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Effect of Bulk Viscosity on the Catalytic Chain Transfer Polymerization of CO_2-Expanded Butyl Methacrylate and Styrene

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ABSTRACT: The catalytic chain transfer polymerization of CO_2-expanded butyl methacrylate and styrene is reported. Experimentally determined values of the chain transfer constant for CO_2-expanded butyl methacrylate are presented at 50 and 60 °C and in the range of pressure from 0.1 to 6 MPa, using a cobaloxime complex as the chain transfer catalyst. Similar data are reported for CO_2-expanded styrene at 50 °C. The chain transfer constants for both expanded monomers are significantly higher than those obtained in the bulk monomers. It is demonstrated that a linear relationship exists between the chain transfer rate coefficient and the inverse of viscosity. These results provide significant evidence that the rate-determining step in the chain transfer process is diffusion-controlled.

Introduction

Despite decades of research since the discovery of catalytic chain transfer agents, there continues to be some uncertainty surrounding the actual mechanism in catalytic chain transfer (CCT) polymerization. The currently accepted mechanism involves a two-step process in which a Co(II) complex first abstracts a hydrogen atom from a growing polymer radical (eq 1).[1] This reaction is considered to be the rate-determining step and leads to the formation of a polymer with a terminal double bond (P_n). The Co(III) hydride subsequently reinitiates a monomer molecule (M), forming a monomeric radical ($R_1^\bullet$) and regenerating the chain transfer catalyst (eq 2).

$$R_n^\bullet + \mathrm{Co(II)} \xrightarrow{k_{tr}} P_n + \mathrm{Co(III)}{-}\mathrm{H} \qquad (1)$$

$$\mathrm{Co(III)}{-}\mathrm{H} + \mathrm{M} \xrightarrow{k_{fast}} \mathrm{Co(II)} + R_1^\bullet \qquad (2)$$

Notwithstanding this simple mechanism, there are other effects that impact on the chain transfer process. Reversible bond formation between cobalt(II) complexes and propagating radicals appears to be significant for secondary radicals but not for tertiary radicals.[2−4] This effect typically leads to a large reduction in the measured chain transfer constant. Monomer substituents may also lead to lower than expected chain transfer constants via steric hindrance or complexation with the catalyst.[5,6] Other unresolved issues include molecular weight evolution with conversion[2,4,7−10] and medium viscosity effects.[11−14]

In a study on the effect of ester chain length on the chain transfer constants for a series of methacrylate monomers, Heuts et al.[11] demonstrated that an inverse relationship exists between the chain transfer constant and monomer viscosity. They concluded that this relationship is consistent with a diffusion-controlled CCT reaction. This was further supported by the work of Forster et al.,[13] who performed CCT polymerization of methyl methacrylate in supercritical CO_2. The chain transfer constant in their study was an order of magnitude higher than that in bulk methyl methacrylate, and this was attributed to the gaslike viscosities of the supercritical medium. However, the results of both of these studies were later cast into doubt by Roberts et al.,[14] who examined the effect of bulk viscosity by the addition of high molecular weight polymer to the monomer. It was found that the chain transfer constant was unaffected by the bulk viscosity, although they concluded that it could be governed by the monomer friction coefficient.

Recently, we demonstrated that the chain transfer constant in methyl methacrylate increases significantly by first expanding the monomer with dense CO_2.[15]

This technique employs greatly reduced operating pressures, in comparison to the reaction performed in supercritical CO_2 under homogeneous conditions. Furthermore, the increase in the chain transfer constant was correlated with the reduced viscosity of the medium and provided further evidence of a diffusion-controlled mechanism. The aim of the present study is to further explore the effect of bulk viscosity by performing CCT on CO_2-expanded monomers with contrasting structures. Styrene forms secondary radicals while butyl methacrylate forms tertiary radicals. High-pressure phase equilibrium data for each monomer/CO_2 system are also available in the literature.[16,17] Herein, we report experimentally determined values of the chain transfer constant for a cobaloxime complex in CO_2-expanded styrene (50 °C) and butyl methacrylate (50 and 60 °C) in the range of pressure from 0.1 to 6 MPa. The inverse relationship between the chain transfer constant and the expanded monomer viscosity is examined in detail.

