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The Effects of Ester Chain Length and Temperature on the Catalytic Chain Transfer Polymerization of Methacrylates

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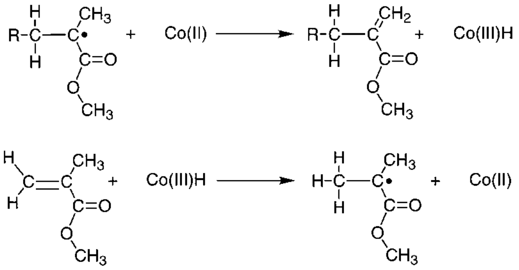
ABSTRACT: The catalytic chain transfer polymerizations of methyl, ethyl, and butyl methacrylates were studied over the temperature range 40−70 °C with cobaloxime boron fluoride (COBF) and its tetraphenyl derivative (COPhBF). It was found that for both catalytic chain transfer agents the chain transfer constant decreases in going from methyl to butyl methacrylate, and that there is no significant temperature effect on the observed chain transfer constants. The results are consistent with a diffusion-controlled rate coefficient for the chain transfer reaction.

Introduction

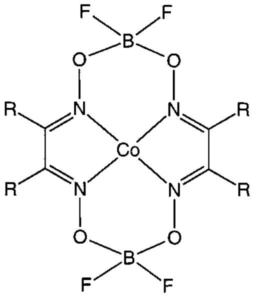
Catalytic chain transfer polymerization is a relatively recent technique for the production of vinyl end-functionalized low-molecular weight polymers via free-radical polymerization.[1−5] This technique is based upon the property of certain low-spin Co(II) complexes to catalyze the chain transfer to monomer reaction (shown in Scheme 1 for the polymerization of methyl methacrylate).[1−3,6−10] It has been well-established that virtually all chains are initiated by a hydrogen atom and terminated by a vinyl end group,[6−8] but despite many efforts,[6−19] most notably those by Gridnev and coworkers [20−27] a fully consistent and unambiguous mechanism has not yet appeared.

In mechanistic studies, the Arrhenius parameters of the overall reaction rate coefficient provide very valuable information about the kinetics and character of the rate-determining step and the nature and importance of substituent effects (for example in a homologous series of monomers). To our knowledge, only three studies of the Arrhenius parameters[11,18,19] and one study of the catalytic chain transfer polymerization of a homologous series of methacrylates[13] have been published to date. In one study[18] a very strong temperature dependence of the catalytic chain transfer reaction in methyl methacrylate was reported. This result was contradicted in two subsequent studies,[11,19] based on a limited data sets, which found only a weak temperature dependence. The effect of the size of the ester group in a series of methacrylates was studied by Mironychev et al.,[13] and it was found that the chain transfer constant (C_S) of a cobalt(II) porphyrin in the catalytic chain transfer polymerization of alkyl methacrylates decreases with increasing size of the ester group. However, the published interpretation of this observation,[13] i.e., a specific complexation between the catalyst and monomer, appears unlikely when considered in the light of recent findings.[28] Since no temperature dependence was determined in the earlier work,[13] it has never been established whether the reported trend in C_S is constant with temperature (which is unlikely if complex formation plays an essential part in the mechanism).

Scheme 1



In the present paper the temperature dependences of the chain transfer constants for both cobaloxime boron fluoride (COBF, **1a**) and its tetraphenyl derivative (COPhBF, **1b**) in the catalytic chain transfer polymerizations of methyl, ethyl, and butyl methacrylate have been determined.



COBF, **1a** : R = methyl

COPhBF, **1b** : R = phenyl

Experimental Section

Materials. The bis(methanol) complexes of COBF (**1a**) and COPhBF (**1b**) were prepared as described previously.[12,17,29,30] Methyl (MMA; Aldrich, 99%), ethyl (EMA; Aldrich, 99%), and butyl methacrylate (BMA; Aldrich, 99%) were passed through a column of activated basic alumina (ACROS, 50−200 μm) and purged with high purity nitrogen (BOC) for 1.5 h prior to use. AIBN (DuPont) was recrystallized twice from methanol and used as initiatior.

