Conventional and catalytic chain transfer in the free-radical polymerization of 2-phenoxyethyl methacrylate

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Abstract

A comparative study was conducted on chain transfer mechanisms in the free radical polymerization of a viscous methacrylate, viz. 2-phenoxyethyl methacrylate. Two chain transfer agents were subjected to investigation: *n*-dodecanethiol (DDM) and bis[(difluoroboryl)diphenylglyoximato]cobalt (II) (COPhBF). The chain transfer constant (C_S) for DDM was found to be 0.7 (at 60°C); a value comparable with the C_S value obtained for a low viscosity methacrylate, methyl methacrylate, under similar conditions. In contrast, the C_S value for COPhBF was found to be 2×10^3 (at 60°C) which is one order of magnitude lower than the C_S value published for methyl methacrylate. This result is explained in terms of the different chain transfer mechanisms operating in the two polymerizing systems. Radical reactions with DDM involve a chemically controlled hydrogen transfer event, whereas experimental results obtained for the reaction of methacrylate radicals with COPhBF indicate a diffusion-controlled, rate determining step in the hydrogen transfer process. Thus in the reaction of COPhBF with 2-phenoxyethyl methacrylate radicals, the high viscosity reaction medium (monomer) has a significant influence on the transfer rate. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Catalytic chain transfer; Thiol; Cobaloxime

1. Introduction

The manufacture of low molecular weight polymers has assumed significant importance in recent years, with developments in powder, UV-curable, high-solids and dispersion coatings formulations for a wide range of industrial end-uses. The conventional approaches to molecular weight reduction involve either increasing initiator concentration or including a chain transfer agent, such as a thiol, into the reaction mixture. The elementary processes that constitute the chain transfer process have been known for many years and can be represented by Eq. (1) [1,2].

$$R\cdot_n + S \xrightarrow{k_{tr,S}} P_n + S\cdot. \tag{1}$$

This reaction, proceeds via the transfer of a hydrogen or halogen atom as the growing n-meric radical reacts with a chain transfer agent, S, to yield a dead polymer chain with the same chain length n, and a new small radical $S\cdot$. This process leads to a decrease in the number average degree of polymerization (DP_n). A quantitative expression describing this effect is the Mayo equation [3]:

$$\frac{1}{DP_n} = (1 + \lambda)\frac{\langle k_t \rangle [R\cdot]}{k_p[M]} + C_M + C_S\frac{[S]}{[M]}. \tag{2}$$

In this equation, λ is the fraction of termination by disproportionation, $\langle k_t \rangle$ the average termination rate coefficient, k_p the propagation rate coefficient, $[R\cdot]$ the total radical concentration, C_M the chain transfer constant to monomer and $C_S(= k_{tr,S}/k_p)$ the chain transfer constant to the chain transfer agent. In polymerizations dominated by chain transfer the molecular weight is governed by both the chain transfer constant and the concentration of S.

The thiol family of compounds is widely used for controlling molecular weight in free radical polymerizations. The chain transfer process comprises of two contiguous steps; transfer of the thiyl hydrogen to the growing polymer chain followed by re-initiation, whereby a thiyl radical adds to a monomeric double bond. The thiol is thus incorporated into the polymer chain. Typically [4], $C_S \approx 10^{-1}$–10 for thiols in the free-radical polymerization of methyl methacrylate. Consequently, significant amounts of chain transfer agent are often required for the production of oligomers.

Catalytic chain transfer (CCT), an extremely efficient alternative to conventional chain transfer, emerged in the

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early 1980s. Catalytic chain transfer derives from the ability of certain low-spin cobalt(II) complexes to catalyze chain transfer to monomer [5,6]. The generally accepted mechanism of the catalytic chain transfer process involves two elementary steps. Firstly the Co(II) catalyst abstracts a hydrogen atom from a β-carbon (preferably an α-methyl group) on the growing radical, yielding a dead polymer chain with a vinyl end-group, and a Co(III)H complex:

$$R_n\cdot + \text{Co(II)} \xrightarrow{k_{tr,Co}} P_n + \text{Co(III)H}. \qquad (3)$$

This Co(III)H intermediate subsequently transfers the hydrogen atom to a monomer molecule, thereby initiating a new chain:

$$\text{Co(III)H} + M \rightarrow \text{Co(II)} + R\cdot_1 . \qquad (4)$$
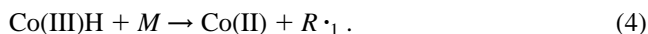
A comparison of CCT with conventional chain transfer processes results in three important observations:

(i) The dead chain formation is similar-in both cases (except for the resulting end-group), i.e. the chain transfer process involves a reaction between a growing radical and a chain transfer agent, yielding dead polymer. Thus, the Mayo equation (2) applies in both cases.