Experimental Section

Materials. Butyl methacrylate (99%) and styrene (99%) were obtained from Sigma-Aldrich and passed through a column of activated basic alumina to remove polymerization inhibitors. Liquid CO_2 (99.995%) was obtained from Linde Gases and used as the source of high-purity CO_2. The polymerization initiator, AIBN, was sourced from Dupont and purified by recrystallization from methanol. The chain transfer catalyst, bis[(difluoroboryl)diphenylglyoximato]cobalt(II) (COPhBF, **1**), was prepared according to the procedure described by Bakac et al.,[18] using diphenylglyoxime instead of dimethylglyoxime in the given procedure. After removal of the inhibitor, styrene was further purified by polymerization in the presence of AIBN and COPhBF to a low conversion, followed by distillation under reduced pressure.

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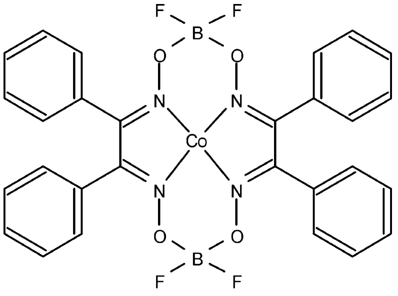

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General Polymerization Procedure. The CCT polymerization of CO_2-expanded butyl methacrylate (BMA) and styrene was carried out in a 300 mL stirred autoclave reactor. A detailed description of the actual reactor setup is given elsewhere.[15] The reactor was cooled to 5 °C prior to the addition of any materials. An amount of 100 mg of AIBN (6.1×10^{-3} M) was added to the reactor followed by the addition of 90−100 mL of monomer, depending on the volume of catalyst solution injected at a later stage. The reactor was sealed and stirring was initiated to mix the AIBN and monomer. The reactor contents were purged with high-purity CO_2 (0.1 MPa) to remove oxygen. A known volume of oxygen-free catalyst stock solution (2.5×10^{-4} g of COPhBF/g of BMA or 4.2×10^{-4} g of COPhBF/g of styrene) was added to the reactor, making a total liquid volume of 100 mL. This was followed by purging with CO_2. The reactor was then pressurized with CO_2 to an intermediate level of pressure.

The system was heated to the target temperature (50 or 60 °C) with continuous stirring to maintain equilibrium between the monomer and the CO_2 atmosphere. Stirring was slowed to 100 rpm once the desired operating temperature and pressure had been reached (∼10 min). In preliminary work, it was established that negligible polymerization of the monomer occurred during this heating stage. The actual polymerization was carried out for a period of 1 h. This was followed by cooling of the reactor to ambient temperature in order to terminate the polymerization (∼10 min) and subsequent depressurization.

A sample of the partially polymerized monomer was collected and evaporated in the presence of hydroquinone to isolate the polymer. Subsequently, the polymer samples were placed in a vacuum oven (60 °C) until constant weight was attained. Conversion was calculated on a mass basis and maintained below 5%. Control experiments were also performed on bulk BMA and bulk styrene in the presence of high-purity CO_2 at atmospheric pressure (0.1 MPa). The same apparatus and procedure as that described above was employed for this purpose. These experiments involve no expansion of the monomer with CO_2 and thus represent the conventional way of performing CCT.

Homogeneous Expansion Limits. The dissolution of CO_2 in hydrophobic monomers at elevated pressure is accompanied by a significant volumetric expansion of the liquid phase.[19,20] This process leads to the well-known antisolvent effect in which the precipitation of a solute can be induced once a sufficient concentration of CO_2 is attained in the solvent.[21,22] Precipitation of polymer from an expanded monomer/polymer mixture is usually preceded by phase separation. This condition is characterized by a cloudy appearance in the mixture and represents the formation of two immiscible liquid phases. The operating pressure at which phase separation occurs marks the limit of homogeneous expansion of the monomer/polymer mixture.

Homogeneous expansion limits for monomer/polymer mixtures synthesized under actual reaction conditions were determined by direct observation in a high-pressure sight gauge. At the completion of a polymerization experiment, a sample of the partially reacted monomer was taken from the reactor and introduced into a high-pressure sight gauge. Details of the apparatus and procedure used for expanding the mixture with CO_2 have been described previously.[15,20] The pressure limit for homogeneous expansion was found to be greater than 7 MPa in all cases. In general, the pressure limit decreased with an increase in the molecular weight and concentration of the polymer, and this was consistent with our earlier study.