General Polymerization Procedure. Polymerizations were carried out as described previously.[12,17,30] Two stock

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Table 1. Experimental Results for the Determination of the Chain Transfer Constant of COBF at 60 °C for Methyl, Ethyl, and Butyl Methacrylate

methyl methacrylate			ethyl methacrylate			butyl methacrylate		
[Co]/[M]	$M_n/10^3$	$M_w/10^3$	[Co]/[M]	$M_n/10^3$	$M_w/10^3$	[Co]/[M]	$M_n/10^3$	$M_w/10^3$
0.00	268	469	0.00	325	514	0.00	523	998
9.84×10^{-8}	31.8	54.7	1.42×10^{-7}	28.1	52.6	1.82×10^{-7}	54.2	91.0
1.92×10^{-7}	16.0	28.1	2.77×10^{-7}	13.1	27.8	3.55×10^{-7}	26.4	45.1
2.81×10^{-7}	7.2	17.6	4.06×10^{-7}	11.2	19.7	5.19×10^{-7}	18.1	32.4
3.67×10^{-7}	7.6	16.8	5.30×10^{-7}	7.5	15.5	6.77×10^{-7}	12.7	26.7
$C_S =$	40×10^3	34×10^3	$C_S =$	27×10^3	27×10^3	$C_S =$	16×10^3	16×10^3

Table 2. Experimental Results for the Determination of the Chain Transfer Constant of COPhBF at 60 °C for Methyl, Ethyl, and Butyl Methacrylate

methyl methacrylate			ethyl methacrylate			butyl methacrylate		
[Co]/[M]	$M_n/10^3$	$M_w/10^3$	[Co]/[M]	$M_n/10^3$	$M_w/10^3$	[Co]/[M]	$M_n/10^3$	$M_w/10^3$
0.00	243	420	0.00	397	684	0.00	499	921
1.01×10^{-7}	46.6	83.0	1.31×10^{-7}	54.8	110	1.73×10^{-7}	78.4	183
1.96×10^{-7}	35.3	63.3	2.55×10^{-7}	24.9	49.2	3.37×10^{-7}	38.6	76.4
2.88×10^{-7}	22.1	39.6	3.74×10^{-7}	19.2	36.3	4.94×10^{-7}	27.3	54.1
3.75×10^{-7}	11.2	25.4	4.87×10^{-7}	12.6	25.7	6.43×10^{-7}	22.4	43.4
$C_S =$	21×10^3	19×10^3	$C_S =$	18×10^3	17×10^3	$C_S =$	9.7×10^3	10×10^3

solutions were prepared: (i) an initiator stock solution, and (ii) a catalyst stock solution (i) The initiator solution was prepared by dissolution of approximately 400 mg of AIBN in 150 mL of monomer. (ii) The catalyst stock solution was prepared by dissolution of approximately 3 mg of catalyst into 10 mL of solution i and a subsequent 10-fold dilution with solution i. Five reaction mixtures were then prepared, each containing 4.0 mL of initiator solution i and 0.00, 0.10, 0.20, 0.30, and 0.40 mL of catalyst solution ii, respectively. The reaction ampules, specially modified for use with standard Schlenk equipment, were deoxygenated by two freeze−pump−thaw cycles and subsequently placed in a thermostated waterbath. Final conversions were maintained below 10%.

Molecular Weight Analysis. Molecular weight distributions were determined by size exclusion chromatography using 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), and a Shimadzu RID-10A differential refractive index detector. Tetrahydrofuran (BDH, HPLC grade) was used as the eluent at 1 mL/min. Calibration of the SEC equipment was performed with narrow poly(methyl methacrylate) standards (Polymer Laboratories, molecular weight range: 200 to 1.6×10^6). Mark−Houwink−Sakurada parameters used for the universal calibration are as follows: $K_{MMA} = 12.8 \times 10^{-5}$ mL·g^{-1}, $a_{MMA} = 0.697$; $K_{EMA} = 15.5 \times 10^{-5}$ mL·g^{-1}, $a_{EMA} = 0.679$; and $K_{BMA} = 14.8 \times 10^{-5}$ mL·g^{-1}, $a_{BMA} = 0.664$.[31]