(ii) The re-initiation steps are very different. In conventional chain transfer, the thiol is consumed in the re-initiation process. In contrast, re-initiation in CCT regenerates the original cobalt(II) complex, and no fragment of the CCT agent are incorporated into the polymer chain.

(iii) There is a significant difference in the reactivity of a thiol compared to that of a catalytic chain transfer agent. A comparison of the chain transfer constants in methyl methacrylate at 60°C of *n*-dodecanethiol and COPhBF, (**1**), denoted as $C_{DDM,MMA}$ and $C_{Co,MMA}$ in the remainder of this paper, yields values of about 0.8 [7,8], and 20×10^3, respectively [9]. This translates into values for the corresponding chain transfer rate coefficients $k_{tr,DDM}$ and $k_{tr,Co}$ of 660 and 2×10^7 dm^3 mol^{-1} s^{-1}, respectively (using k_p at 60°C ≈ 830 dm^3 mol^{-1} s^{-1}) [10], indicating that the catalytic chain transfer agent is about four orders of magnitude more reactive than the thiol.

The work reported in this paper mainly relates to an investigation of (iii). The values for $k_{tr,Co}$ are close to the rate coefficients observed for bimolecular termination in free-radical polymerization, which are known to be diffusion-controlled [11,12]. Previous work [9,13] provided evidence that the chain transfer process in the catalytic chain transfer polymerization of methacrylates may be diffusion-controlled. Recent results for the Arrhenius parameters of $k_{tr,Co}$ in methyl (MMA), ethyl (EMA) and butyl methacrylate (BMA) [14] are consistent with a diffusion-controlled chain transfer mechanism. The C_{Co} value was found to decrease with increasing size of the ester group in a homologous series of the methacrylates [14]; this effect was found to be constant over the investigated temperature
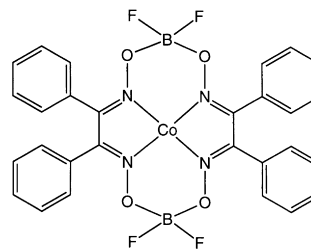
COPhBF, **1**
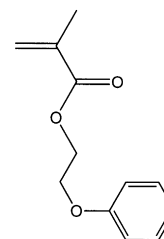
2-Phenoxyethyl methacrylate, **2**

range of 40–70°C. A similar result, at 60°C, was reported previously by Myronichev et al. [15], who explained the observation in terms of steric hindrance and a specific complexation of the monomer with the catalyst. However, Arrhenius parameters for the chain transfer reaction ($A \sim 10^{10}$ dm^3 mol^{-1} s^{-1}, $E_{act} \sim 23$ kJ mol^{-1}) [14] are not compatible with this explanation. Instead, they indicate a diffusion-controlled reaction. Further, relationship (5) was found to be valid for the chain transfer constants of COPhBF in MMA, EMA and BMA over a range of temperatures:

$$C_{Co}k_p\eta \approx \text{constant}, \qquad (5)$$

where η is the monomer viscosity. This relationship is derived on the basis that in diffusion-controlled reactions the rate coefficient should be roughly proportional to the inverse of the monomer viscosity [16,17].

In contrast, the conventional chain transfer reactions of alkyl methacrylates with *n*-dodecanethiol are chemically controlled. Transition state theory predicts [18] that the chain transfer constant of a thiol in a homologous series should be nearly constant. The transition states of the chain transfer and the propagation reactions are similar enough for the changes in $k_{tr,DDM}$ and k_p caused by a changing monomer to cancel. This argument is substantiated by experimental results from Hutchinson et al. [7] who measured a constant C_{DDM} (~0.7) for MMA, EMA and BMA.