Since the polymerization experiments were restricted to pressures no higher than 6 MPa, it was concluded that phase separation was absent in the range of conditions investigated. Note that the homogeneity of the liquid phase is necessary to properly determine the chain transfer constant. When phase separation occurs, different molecular weight distributions are generated in each phase, leading to an unrepresentative estimate of the chain transfer constant.

Chain Transfer Constants. 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_{tr}) and propagation (k_p). The standard method for evaluating chain transfer constants is via the Mayo equation.[23] A simplified form of this equation is as follows:

$$\frac{1}{DP_n} = \frac{1}{DP_{n,0}} + C_s\frac{[S]}{[M]} \tag{3}$$

where DP_n ($= M_n/M_0$) is the number-average degree of polymerization, M_n is the number-average molecular weight, M_0 is the molecular mass of the monomer, $DP_{n,0}$ is the number-average degree of polymerization 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 monomer.

DP_n can be determined using the number-average molecular weight or weight-average molecular weight, as determined by the molecular weight distribution analysis. In this study, the latter method was used since it is less prone to baseline subtraction errors, thus giving more accurate results.[2,24,25] In chain transfer controlled systems, the polydispersity index is very close to 2 and thus $DP_n = M_w/2M_0$. This method was also used for styrene, even though the polydispersity index was larger than 2. The value of DP_n at a given set of conditions was calculated from the mean of at least two runs, with a relative standard deviation of less than 10%. On the basis of the uncertainty in DP_n and the experimental values of [S]/[M] (±2%), the values of C_s generated from the Mayo plots have an uncertainty of less than 20%.

Estimation of Viscosity. The viscosity of CO_2-expanded BMA was calculated using the modified Andrade equation

$$\ln \eta_{mix} = \sum_{i=1}^{N} x_i \ln \eta_i + \sum_{i=1}^{N}\sum_{j=1}^{N}(k_{ij}x_ix_j + m_{ij}x_i^2x_j^2) \tag{4}$$

where η_i is the pure component viscosity, x_i is the mole fraction of component i, and N is the number of components.[26] k_{ij} and m_{ij} are binary interaction parameters that are normally regressed from experimental data. To the best of our knowledge, experimental data on the viscosity of CO_2-expanded BMA are unavailable in the open literature, and so the interaction parameters were set to zero. Data on the viscosity of BMA at 40−70 °C are reported by Heuts et al.[11] Husain et al.[17] have measured the solubility of CO_2 in BMA at elevated pressure and for temperatures of 50 and 60 °C.

The viscosity of CO_2-expanded monomer depends on pressure as well as temperature. The pressure dependence of η_{mix} was accounted for using the viscosity of CO_2. For supercritical temperatures, Orbey and Sandler[27] propose the following empirical equations

$$\eta_{CO_2}(T,P) = \eta_{CO_2}(T,P = 0.1\ \text{MPa}) + (5.02 \times 10^{-3} - 1.02 \times 10^{-5}T)P \tag{5}$$

$$\eta_{CO_2}(T,P = 0.1\ \text{MPa}) = 1.97 \times 10^{-3} + 4.4 \times 10^{-5}T \tag{6}$$

where the units for T, P, and η are K, MPa, and mPa·s (cP), respectively.

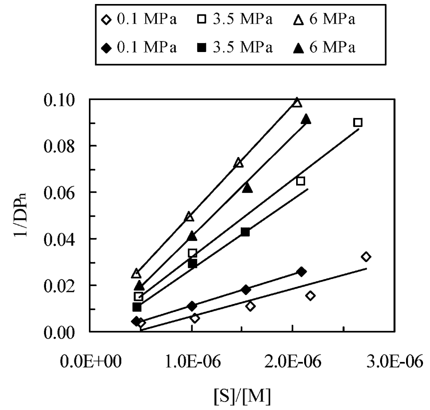

Figure 1. Mayo plots for COPhBF in CO_2-expanded BMA at 50 °C (open symbols) and 60 °C (closed symbols). The solid lines indicate the lines of best fit.