Viscosity Measurements. Absolute monomer viscosities were measured using an Ostwald viscometer (size A) immersed in a temperature-controlled water bath.[32] The accuracy of the calibration was verified by cross-checking the viscosity obtained for MMA with previously published values by Stickler et al.[33]

Results and Discussion

As stated in the Introduction, many mechanistic aspects of catalytic chain transfer polymerization have not yet been established unambiguously. However, most of the experimental evidence thus far suggests that the chain transfer process consists of two steps, i.e., a hydrogen-abstraction reaction from the growing polymeric radical ($R_n^\bullet$) by the Co(II) complex (similar to a disproportionation reaction) and a hydrogen-transfer reaction from the resulting Co(III)−H species to a monomer molecule (M):[3,4,9−12,21,23−27]

$$R_n^\bullet + \mathrm{Co(II)} \xrightarrow{k_s} P_n + \mathrm{Co(III)}\text{−}\mathrm{H} \qquad (1)$$

$$\mathrm{Co(III)}\text{−}\mathrm{H} + \mathrm{M} \rightarrow \mathrm{Co(II)} + R_1^\bullet \qquad (2)$$

If this mechanism is included as a chain stopping event in the overall kinetic scheme of free-radical polymerization, the following expression applies for the average degree of polymerization, DP_n:[34]

$$\frac{1}{DP_n} = (1 + \lambda)\frac{\langle k_t\rangle[R^\bullet]}{k_p[M]} + C_M + C_s\frac{[\mathrm{Co(II)}]}{[M]} \qquad (3)$$

In this equation (i.e., the Mayo equation),[35] λ is the fraction of termination by disproportionation, $\langle k_t\rangle$ the average termination rate coefficient, k_p the propagation rate coefficient, $[R^\bullet]$ the total radical concentration, C_M the chain transfer constant to monomer and C_S ($=k_S/k_p$) the chain transfer constant to the catalytic chain transfer agent. From this equation it is evident that a value for C_S can be obtained by measurement of DP_n^{-1} as a function of [Co(II)]/[M], and if the former is plotted against the latter, C_S can be obtained from the slope of this plot (often termed a Mayo plot). A note needs to be made regarding the determination of DP_n in the Mayo procedure. The number average degree of polymerization can either be calculated from the number average molecular weight, M_n, or the weight average molecular weight, M_w, by dividing the former by the monomer mass and the latter by twice the monomer mass. Using M_w/(2 monomer mass) as an estimate for DP_n is only justified in systems which are fully controlled by chain transfer (i.e., the polydispersity index, M_w/M_n, is equal to 2), but it has been found that this estimate gives more reliable results than the estimate based on M_n.[12,17,36−39]

Effect of Alkyl Chain Length in Ester Group. One objective of this paper is to investigate whether there is a systematic effect on the observed chain transfer constant with increasing size of the ester group in the methacrylate monomer. In Tables 1 and 2, experimental results are shown for the chain transfer constant measurements of COBF and COPhBF, respectively, in the free-radical polymerizations of methyl, ethyl, and butyl methacrylate at 60 °C. It is clear from

Table 3. Chain Transfer Constants of COBF for Methyl, Ethyl, and Butyl Methacrylate in the Temperature Range 40−70 °C

	methyl methacrylate		ethyl methacrylate		butyl methacrylate	
temp[a]	$C_S(M_n)$[b]	$C_S(M_w)$	$C_S(M_n)$[b]	$C_S(M_w)$[c]	$C_S(M_n)$[b]	$C_S(M_w)$
40	38×10^3	33×10^3	30×10^3	27×10^3	14×10^3	15×10^3
50	44×10^3	39×10^3	30×10^3	30×10^3	15×10^3	16×10^3
60	40×10^3	34×10^3	26×10^3	24×10^3	16×10^3	16×10^3
			27×10^3	27×10^3		
70	31×10^3	28×10^3	26×10^3	24×10^3	16×10^3	15×10^3
	28×10^3	27×10^3	24×10^3	22×10^3		

[a] Temperature in °C. [b] Chain transfer constant of COBF determined using $DP_n = M_n/(\text{monomer mass})$. [c] Chain transfer constant of COBF determined using $DP_n = M_w/(2\ \text{monomer mass})$.