Earlier work on catalytic chain transfer only focused on

monomers with a relatively low viscosity. In the current paper, a very viscous monomer, 2-phenoxyethyl methacrylate (POEMA, **2**), was selected for study to test the earlier prediction of a diffusion-controlled mechanism for catalytic chain transfer polymerizations involving methacrylate derivatives.

2. Experimental

2.1. Materials

COPhBF was prepared as described previously [19,20]. The monomer 2-phenoxyethyl methacrylate (POEMA; Sartomer) was purified by vacuum distillation prior to use, *n*-dodecanethiol (DDM; Aldrich, 98%) was used without further purification, and 2,2'-azobisisobutyronitrile (AIBN; DuPont) was recrystallized twice from methanol and used as initiator.

2.2. Measurement of chain transfer constant to DDM

A stock solution of approximately 100 mg AIBN in 130 ml POEMA was prepared from which four samples of ~5 ml were transferred into glass ampoules (all quantities were accurately weighed). To each of these solutions a quantity of *n*-dodecanethiol (ranging roughly from 20 to 100 mg) was added and the solutions were subsequently purged with high purity nitrogen gas (BOC gases) for 10 min. The ampoules were subsequently sealed with rubber septa and placed in a constant temperature water bath. Conversions were maintained below 5%.

2.3. Measurement of chain transfer constant to COPhBF

Measurements of the chain transfer constant to COPhBF were carried out as described previously [19,21,22]. Two stock solutions were prepared: (a) an initiator stock solution I; and (b) a catalyst stock solution II. The initiator solution was prepared by dissolution of approximately 100 mg of AIBN in 130 ml of monomer ($\sim 5 \times 10^{-3}$ M)—solution I. 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 dillution with solution I and solution II. Five reaction mixtures were then prepared, each containing 4.0 ml of initiator solution I and 0.10, 0.20, 0.30, 0.40 and 0.50 ml of catalyst solution II, respectively. The reaction ampoules, specially modified for use with standard Schlenk equipment, were deoxygenated by two freeze-pump-thaw cycles and subsequently placed in a temperature-controlled water bath. Final conversions were maintained below 10%.

2.4. 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^2 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 eluent at 1 ml min. Calibration of the SEC equipment was performed with narrow poly-(methyl methacrylate) standards (Polymer Laboratories, molecular weight range: 200–1.6×10^6). No special consideration was given to the Mark–Houwink–Sakurada parameters of poly(POEMA), but it is expected that the errors introduced by this approximation are small.

2.5. Viscosity measurements

Absolute monomer viscosities were measured using an Ostwald viscometer (size A) immersed in a temperature-controlled water bath at 60°C [23]. The calibration of the capillary was verified by cross-checking the viscosity of MMA with those obtained by Stickler et al. [24].

2.6. Pulsed laser polymerization

The propagation rate coefficient (k_p) of POEMA at 60°C was measured using pulsed laser polymerization [25]. Purified monomer and benzoin were weighed into pyrex sample tubes (10 mm diameter by 60 mm height), which were then purged with high purity nitrogen for 5 min and sealed with rubber septa. The reaction mixtures were equilibrated at the reaction temperature prior to laser exposure. The polymerizations were initiated by a pulsed Nd:Yag laser (Continuum Surelite I-20) with a harmonic generator (a Surelite SLD-1 and SLT in series), which was used to produce the 355 nm UV laser radiation, and a wavelength separator (Surelite SSP-2), which was used to isolate the 355 nm beam. Constant pulsing frequencies of 10 and 6.67 Hz were used. Polymerization was terminated by removing the sample from the laser, and precipitating the polymer into methanol. The molecular weight distributions of these polymers were subsequently determined by size exclusion chromatography.