Table 1. Chain Transfer Constants for COPhBF in CO_2-Expanded BMA

P (MPa)	C_s (50 °C)	C_s (60 °C)
0.1	11 900	13 200
3.5	33 400	30 100
6.0	46 700	43 000

Molecular Weight Analysis. Molecular weight distributions were determined by size exclusion chromatography (SEC). The SEC equipment consisted of a Shimadzu LC-10 AT VP pump, a Shimadzu SIL-10AD VP autoinjector, a column set consisting of a Polymer Laboratories 5.0 μm bead-size guard column (50 × 7.5 mm) followed by three linear PL columns (10^5, 10^4, and 10^3 Å) in a column oven at 40 °C, and a Shimadzu RID-10A differential refractive index detector. Tetrahydrofuran (Ajax, HPLC grade) was used as eluent at 1.0 mL/min. Calibration was performed with narrow polystyrene standards (Polymer Laboratories), with molecular weights (M_p) in the range 750−1.95 × 10^6 g/mol. The following Mark−Houwink−Sakurada constants in conjunction with the universal calibration were used to calculate the weight-average molecular weight of the samples: $K = 14.1 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.7$ for polystyrene; $K = 14.8 \times 10^{-5}$ dL g^{-1}, $\alpha = 0.664$ for poly(butyl methacrylate).

Results and Discussion

Chain Transfer Constants. The experimentally determined values of the chain transfer constant for COPhBF in CO_2-expanded BMA are listed in Table 1. The corresponding Mayo plots are shown in Figure 1. Beginning with the control experiments on bulk BMA (0.1 MPa), the chain transfer constant exhibits negligible temperature dependence when experimental error is taken into account. This is consistent with previous studies on methacrylates.[11] The values of C_s for COPhBF in bulk BMA are also comparable with those previously reported and confirm both the purity of the catalyst and the validity of the experimental procedure.

The positive influence of CO_2 on the CCT process is evident from the data in Table 1. At 50 °C, C_s in expanded BMA increases by a factor of around 4 when the pressure is increased to 6 MPa. The corresponding increase in C_s at 60 °C is slightly lower (~3) due to a reduction in the solubility of CO_2 in the monomer (see Table 3). Beuermann et al.[28] have shown that k_p for MMA in dense CO_2 decreases by around 40% at a pressure of 100 MPa. If a similar reduction applies to BMA, then this effect is probably negligible at pressures below 10 MPa. This indicates that an increase in k_{tr} most likely accounts for the increase in C_s in the expanded monomer.

Table 2. Chain Transfer Constants for COPhBF in CO_2-Expanded Styrene

P (MPa)	C_s	PDI
	1 h reaction time	
0.1	400	2.6
3.5	600	2.8
6.0	1200	2.3
	2 h reaction time	
0.1	100	4.5
3.5	200	4.1
6.0	400	4.2

Table 3. Viscosity of CO_2-Expanded BMA (η_{mix}) as a Function of Pressure

P (MPa)	x_{CO_2}[a]	η_{BMA}[b]	η_{CO_2}[c]	η_{mix}[d]	k_{tr} (dm^3 mol^{-1} s^{-1})[e]
			$T = 50$ °C		
0.1	0.000	0.62	0.016	0.620	9.00×10^6
3.5	0.411	0.62	0.022	0.158	2.53×10^7
6.0	0.631	0.62	0.027	0.085	3.53×10^7
			$T = 60$ °C		
0.1	0.000	0.55	0.017	0.550	1.29×10^7
3.5	0.373	0.55	0.022	0.166	2.94×10^7
6.0	0.575	0.55	0.026	0.096	4.20×10^7

[a] Solubility of CO_2 in BMA at 50 °C.[17] [b] The viscosity of pure BMA[11] is assumed to be independent of pressure. [c] The viscosity of pure CO_2 is calculated using eqs 5 and 6. [d] Calculated using eq 4. [e] $k_{tr} = C_s\, k_p$ where k_p (50 °C) = 756 dm^3 mol^{-1} s^{-1} and k_p (60 °C) = 976 dm^3 mol^{-1} s^{-1}.[30]

Previous measurements of the chain transfer rate coefficients for cobaloxime catalysts have led to speculation that the rate-determining step is diffusion-controlled in the case of methacrylates. This is based on the high value of the chain transfer rate coefficient, on the order of 10^7 dm^3 mol^{-1} s^{-1}, being very similar in magnitude to the rate coefficient for termination, which is widely accepted as diffusion-controlled. In this situation, the rate coefficient is considered to be inversely proportional to the viscosity of the medium (see below). It is well-known that supercritical CO_2 exhibits gaslike viscosities, and the viscosity of CO_2-expanded BMA is also much lower in comparison to the bulk monomer (see Table 3). The proposed increase in k_{tr} is therefore consistent with the reduced viscosity of the expanded monomer.

