gauge similar to that reported previously [7]. The data in Figure 2 demonstrate that MMA can be expanded with dense  $CO_2$  to around three times its initial volume at 50°C and 7 MPa. This is attributed to the dissolution of  $CO_2$  in the liquid phase. At these particular conditions, the solubility of  $CO_2$  in the liquid phase is around 77 mol%. The influence of small quantities of poly(methyl methacrylate) (PMMA) on the expansion behaviour of MMA is also shown in Figure 2. Expansion data are presented for MMA containing 2 % PMMA with a weight-average molecular weight ( $M_w$ ) of 30000 g/mol and 5 % PMMA with a  $M_w$  of 4000 g/mol. The two PMMA/MMA/ $CO_2$  systems represent two extremes, in terms of molecular weight distributions and monomer conversions, during CCT polymerisation of MMA.

In both cases, it can be seen that there is a slight reduction in the volumetric expansion of MMA due to the presence of PMMA at the given concentrations. However, both sets of expansion data terminate abruptly at 6.9 MPa and 5.5 MPa for the 5% and 2% PMMA solutions, respectively. These end points marked the transition from a vapour-liquid system to a vapour-liquid-liquid system which was characterised by a cloudy appearance in the main liquid phase. The cloudiness was due to the formation of the second liquid phase in the form of small droplets dispersed within the main liquid phase. It was presumed that the dispersed liquid phase was richer with respect to PMMA. At pressures higher than the indicated end-points, the actual precipitation of solid polymer was observed.

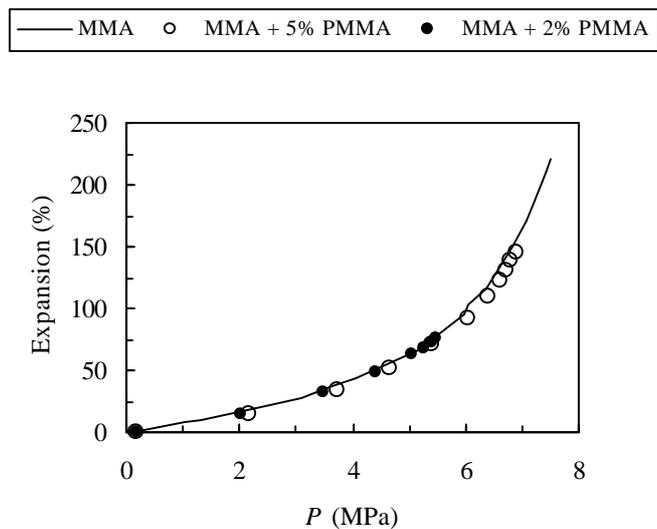
In view of these findings, the polymerisation experiments were restricted to pressures below 5.5 MPa and for monomer conversions less than 5%. This was also considered necessary in order to properly determine the chain transfer constant. In the Mayo equation, it is assumed that the catalyst is evenly distributed in the monomer. However, the separation of the liquid phase into two immiscible liquid phases creates the possibility of partitioning of the catalyst between the phases. Under such conditions, one would expect different molecular weight

distributions in each phase, leading to an unrepresentative estimate of the chain transfer constant at the given experimental conditions.

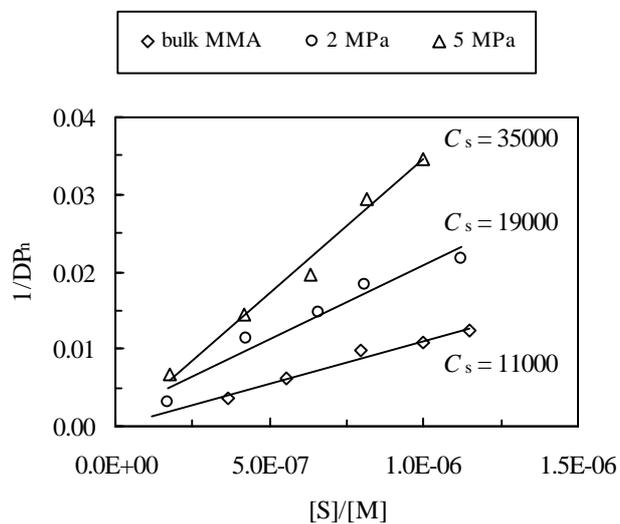
**Synthesis of Oligomers.** Mayo plots for CO<sub>2</sub>-expanded MMA are shown in Figure 3. Each data point in the figure represents the mean of duplicate runs in which the conversion of the monomer was kept below 4%. The resulting  $M_w$  of the polymer was generally less than 30,000 g/mol. The value of  $C_s$  for CPhBF in bulk MMA (11,000) is substantially lower than the literature value of around 20,000. The activity of CPhBF, in its solid form, degrades slowly in the presence of air and thus the value of  $C_s$  is influenced by the amount of time that the catalyst has been stored. In solution, the catalyst is extremely sensitive to the presence of oxygen. The efficiency of the technique for purging oxygen from the reactor is another factor that influences the degree of molecular weight reduction. The control experiment takes into account these factors and serves as a reference value for the experiments conducted on CO<sub>2</sub>-expanded MMA. It is evident from Figure 3 that  $C_s$  for CPhBF in CO<sub>2</sub>-expanded MMA varies with pressure and increases by a factor of around 3 at 5 MPa. At a given concentration of catalyst, the average molecular weight at 5 MPa is reduced by a similar factor. Beuermann et al. [8] have shown that there is some reduction in  $k_p$  for MMA in dense CO<sub>2</sub>. However, it is unlikely that this alone accounts for the magnitude of the increase in  $C_s$  reported here.