3. Results and discussion

Chain transfer constants were obtained using the Mayo Eq. (2); the plots are shown in Fig. 1 and the basic data and derived C_{Co} values are given in Table 1. The reproducibility of the data is excellent and $C_{Co,POEMA}$ is found to be $\sim 2 \times 10^3$. This value is significantly smaller than $C_{co,MMA}$, previously determined as 20×10^3 [9]. This result is consistent with the hypothesis of a diffusion-controlled catalytic chain transfer reaction for the methacrylate series of monomers. The measured viscosity of POEMA, $\eta_{POEMA} = 2.51$ cP, can be contrasted with the viscosity of MMA, $\eta_{MMA} = 0.37$ cP. If the chain transfer reaction is indeed diffusion controlled, the relationship given by Eq. (5), shown to be applicable to MMA, EMA and BMA, should also apply in the present case, provided that no
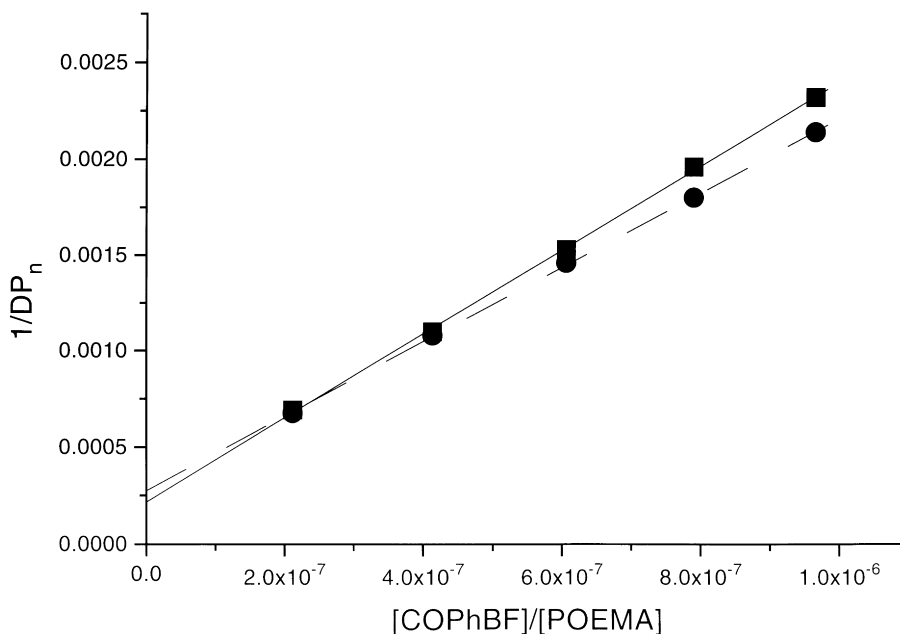
Fig. 1. Mayo plots for POEMA polymerization in the presence of COPhBF. ●: Molecular weight data based on M_n and ■: molecular weight data based $M_w/2$.

extraneous solvent effect is exerted by the phenyl ring. In other words, Eq. (6) should apply:

$$(C_{Co}k_p\eta)_{POEMA} \approx (C_{Co}k_p\eta)_{MMA} \tag{6}$$

The value of the propagation rate coefficient, k_p, of POEMA at 60°C is required to test Eq. (6). This k_p value was determined via pulsed laser polymerization (PLP) using the inflection point molecular weight (M_{inf}) as a measure of the characteristic chain length L_0 (i.e. $L_0 = M_{inf}/$monomer mass) in Eq. (7):

$$k_p = \frac{L_0\nu}{[M]}, \tag{7}$$

where ν is the pulsing frequency of the laser. Typical molecular weight distributions analysed with a polyMMA calibration curve are shown in Fig. 2. All of the characteristic features of classical PLP are observed. In Table 2 the experimental results obtained from the PLP experiments are listed and from these a propagation rate coefficient of 953 ± 30 dm^3 mol^{-1} s^{-1} (NB. k_p from a poly-MMA calibration curve!) can be estimated.

This value for k_p can now be substituted into Eq. (6) as shown below, for MMA and POEMA:

$$\text{MMA}: \quad C_{Co} \times k_p \times \eta = 18.5 \times 10^3 \times 833 \times 0.37$$

$$= 5.7 \times 10^6, \tag{8a}$$

$$\text{POEMA}: \quad C_{Co} \times k_p \times \eta = 2 \times 10^3 \times 953 \times 2.5 = 4.8 \times 10^6. \tag{8b}$$