The mechanism for styrene is similar to that for methacrylates, with a few important differences. Styrene forms secondary radicals due to the absence of an α-methyl group, and hydrogen abstraction is thought to occur from an internal β-H on the backbone.[4] Styrene radicals also form reversible cobalt−carbon bonds with the chain transfer catalyst, producing an organometallic species:

$$R_n^{\bullet} + \mathrm{Co(II)} \leftrightarrow R_n{-}\mathrm{Co(III)} \tag{7}$$

This renders part of the catalyst molecules inactive. For this reason only an apparent chain transfer constant can be determined which is lower than the real value. The equilibrium in eq 7 is considered to be fully established at a conversion of around 5%. At lower conversions, the chain transfer constant generally decreases with increasing initiator concentration and monomer conversion.[29]

Experimentally determined values of the apparent chain transfer constant for COPhBF in CO_2-expanded styrene at 50 °C are listed in Table 2. The corresponding Mayo plots are shown in Figure 2. All of the experiments were performed at a constant initiator concentration of 6.1×10^{-3} M, taking into account the expansion of the liquid phase at different operating pressures. Two levels of conversion were considered by extending the reaction time from 1 to 2 h, although the conversion was generally less than 1% in both cases. As shown in Figure 2, only a single catalyst concentration was used for

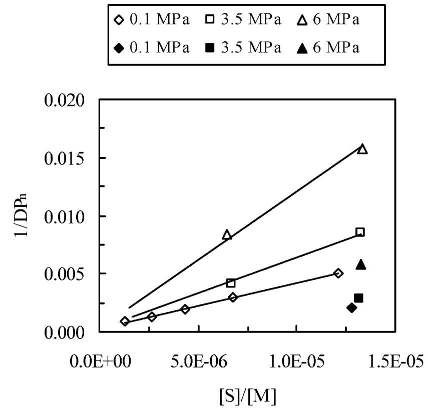

Figure 2. Mayo plots for COPhBF in CO_2-expanded styrene at 50 °C. Reaction times vary from 1 h (open symbols) to 2 h (closed symbols). The solid lines indicate the lines of best fit.

the higher conversion data. In this case, C_s was determined from the slope of a line having the same intercept as the data for bulk styrene (0.1 MPa, 1 h reaction time).

It is evident from Table 2 that C_s decreases with increasing conversion as expected. The increase in PDI with time also indicates progressive catalyst inactivation. It can be seen that C_s in expanded styrene increases by a factor of around 3 at a pressure of 6 MPa. The magnitude of this increase is comparable to that for BMA. These results suggest that the hydrogen abstraction step for styrene may be diffusion-controlled, even though much of the catalyst is unavailable for chain transfer. Again, this assumes that k_p is constant in the expanded monomer.

Effect of Bulk Viscosity. In the conventional CCT polymerization of methacrylates, the relationship between the chain transfer constant and the bulk viscosity of the solution is given by the following equation:

$$C_s k_p \eta^{\alpha} \approx \text{constant} \tag{8}$$

or

$$k_{tr} \propto \frac{1}{\eta^{\alpha}} \tag{9}$$

where α varies from 0.5 to 1.0. This equation is based on the notion that in a diffusion-controlled reaction the rate coefficient is proportional to the diffusion coefficients of the reactants, which in turn are considered to be inversely proportional to the medium viscosity. The bulk viscosity of the pure monomer is commonly used in eq 9.[11]

A useful feature of CO_2-expanded monomers is that the validity of eq 9 can be assessed over a relatively wide range of viscosity. The values of viscosity for CO_2-expanded BMA calculated using eqs 4−6 are presented in Table 3 along with calculated values of k_{tr}. The viscosity of the CO_2-expanded monomer decreases with increasing pressure even though the viscosity of pure CO_2 increases slightly in the same range of pressure. At 6 MPa, the expansion process decreases the viscosity of the monomer by a factor of 6−7 at the temperatures considered.

The value of α in eq 9 can be determined from the slope of a plot of ln k_{tr} vs ln η_{mix}. The data in Figure 3 reveal that the value of α is independent of temperature. The proportionality constant required in eq 9 is obtained from the intercept of the plot and appears to be temperature dependent. This is not surprising because at a fixed viscosity the rate coefficient is expected to increase in accordance with the Arrhenius equation. The increase is relatively minor over the range of temperature considered, in conjunction with the estimated activation energy of 23 kJ mol^{-1} for the chain transfer reaction.[11] It is therefore reasonable to determine an average proportionality constant from the line of best fit for the combined set of data. In this case, values of 0.69 and 7.5 × 10^6 are obtained for α and the proportionality constant, respectively. The latter is in close agreement with the value of 10^7 reported for methacrylate esters by Heuts et al.[11] We note also that the estimation of bulk viscosity from eq 4, with interaction parameters set to zero, yields a satisfactory outcome in this analysis.

