CATALYTIC CHAIN TRANSFER POLYMERISATION OF CO$_2$-EXPANDED MONOMERS

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The catalytic chain transfer polymerisation (CCTP) of CO$_2$-expanded styrene and butyl methacrylate (BMA) were investigated in this study. The reactions were conducted in an autoclave reactor in the range of pressure from 0.1 to 6 MPa with varying amounts of a cobaloxime catalyst. Experimentally determined values of the chain transfer constant (C_s) for CO$_2$-expanded styrene (50°C) and BMA (50 and 60°C) are reported, along with volumetric expansion measurements for the polymer/monomer/CO$_2$ systems. The values of C_s in CO$_2$-expanded BMA are significantly higher than that in the bulk monomer. This effect can be correlated with the decrease in the liquid-phase viscosity and provides further evidence of a diffusion-controlled mechanism. Furthermore, the CCT process is facilitated by CO$_2$ even in the presence of cobalt-carbon bond formation in the case of styrene.

INTRODUCTION

Catalytic chain transfer polymerisation (CCTP) is a highly efficient method for the production of low molecular weight polymers (oligomers) [1]. A particular advantage of CCT is that it employs low concentrations (ppm quantities) of generally nontoxic cobaloxime catalysts. In contrast, a similar reduction in molecular weight requires several weight percent of toxic and malodorous sulphur-containing chain transfer agents. The latter are non-catalytic and become incorporated in the oligomer molecular structure, adversely affecting its properties. Oligomers are employed as additives in products such as detergents, paints and coatings. There is a growing need to further decrease the molecular weight of oligomeric additives in such products. For example, the reduction of organic solvents in coatings is leading to the development of high solids coatings (60-80% solids). The main limiting factor in high solids coatings is the increased viscosity that can only be reduced by employing lower molecular weight additives.

The efficiency of CCTP for the synthesis of oligomers is expressed in terms of the chain transfer constant (C_s). In previous work, we demonstrated that the value of C_s can be increased significantly by first expanding the monomer with dense CO$_2$ [2]. This approach offers environmental and process benefits. The CO$_2$-expanded monomer offers 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 CO$_2$ under homogeneous conditions [3]. Previous work on CCTP, with and without CO$_2$, has provided strong evidence of a diffusion controlled mechanism. The objective of this study is to perform CCTP on CO$_2$-expanded monomers with contrasting structures to demonstrate the mechanism more clearly. Herein we report experimentally determined values of C_s in CO$_2$-expanded styrene (50°C) and butyl methacrylate (BMA) (50 and 60°C) in the range of pressure from 0.1 to 6 MPa.

MATERIALS AND METHODS

Materials. BMA (99%) and styrene (99%) were obtained from Sigma-Aldrich and passed through a column of activated basic alumina to remove the polymerisation inhibitor (methyl ethyl hydroquinone and 4-tert-butyl catechol, respectively). Styrene was further purified by polymerisation in the presence of the CCT agent to a low conversion and then distilled under reduced pressure. 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. The reader is referred to elsewhere for the method of preparing COPhBF [4]

Apparatus and Procedure. CCTP of CO_2-expanded BMA and styrene 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_2 [5]. As a control experiment, CCTP of bulk BMA and styrene were also carried out in the presence of high purity CO_2 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 monomer. The reactor contents were purged with high-purity CO_2 (0.2 MPa) to remove oxygen. A known volume of a catalyst stock solution (monomer + COPhBF) was added to the reactor followed by purging with CO_2. The reactor was then pressurised with CO_2 to an intermediate level of pressure.

The system was heated to the target temperature with continuous stirring in order to maintain equilibrium between the liquid and vapour phases. Stirring was slowed down to 100 rpm once the desired operating temperature and pressure had been reached (~ 10 min). 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 1 hour. This was followed by cooling of the reactor to ambient temperature, in order to terminate the polymerisation (~10 min), and depressurisation. A sample of the partially polymerised monomer was collected and evaporated in the presence of inhibitor (hydroquinone 99%) 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 catalytic 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:

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

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. Volumetric expansion data for BMA and styrene with CO_2 are presented in Figures 1 and 2. The expansion data were measured in a high-pressure sight gauge similar to that reported previously [7]. The data for BMA show the expected trend of a decrease in the volumetric expansion with an increase in temperature at constant pressure, due to a reduction in the solubility of CO_2 in the liquid phase. BMA can be expanded with CO_2 to around twice its initial volume at 50°C and 7.2 MPa. Styrene displays similar behaviour to BMA but its expansion rate is lower. The homogeneity of expanded monomer/polymer solutions under actual reaction conditions was confirmed by direct observation in the sight gauge. Samples of partially reacted monomer were taken from the reactor and introduced into the sight gauge at an equivalent loading (mass solution/volume vessel). The conversions of BMA and styrene in these samples were typically less than 5% and 2%, respectively. Representative expansion data for monomer/polymer solutions are also shown in Figures 1 and 2.