It is evident that these two values (8a) and (8b) are very

Table 1
Summary of experimental results for the determination of the chain transfer constant to COPhBF at 60°C

|	Solution I (ml)	Solution II (ml)	[Co]/[M]	M_n	M_w
Experiment 1					
a	0.1	4.0	2.12×10^{-7}	198×10^3	610×10^3
b	0.2	4.0	4.15×10^{-7}	168×10^3	382×10^3
c	0.3	4.0	6.07×10^{-7}	127×10^3	282×10^3
d	0.4	4.0	7.91×10^{-7}	113×10^3	229×10^3
e	0.5	4.0	9.67×10^{-7}	94.8×10^3	192×10^3
C_{Co}				1.5×10^3	1.9×10^3
Experiment 2					
a	0.1	4.0	2.12×10^{-7}	264×10^3	595×10^3
b	0.2	4.0	4.15×10^{-7}	174×10^3	375×10^3
c	0.3	4.0	6.07×10^{-7}	130×10^3	269×10^3
d	0.4	4.0	7.91×10^{-7}	102×10^3	210×10^3
e	0.5	4.0	9.67×10^{-7}	85.9×10^3	178×10^3
C_{Co}				2.2×10^3	2.2×10^3
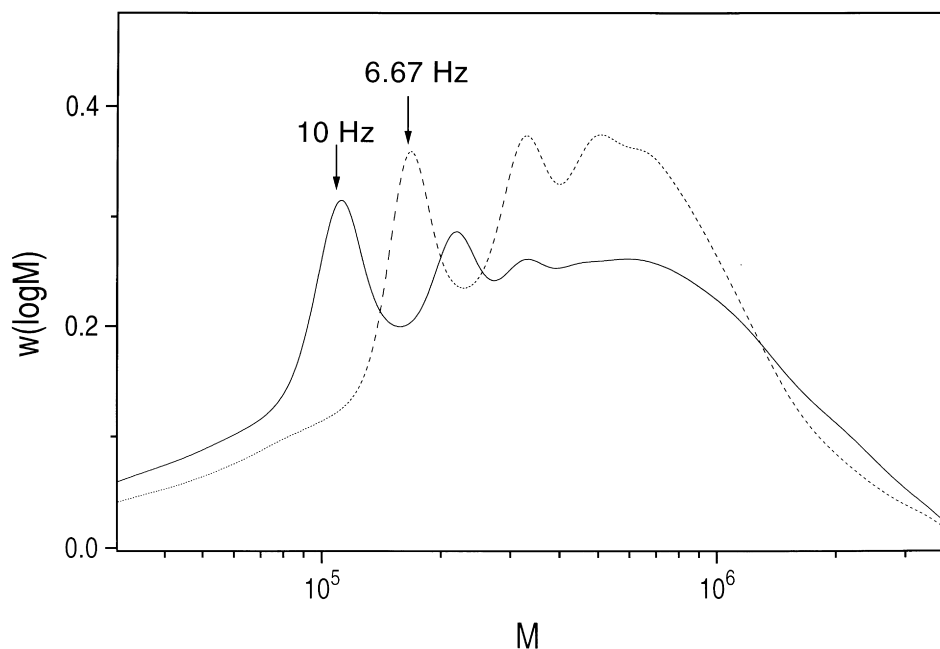
Fig. 2. Typical molecular weight distributions obtained from PLP experiments with POEMA.

similar. This provides strong evidence that viscosity effects are very important in the catalytic chain transfer reaction of these two monomers, confirming the previous data obtained for the lower *n*-alkyl methacrylate monomers. It is noteworthy that the molecular weight distributions obtained from both transfer and PLP experiments were not analyzed using appropriate Mark–Houwink constants for poly-POEMA. However, as the molecular weight ranges obtained in our CCT and PLP are very similar (see Tables 1 and 2), the important final result should be independent of the

SEC calibration. As $C_{Co} \propto$ molecular weight^{-1} and $k_p \propto$ molecular weight, the product of C_S and k_p is unlikely to be affected significantly by the universal calibration procedure.