these results that the chain transfer constants for both COBF and COPhBF decrease with increasing size of the ester group. This result is in accordance with the data previously reported by Mironychev et al.[13] for the chain transfer constants of a cobalt(II) porphyrin in the free-radical polymerization of a wide range of methacrylates at 60 °C. These workers ascribed the reduction in chain transfer constant mainly to an increasing steric hindrance with bulky ester side chains and an enhanced stability of the complex formed upon axial ligation of the monomer with the Co(II) center.[13] Although the possibility that these factors play a role cannot be discounted, it is doubtful that they dominate. A previous study[28] showed that direct participation of monomer molecules in the hydrogen-abstraction step is unlikely and that solvent effects through axial ligation are small unless strong ligands, such as pyridine, are included in the reaction mixture. An alternative interpretation of the data, is that the results are consistent with a diffusion-controlled hydrogen-abstraction rate coefficient.

Temperature Effects. In Tables 3 and 4, we have listed the chain transfer constants determined for COBF and COPhBF, respectively, with the three monomers at 40, 50, 60, and 70 °C. It is clear from these results (Figures 1 and 2), that, to within experimental error, no significant temperature effects are observed for either catalyst in any of the studied monomers. This conclusion accords with results obtained in previous studies[11,19] (i.e., only a small temperature dependence was reported for COBF in methyl methacrylate). However, this finding contradicts conclusions made in a different study where an activation energy for the chain transfer constant of COBF in methyl methacrylate of $-10.1\ \text{kJ}\cdot\text{mol}^{-1}$ was reported.[18] This apparent anomaly was investigated by re-analyzing the earlier data,[18] yielding C_S values of 33.5×10^3, 32.8×10^3, 35.2×10^3, and 32.5×10^3 at 60, 70, 80, and 90 °C, respectively, indicating the absence of any significant temperature dependence.

To facilitate discussion of the Arrhenius parameters it is useful to introduce the important parameters by means of eq 4, where A_S, A_p, and A are the preexponential factors of the chain transfer rate coefficient, propagation rate coefficient and chain transfer constant, respectively, and E_S, E_p, and E_{act} are the activation energies of the chain transfer rate coefficient, propagation rate coefficient and chain transfer constant, respectively. From the chain transfer constants listed in Tables 3 and 4 it is clear that $E_{act} \approx 0$ in all cases and therefore $E_S \approx E_p$ for all three monomers. Since the activation energies for propagation of these three monomers are not significantly different,[40−42] the activation energy for the chain transfer reaction is close to 23 $\text{kJ}\cdot\text{mol}^{-1}$ ($E_S \approx E_p \approx 23\ \text{kJ}\cdot\text{mol}^{-1}$). This in turn implies that the preexponential factor of the chain transfer rate coefficient is approximately given by

$$C_s = \frac{k_s}{k_p} = \frac{A_S}{A_p} \exp\left(-\frac{E_S - E_p}{RT}\right) = A \exp\left(-\frac{E_{act}}{RT}\right) \quad (4)$$

$$A_S \approx C_S A_p \quad (5)$$

Using this expression yields values for A_S of the order of $\sim 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$ for all three monomer systems, which is in agreement with previous work.[18,19]

Mechanistic Interpretation. The value of the activation energy, $E_S \approx 23\ \text{kJ}\cdot\text{mol}^{-1}$, for the chain transfer reaction, simply indicates the presence of a reaction barrier; unfortunately it is not possible to draw significant mechanistic conclusions on the basis of this result alone. More information can be obtained from the preexponential factor A_S which is on the order of $\sim 10^{10}$ $\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$. This value is atypical for a chemically controlled bimolecular (elementary) reaction between a polymeric radical and a small molecule, as experimental data,[40,43−46] backed up by theoretical transition state theory arguments,[47−51] suggest that typical preexponential factors are several orders of magnitude lower (i.e., $\sim 10^6 - 10^8\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$). The much higher value for A_s reported here is therefore indicative of an unusual chain transfer mechanism. High A_s values are more likely to signify a unimolecular rate-determining step[47] (in which case the units of A_S should be s^{-1}). A unimolecular rate-determining step is feasible if the mechanism of catalytic chain transfer involves a β-elimination of a hydrogen atom from a radical coordinated to the cobalt center.[27,52] Although this possibility cannot be discarded at present, we will not discuss it further in the present paper.