It can be seen that the presence of polymer at the given concentrations has a negligible influence on the expansion of the monomers. This also suggests that the solubility of CO_2 in the liquid phase is not significantly altered by the polymer in the given ranges of polymer concentration and molecular weight. However, there is a limit to which homogeneous expansion of the monomer/polymer mixture occurs. At the highest pressures reported, phase separation occurs and this is characterised by a cloudy appearance in the liquid phase. The cloudiness is due to the formation of a second liquid phase in the form of small droplets dispersed within the main liquid phase. The pressure at which the maximum homogeneous expansion limit occurs is greater than 7 MPa in all cases. In general, this pressure limit decreases with an increase in the molecular weight and concentration of the polymer. The solutions tested here contained the highest molecular weight polymer produced in the CCTP of the expanded monomers.

The requirement of homogeneity is necessary to properly determine the chain transfer constants. In the Mayo equation, it is assumed that the catalyst is evenly distributed in the monomer. 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. Since the polymerisation experiments were restricted to pressures no higher than 6.0 MPa, it may be concluded that homogeneous conditions were maintained in the CO_2-expanded monomer phases in the determination of chain transfer constants.

Synthesis of Oligomers. Mayo plots for CO_2-expanded BMA at 50°C and 60°C are shown in Figure 3 and the resulting values of C_s are given in Table 1. Each data point in the figure represents the mean of duplicate runs in which the conversion of the monomer was kept below 5%. The resulting M_w of the polymer synthesised in the expanded BMA varied in the range of 3,000 - 30,000 g/mol. Within the range of experimental error, the values of C_s for COPhBF in bulk BMA (1 bar) exhibit very little temperature dependence, and this is

consistent with other studies on methacrylates [8]. The positive influence of CO_2 on the CCT process is clearly evident in Figure 3. At 50°C, C_s in expanded BMA increases by a factor of around 4 at a pressure of 6 MPa. The corresponding increase in C_s at 60°C is slightly lower (~3) and this is due to the reduction of the solubility of CO_2 in the liquid phase.

Mayo plots for styrene at 50°C are presented in Figure 4 and C_s values are given in Table 2. The effect of conversion on C_s was also examined by extending the reaction time from 1 to 2 hrs. The resulting M_w of the polymer synthesised in expanded styrene varied in the range of 10,000 - 80,000 g/mol. For the reactions in expanded styrene at a duration of 1 hr, two catalyst concentrations were chosen and the intercept of the Mayo plot was assumed to be the same as that for bulk styrene. For the extended reaction time, only a single catalyst concentration was considered. The values of C_s in styrene are 1-2 orders of magnitude lower than those for BMA. An increase in styrene conversion also leads to a decrease in C_s. However, at both levels of conversion, C_s in expanded styrene increases by a factor of 3 at a pressure of 6 MPa.

The generally accepted mechanism for CCTP of methacrylates is considered to be a 2-step process (see Eqs 2 and 3). In the first step (k_s), the Co(II) abstracts a hydrogen atom from the growing polymer radical to yield a dead polymer chain. This reaction represents the rate-determining step in the chain transfer process. In the second step (k_{fast}), the chain transfer to monomer is completed by a hydrogen transfer from the Co(III)-H species to form a monomeric radical. Previous measurements of the chain transfer rate coefficients suggest that the rate-determining step is diffusion-controlled. In this situation, k_s ($= C_s k_p$) is considered to be inversely proportional to the viscosity of the monomer (Eq. 4). It can be seen from Table 1 that the equality specified in Eq. 4 is generally valid for expanded BMA and that there is no significant difference between the two temperatures employed. Thus, the increase in C_s in CO_2-expanded BMA can be mainly attributed to the reduction in the liquid-phase viscosity and this provides further evidence of a diffusion-controlled mechanism.

$$\text{R}_n^{\bullet} + \text{Co(II)} \xrightarrow{k_s} \text{P}_n + \text{Co(III)} - \text{H} \tag{2}$$

$$\text{Co(III)} - \text{H} + \text{M} \xrightarrow{k_{fast}} \text{Co(II)} + \text{R}_1^{\bullet} \tag{3}$$