Although the exact mechanism of CCT polymerisation is still the subject of ongoing research, the generally accepted mechanism is illustrated in Scheme 1. The Co(II) complex catalyses the chain transfer to monomer reaction by abstracting a hydrogen atom from the  $\alpha$ -methyl group of the growing polymer radical. This leads to the formation of a dead polymer chain with a vinyl endgroup. The abstracted hydrogen is then transferred from the Co(III)H complex to the monomer, forming a monomeric radical which initiates a new polymer chain. The cobalt(II) complex is regenerated in the second step. The chain transfer reaction is generally very fast and this has led to speculation that the rate-determining step in the chain transfer process, in some systems, is the diffusion of the polymer radical and the catalyst in the solvent.

In a diffusion-controlled reaction, the rate coefficient is considered to be inversely proportional to the viscosity of the medium. It is well-known that dense CO<sub>2</sub> exhibits gas-like viscosities and therefore the viscosity of CO<sub>2</sub>-expanded MMA would be expected to be much lower in comparison to the bulk monomer. The increase in  $C_s$  in CO<sub>2</sub>-expanded MMA is consistent with an increase in  $k_s$  and provides evidence that the chain transfer reaction is diffusion-controlled. This observation is supported by an earlier study on the CCT polymerisation of MMA in supercritical CO<sub>2</sub> under homogeneous conditions [5]. In that study,  $C_s$  for CPhBF in MMA/scCO<sub>2</sub> was enhanced by an order of magnitude, in comparison to bulk MMA, at 50°C and 15 MPa. The larger value of  $C_s$  in MMA/scCO<sub>2</sub>, compared with CO<sub>2</sub>-expanded MMA, is attributed to the much larger concentration of CO<sub>2</sub> required to maintain a single-phase system. Under such conditions one would expect that the viscosity of the medium is much lower than that for CO<sub>2</sub>-expanded MMA.

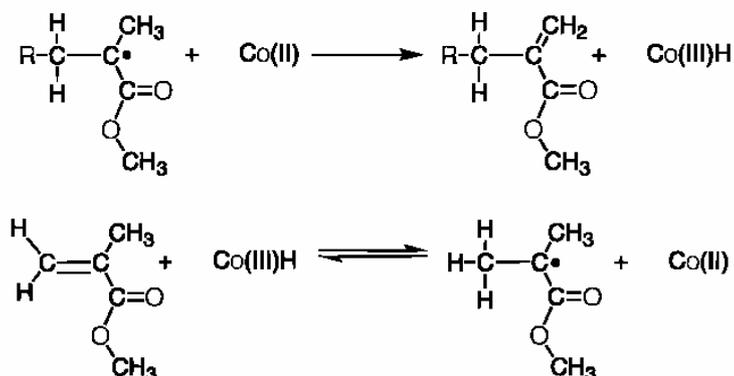


**Figure 2.** The effect of 5% PMMA ( $M_w = 4000$ ) and 2% PMMA ( $M_w = 30000$ ) on the volumetric expansion of MMA with dense  $\text{CO}_2$  at  $50^\circ\text{C}$ .



**Figure 3.** Mayo plots for  $\text{CO}_2$ -expanded MMA at  $50^\circ\text{C}$ .

Scheme 1



## CONCLUSION

The expansion of MMA with dense  $\text{CO}_2$  provides an effective means of increasing the degree of molecular weight reduction during CCT polymerisation of the monomer. This effect is mainly attributed to the enhancement of the chain transfer rate, arising from the reduction in the viscosity of the medium. These findings highlight the potential of  $\text{CO}_2$ -expanded monomers for the synthesis of oligomers via catalytic chain transfer polymerisation. Additional environmental and safety advantages are apparent in this method.  $\text{CO}_2$ -expanded monomers offer the possibility of eliminating the use of organic solvents during polymerisation. The process may also be conducted at greatly reduced operating pressures, in comparison to the reaction performed in supercritical  $\text{CO}_2$  under homogeneous conditions.

## REFERENCES

- [1] LIU, J., HAN, B., ZHANG, R., LIU, Z., JIANG, T., YANG, G. J., *Supercrit. Fluids*, 25, **2003**, 91.
- [2] LIU, J., HAN, B., LIU, Z., WANG, J., HUO, Q., *J. Supercrit. Fluids*, 20, **2001**, 171.
- [3] WEI, M., MUSIE, G.T., BUSCH, D.H., SUBRAMANIAM, B., *J. Am. Chem. Soc.*, 124, **2002**, 2513.
- [4] PHIONG, H-S., LUCIEN, F.P., ADESINA, A.A., *J. Supercrit. Fluids*, 25, **2003**, 155.
- [5] FORSTER, D.J., HEUTS, J.P.A., LUCIEN, F.P., DAVIS, T.P., *Macromolecules*, 32, **1999**, 5514.
- [6] MAYO, F.R., *J. Am. Chem. Soc.*, 65, **1943**, 2324.
- [7] PHIONG, H-S., LUCIEN, F.P., *J. Supercrit. Fluids*, 25, **2003**, 99.
- [8] BEUERMAN, S., BUBACK, M., SCHMALTZ, C., KUCHTA, F.-D., *Macromol. Chem. Phys*, 199, **1998**, 1209.