It is evident from Figure 3 that a clear relationship exists between the chain transfer rate coefficient and the inverse of viscosity. To further illustrate this point, the data for BMA are compared with results from our earlier study on CO_2-expanded MMA (50 °C) in Figure 4. For MMA, values of 0.76 and 7.2 × 10^6 are obtained for α and the proportionality constant, respectively. Within experimental error, it can be seen that the chain transfer rate coefficients for expanded BMA and MMA are identical at 50 °C. Additionally, the linearity of the data provides evidence of a diffusion-controlled rate-determining step in the CCT polymerization of methacrylates. The chain transfer rate coefficients derived from the apparent values of C_s for expanded styrene exhibit a similar dependence on bulk viscosity (not shown here).

The effect of bulk viscosity on C_s differs from that reported by Roberts et al.[14] They examined the effect of bulk viscosity by addition of high molecular weight PMMA during the

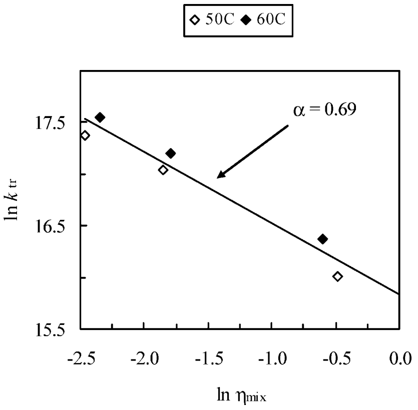

Figure 3. Determination of the value of α in eq 9 for CO_2-expanded BMA. The solid line indicates the line of best fit for the combined set of data.

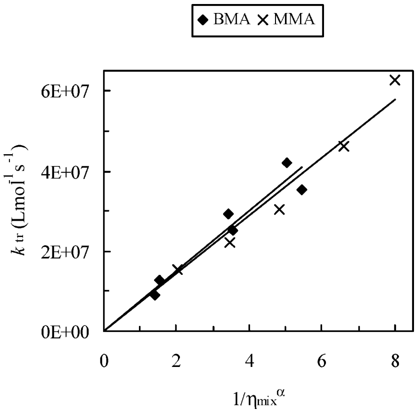

Figure 4. Relationship between the chain transfer rate coefficient and the inverse of bulk viscosity for CO_2-expanded methacrylate esters. The data for MMA are from ref 15. The solid lines indicate the lines of best fit.

cobaloxime-mediated CCT polymerization of the corresponding monomer. In the most extreme case, the bulk viscosity was increased by 3 orders of magnitude by addition of 5 wt % PMMA ($M_w = 4.8 \times 10^6$). The chain transfer constant under these conditions was not significantly affected, suggesting that the reaction is not diffusion-controlled.

However, a closer examination of this finding needs to be made. First, a 5 wt % solution of the given high molecular weight polymer translates to a negligible concentration on a mole basis. This indicates that the local composition in the region surrounding the propagating radicals and chain transfer catalyst is largely unaffected by the presence of the polymer. Accordingly, the local viscosity is similar to the bulk viscosity of the pure monomer, and this largely explains why no change in C_s is observed. In general, the determination of C_s involves the synthesis of oligomers at low conversion. In this study, it is therefore appropriate to use the bulk viscosity of the unreacted expanded monomer in eq 9.

Conclusions

The volumetric expansion of BMA with dense CO_2 provides an effective means of increasing the chain transfer constant during CCT polymerization of the monomer. This effect is mainly attributed to the enhancement of the chain transfer rate coefficient, arising from the reduction in the bulk viscosity of the medium. Furthermore, the CCT process is facilitated by CO_2 even in the presence of cobalt−carbon bond formation in the case of styrene. For both expanded monomers, the chain transfer constants increase by a similar factor in the range of pressure considered. It is demonstrated that a clear linear relationship exists between the chain transfer rate coefficient and the inverse of viscosity. In conjunction with earlier studies on methacrylates, the results of this study provide significant evidence that the rate-determining step in the chain transfer process is diffusion-controlled.