An alternative explanation, already alluded to in previous studies,[2,11,19] is that the chain transfer reaction involving methacrylate monomers is diffusion-controlled. The chain transfer rate coefficients, k_S ($\sim 10^7$ $\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$) are similar to the rate coefficients obtained for bimolecular termination reactions in free-radical polymerization − these are known to be diffusion-controlled.[53]

For a diffusion-controlled reaction, the rate coefficient is often expressed in terms of the Smoluchowski equation,[53−55] which states that the rate coefficient is proportional to the mutual diffusion coefficients of the two reactants, which can be approximated by the sum of the two self-diffusion coefficients:[53]

$$k_s \propto D_{Co} + D_i \quad (6)$$

Here D_{Co} is the diffusion coefficient of the cobalt catalyst and D_i the diffusion coefficient of an i-meric radical. This implies that the temperature dependence of the diffusion coefficients will dictate the temperature behavior of the rate coefficient.[56] An extensive study of the self-diffusion of toluene in a polystyrene solution has shown that the activation energy of the diffusion coefficient is about 11 $\text{kJ}\cdot\text{mol}^{-1}$ at zero polymer concentrations and increases with increasing polymer content.[57] Furthermore, diffusion coefficients at 25 and 40 °C reported by Griffiths et al.[58] for the diffusion of methyl methacrylate and butyl methacrylate oligomers in rubbery polymer

Table 4. Chain Transfer Constants of COPhBF for Methyl, Ethyl, and Butyl Methacrylate in the Temperature Range 40−70 °C

	methyl methacrylate		ethyl methacrylate		butyl methacrylate	
temp[a]	$C_S(M_n)$[b]	$C_S(M_w)$[c]	$C_S(M_n)$[b]	$C_S(M_w)$[c]	$C_S(M_n)$[b]	$C_S(M_w)$[c]
40	18×10^3	19×10^3	15×10^3	17×10^3	6.5×10^3	7.8×10^3
			19×10^3	20×10^3	7.7×10^3	8.1×10^3
					9.4×10^3	8.8×10^3
50	19×10^3	18×10^3	15×10^3	17×10^3	9.2×10^3	10×10^3
			16×10^3	16×10^3	7.5×10^3	10×10^3
					9.0×10^3	10×10^3
60	21×10^3	19×10^3	17×10^3	17×10^3	9.7×10^3	10×10^3
			17×10^3	18×10^3	8.6×10^3	9.5×10^3
			18×10^3	17×10^3	9.9×10^3	11×10^3
70	21×10^3	20×10^3	15×10^3	17×10^3	11×10^3	8.4×10^3
			16×10^3	17×10^3	9.3×10^3	9.5×10^3
			17×10^3	17×10^3	8.2×10^3	8.9×10^3

[a] Temperature in °C. [b] Chain transfer constant of COBF determined using $DP_n = M_n$/(monomer mass). [c] Chain transfer constant of COPhBF determined using $DP_n = M_w$/(2 monomer mass).

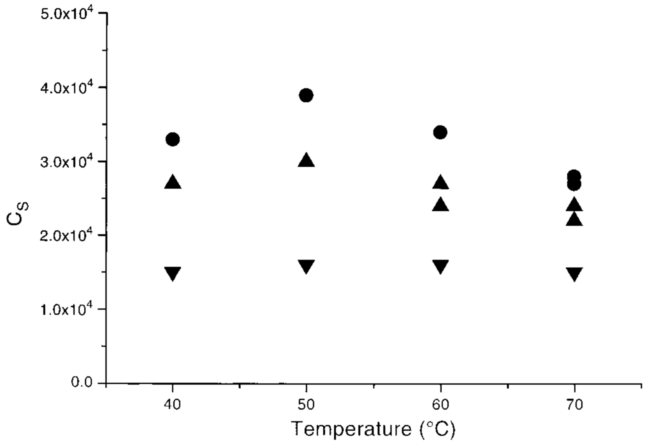

Figure 1. Temperature dependence of the chain transfer constants of COBF in the free-radical polymerizations of (●) MMA, (▲) EMA and (▼) BMA in the temperature range of 40−70 °C.