$$C_s k_p \eta \approx \text{constant} \tag{4}$$

The mechanism of CCTP of styrene is similar to that of methacrylates with a few important differences. Styrene forms secondary radicals, not primary like methacrylates, and forms reversible cobalt-carbon bonds between the polymer radical and Co(II), forming an organometallic species. This renders part of the catalyst molecules inactive and for this reason only apparent chain transfer constants can be measured. The equilibrium for cobalt-carbon bond formation is fully established at a monomer conversion of around 5% [9]. In relation to Figure 4, the decrease in C_s with an increase in conversion can now be explained in terms of progressive catalyst de-activation. This is also supported by an increase in the polydispersity of the polymer formed at the higher level of conversion (see Table 2). Nonetheless, the results presented here suggest that the hydrogen abstraction step in CCTP of styrene is still diffusion-controlled.
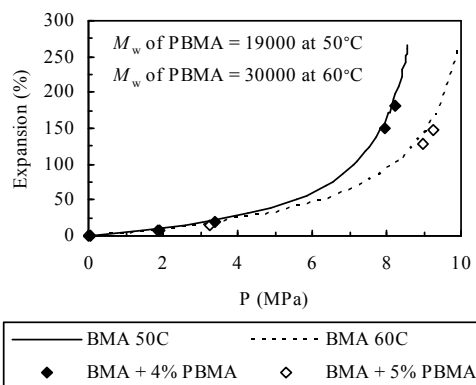
Figure 1. Effect of PBMA on the expansion of BMA with CO_2.

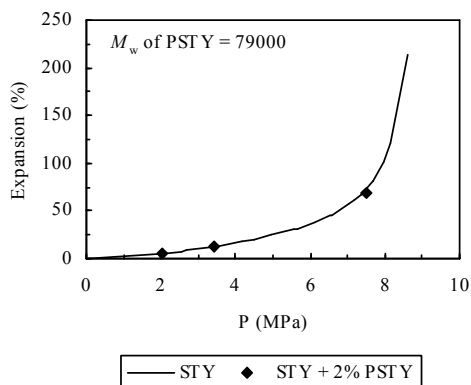

Figure 2. Effect of PSTY on the expansion of STY with CO_2 at 50C.

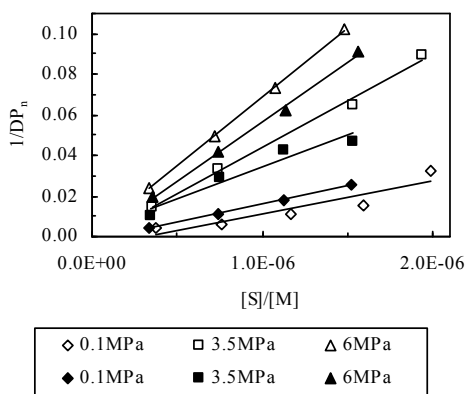Figure 3. Mayo plots for CO_2-expanded BMA at 50C (open symbols) and 60C (closed symbols).

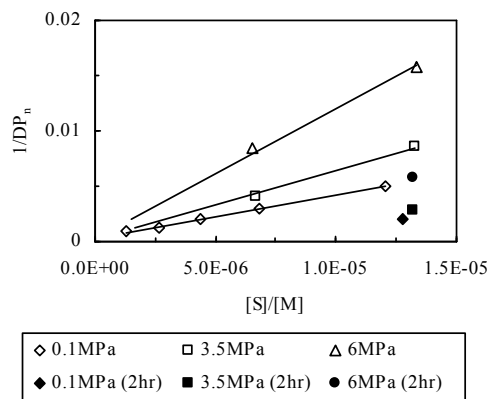

Figure 4. Mayo plots for CO_2-expanded styrene at 50C.

Table 1. Comparison of values of $C_s k_p \eta$ for COPhBF in CO_2-expanded BMA.

T (°C)	P (MPa)	C_s	$C_s k_p \eta$ [a]
50	0.1	16300	8.6×10^6
50	3.5	45600	9.7×10^6
50	6.0	67600	7.6×10^6
60	0.1	18000	1.0×10^7
60	3.5	31300	7.7×10^6
60	6.0	58700	8.1×10^6

[a] Values of k_p (L mol^{-1}s^{-1}) are from [8]. Values of η for CO_2-expanded BMA (cP) were estimated using AspenPlus.

Table 2. Effect of conversion on polydispersity in CCTP of CO_2-expanded styrene at 50°C.

P (MPa)	Reaction time (hrs)	C_s	PDI
0.1	1	400	2.6
3.5	1	600	2.8
6.0	1	1200	2.3
0.1	2	140	4.5
3.5	2	190	4.1
6.0	2	420	4.2

CONCLUSION

The volumetric expansion of BMA with dense CO_2 provides an effective means of increasing the chain transfer constant during the CCTP of the monomer. This effect can be correlated with the decrease in the liquid-phase viscosity and provides further evidence of a diffusion-controlled mechanism. Furthermore, the CCT process is facilitated by CO_2 even in the presence of cobalt-carbon bond formation in the case of styrene. The process may also be conducted at greatly reduced operating pressures, in comparison to the reaction performed in supercritical CO_2 under homogeneous conditions.

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