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References and Notes

(1) Gridnev, A. A.; Ittel, S. D. *Chem. Rev.* **2001**, *101*, 3611−3659.
(2) Heuts, J. P. A.; Forster, D. J.; Davis, T. P.; Yamada, B.; Yamazoe, H.; Azukizawa, M. *Macromolecules* **1999**, *32*, 2511−2519.
(3) Roberts, G. E.; Heuts, J. P. A.; Davis, T. P. *Macromolecules* **2000**, *33*, 7765−7768.
(4) Kukulj, D.; Davis, T. P. *Macromol. Chem. Phys.* **1998**, *199*, 1697−1708.
(5) Roberts, G. E.; Davis, T. P.; Heuts, J. P. A.; Ball, G. E. *Macromolecules* **2002**, *35*, 9954−9963.
(6) Biasutti, J. D.; Roberts, G. E.; Lucien, F. P.; Heuts, J. P. A. *Eur. Polym. J.* **2003**, *39*, 429−435.
(7) Muratore, L. M.; Heuts, J. P. A.; Davis, T. P. *Macromol. Chem. Phys.* **2000**, *201*, 985−994.
(8) Heuts, J. P. A.; Muratore, L. M.; Davis, T. P. *Macromol. Chem. Phys.* **2000**, *201*, 2780−2788.
(9) Kowollik, C.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3303−3312.
(10) Pierik, S. C. J.; van Herk, A. M. *J. Appl. Polym. Sci.* **2004**, *91*, 1375−1388.
(11) Heuts, J. P. A.; Forster, D. J.; Davis, T. P. *Macromolecules* **1999**, *32*, 3907−3912.
(12) Forster, D. J.; Heuts, J. P. A.; Davis, T. P. *Polymer* **2000**, *41*, 1385−1390.
(13) Forster, D. J.; Heuts, J. P. A.; Lucien, F. P.; Davis, T. P. *Macromolecules* **1999**, *32*, 5514−5518.
(14) Roberts, G. E.; Davis, T. P.; Heuts, J. P. A.; Russell, G. T. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 782−792.
(15) Zwolak, G.; Jayasinghe, N. S.; Lucien, F. P. *J. Supercrit. Fluids* **2006**, *38*, 420−426.
(16) Akgün, M.; Emel, D.; Baran, N.; Akgün, N. A.; Deniz, S.; Dinçer, S. *J. Supercrit. Fluids* **2004**, *31*, 27−32.
(17) Husain, A. Z.; Zwolak, G.; Lucien, F. P. *J. Chem. Eng. Data* **2006**, *51*, 718−721.
(18) Bakac, A.; Brynildson, M. E.; Espenson, J. H. *Inorg. Chem.* **1986**, *25*, 4108−4114.
(19) Phiong, H.-S.; Lucien, F. P. *J. Supercrit. Fluids* **2003**, *25*, 99−107.
(20) Zwolak, G.; Lioe, L.; Lucien, F. P. *Ind. Eng. Chem. Res.* **2005**, *44*, 1021−1026.
(21) Xu, Q.; Han, B.; Yan, H. *J. Appl. Polym. Sci.* **2003**, *88*, 2427−2433.
(22) Yeo, S.-D.; Kiran, E. *J. Supercrit. Fluids* **2005**, *34*, 287−308.
(23) Mayo, F. R. *J. Am. Chem. Soc.* **1943**, *65*, 2324−2329.
(24) Suddaby, K. G.; Maloney, D. R.; Haddleton, D. M. *Macromolecules* **1997**, *30*, 702−713.
(25) Heuts, J. P. A.; Kukulj, D.; Forster, D. J.; Davis, T. P. *Macromolecules* **1998**, *31*, 2894−2905.
(26) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The Properties of Gases and Liquids*, 4th ed.; McGraw-Hill: New York, 1987.
(27) Orbey, H.; Sandler, S. I. *Can. J. Chem. Eng.* **1993**, *71*, 437−446.
(28) Beuermann, S.; Buback, M.; Schmaltz, C.; Kuchta, F.-D. *Macromol. Chem. Phys.* **1998**, *199*, 1209−1216.
(29) Roberts, G. E.; Heuts, J. P. A.; Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 752−765.
(30) Beuermann, S.; Buback, M.; Davis, T. P.; Gilbert, R. G.; Hutchinson, R. A.; Kajiwara, A.; Klumperman, B.; Russell, G. T. *Macromol. Chem. Phys.* **2000**, *201*, 1355−1364.

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