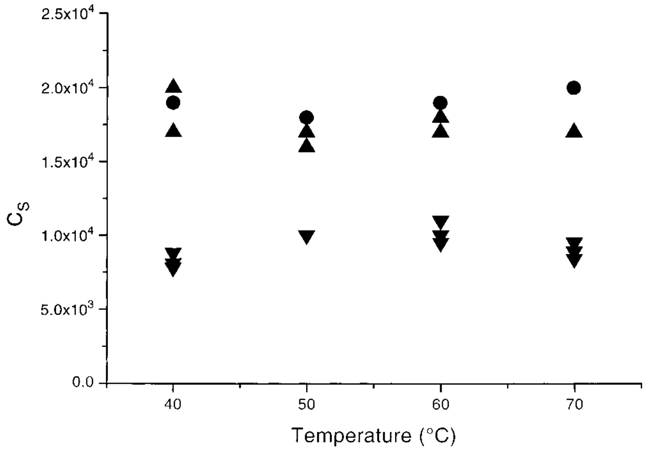

Figure 2. Temperature dependence of the chain transfer constants of COPhBF in the free-radical polymerizations of (●) MMA, (▲) EMA and (▼) BMA in the temperature range of 40−70 °C.

matrixes suggest that the activation energy for the diffusion of these species has a value between about 10 and 40 kJ·mol^{-1}. Hence, an activation energy of ∼23 kJ·mol^{-1} is not inconsistent with a diffusion-controlled reaction. An estimated value for the preexponential factor in a diffusion-controlled reaction can be obtained from the reaction rate coefficient for the recombination reaction of two primary radicals, which is of the order of 10^9 dm^3 mol^{-1} s^{-1}.[53] In conjunction with an activation energy of about 11 kJ·mol^{-1} (taken from the toluene study, vide supra), this corresponds to a preexponential factor of about 10^{10} to 10^{11} dm^3 mol^{-1} s^{-1}. The estimate from the current study, i.e., $A_S \approx 10^{10}$ dm^3 mol^{-1} s^{-1}, is consistent with this value.

Further indications of a diffusion-controlled chain transfer reaction can be found by comparing the chain transfer constants obtained for the three different monomers. It is evident from Tables 1−4 that the larger the ester group in this homologous series, the smaller the chain transfer constant. This decrease in chain transfer constant can only be partially explained by an increasing propagation rate coefficient upon increasing size of the ester group.[42] Since the chain transfer constants contain the rate coefficients of both chain transfer and propagation, the discrepancy can only be ascribed to the chain transfer rate coefficients, as indicated in eq 7, where the chain transfer constants for methyl and butyl methacrylate are compared. At 40 °C, $C_{S,MMA}/C_{S,BMA} \approx 2.0-2.2$ (see Tables 3 and 4) and $k_{p,BMA}/k_{p,MMA} \approx 1.3$,[40,42] which leaves a factor of about 1.7 unaccounted for. This factor should then correspond to the ratio $k_{S,MMA}/k_{S,BMA}$,. If these chain transfer rate coefficients are diffusion-limited, then they should be proportional to the diffusion coefficients in these systems (see eq 6), which in turn are generally found to be roughly proportional to the inverse of the solvent viscosity η[59]

$$\frac{C_{S,MMA}}{C_{S,BMA}} = \frac{k_{S,MMA}}{k_{S,BMA}}\frac{k_{p,BMA}}{k_{p,MMA}} \tag{7}$$

$$D \propto \frac{1}{\eta^{\alpha}} \tag{8}$$

where α lies generally between 0.5 and 1.0.[59] Since the chain transfer rate coefficient is proportional to the sum of the self-diffusion coefficients of the cobalt complex and the i-meric radicals (see eq 6), it should also be roughly proportional to $\eta^{-\alpha}$ (i.e., $k_S \propto \eta^{-\alpha}$). Hence, if the chain transfer reaction is diffusion controlled, eq 9 should apply:

$$C_S \propto \frac{1}{k_p \eta^{\alpha}} \tag{9}$$

Equation 9 in turn implies the following:

Table 5. Summary of Relevant Kinetic and Physical Data of the Studied Methacrylates at 40, 50, 60 and 70 °C

	methyl methacrylate			ethyl methacrylate			butyl methacrylate		
temp[a]	C_s[b]	k_p[c]	η[d]	C_s[b]	k_p[c]	η[e]	C_s[b]	k_p[c]	η[e]
40	33×10^3	497	0.45	27×10^3	555	0.48	15×10^3	676	0.70
50	39×10^3	649	0.40	30×10^3	728	0.44	16×10^3	863	0.62
60	34×10^3	833	0.37	26×10^3	946	0.39	16×10^3	1085	0.55
70	27×10^3	1054	0.33	23×10^3	1196	0.35	16×10^3	1347	0.49

[a] Temperature in °C. [b] Chain transfer constant of COBF taken from Table 3 (M_w results). [c] Propagation rate coefficient (dm^3 mol^{-1} s^{-1}) taken from ref 31. [d] Absolute viscosity (centipoise) of MMA taken from ref 32. [e] Absolute viscosity of the monomer (centipoise) determined in the present study.

Table 6. Comparison of Values for $C_s k_p \eta^a$ for the COBF-Mediated Free-Radical Polymerizations of Methyl, Ethyl, and Butyl Methacrylate

	temp[a]	MMA	EMA	BMA
$C_s k_p \eta$	40	7.8×10^6	7.2×10^6	7.3×10^6
	50	1.0×10^7	9.5×10^6	8.5×10^6
	60	1.0×10^7	1.0×10^7	9.3×10^6
	70	9.7×10^6	9.7×10^6	1.0×10^7
$C_s k_p \eta^{0.7}$	40	9.9×10^6	9.0×10^6	8.1×10^6
	50	1.3×10^7	1.2×10^7	9.9×10^6
	60	1.4×10^7	1.3×10^7	1.1×10^7
	70	1.3×10^7	1.3×10^7	1.3×10^7
$C_s k_p \eta^{0.5}$	40	1.2×10^7	1.0×10^7	8.7×10^6
	50	1.6×10^7	1.4×10^7	1.1×10^7
	60	1.7×10^7	1.6×10^7	1.3×10^7
	70	1.7×10^7	1.7×10^7	1.5×10^7

[a] Temperature in °C.

$$C_S k_p \eta^\alpha \approx \text{constant} \tag{10}$$

In Table 5, the individual values for C_S, k_p, and measured monomer viscosities are listed. The equality specified in eq 10 is tested for MMA, EMA, and BMA at 40−70 °C using three different values for α, viz. 1, 0.7, and 0.5.;[59] the results are shown in Table 6. The data in Table 6 clearly suggest the validity of Eq 10 within experimental uncertainty, which provides further evidence for a diffusion-controlled chain transfer reaction. This is the case for both COBF and COPhBF, the latter consistently displaying chain transfer constants about 50% less than those observed with COBF (see Tables 1−4). A possible explanation for this observation was previously published by Haddleton et al.,[11] who suggested that the lower chain transfer constants for COPhBF may be ascribed to a larger cross-sectional area of COPhBF compared to COBF, slowing down the diffusion process.

Conclusions

The data presented in this paper clearly show a dependence of the catalytic chain transfer constant on the size of the ester group in the methacrylate series, i.e., $C_{S,MMA} > C_{S,EMA} > C_{S,BMA}$. Furthermore, a virtually constant C_S value was observed with changing temperature, yielding a preexponential factor A of about 10^{10} and an activation energy of about 23 kJ mol^{-1} for the rate-determining step in the chain transfer reaction. These observations are consistent with a diffusion-controlled rate-determining step in the catalytic chain transfer reaction of methacrylates. This conclusion is reinforced by an inverse correlation of the C_S values with monomer viscosity, as $\eta_{MMA} < \eta_{EMA} < \eta_{BMA}$. Furthermore, it was shown that for a diffusion-controlled chain transfer reaction, the product of C_S, k_p and η^α should be constant − which was confirmed in the current experiments for all three monomers over the range 40−70 °C.

In conclusion, all results presented in this paper are consistent with a diffusion-controlled catalytic chain transfer reaction for MMA, EMA, and BMA.

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