The chain transfer constant of *n*-dodecanethiol in POEMA was measured to confirm that the large decrease in the catalytic chain transfer constant was not caused by an unusual solvent effect. The Mayo plots are shown in Fig. 3 and the data are listed in Table 3. A chain transfer constant $C_{DDM,POEMA}$ of 0.7 is obtained, which is similar to values
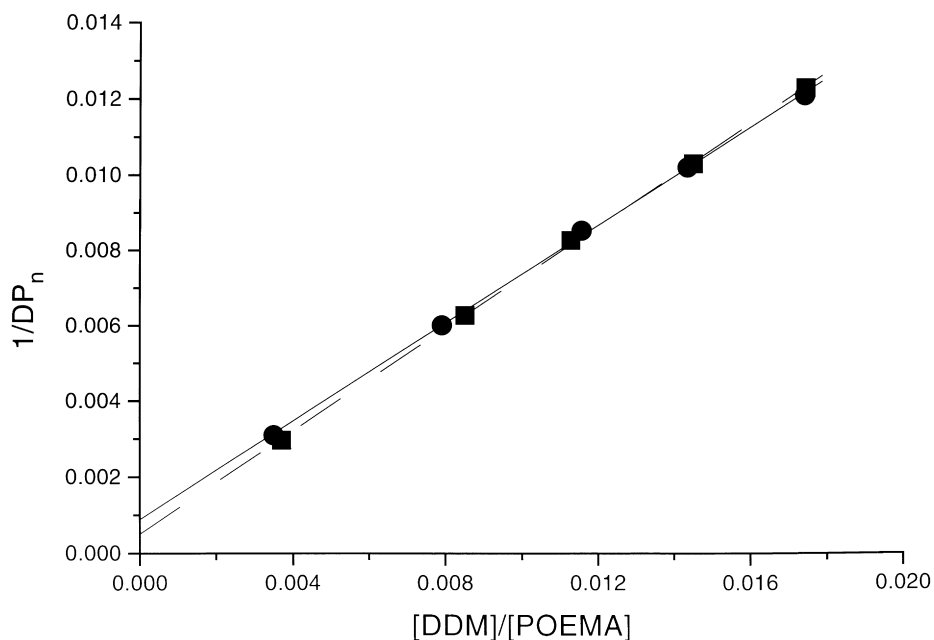

Fig. 3. Mayo plots for POEMA polymerization in the presence of DDM. ●: Molecular weight data based on M_n and ■: molecular weight data based $M_w/2$.

Table 2
Summary of experimental pulsed laser polymerization results at 60°C

Experiment	ν [a]	ρ [b]	$[M]$ [c]	$M_{\text{inf,1}}$ [d]	k_p [e]	$M_{\text{inf,2}}$ [f]	k_p [g]
1	10	1.046	5.07	98×10^3	938	194×10^3	926
2	10	1.046	5.07	104×10^3	998	209×10^3	1000
3	6.67	1.046	5.07	149×10^3	948	290×10^3	923
4	6.67	1.046	5.07	150×10^3	955	292×10^3	931

[a] Pulsing frequency in Hz.
[b] Monomer density in g ml^{-1}.
[c] Monomer concentration in mol dm^{-3}.
[d] First inflection point.
[e] Propagation rate coefficient derived from first inflection point (dm^3 mol^{-1} s^{-1}).
[f] Inflection point of first overtone.
[g] Propagation rate coefficient derived from inflection point of first overtone (dm^3 mol^{-1} s^{-1}).

Table 3
Summary of experimental results for the determination of the chain transfer constant to DDM at 60°C

	m_{DDM} (g)	m_{POEMA} (g)	$[\text{DDM}]/[M]$	M_n	M_w
Experiment 1					
a	0.0210	5.7670	3.71×10^{-3}	68.2×10^3	139×10^3
b	0.0479	5.7223	8.52×10^{-3}	36.5×10^3	65.6×10^3
c	0.0647	5.8307	11.3×10^{-3}	28.5×10^3	49.8×10^3
d	0.0814	5.7104	14.5×10^{-3}	23.6×10^3	39.9×10^3
e	0.0984	5.7366	17.5×10^{-3}	19.4×10^3	33.5×10^3
C_{DDM}				0.55	0.68
Experiment 2					
a	0.0198	5.7534	3.50×10^{-3}	64.8×10^3	133×10^3
b	0.0445	5.7166	7.93×10^{-3}	37.9×10^3	68.5×10^3
c	0.0648	5.6949	11.6×10^{-3}	27.1×10^3	48.4×10^3
d	0.0802	5.6840	14.4×10^{-3}	23.5×10^3	40.6×10^3
e	0.0979	5.7146	17.4×10^{-3}	20.2×10^3	34.2×10^3
C_{DDM}				0.51	0.64

previously obtained in MMA (0.7[7] and 0.8[8]). This is consistent with theoretical predictions (vide supra). This result confirms the absence of any anomalous steric or electronic effects in conventional transfer reactions with POEMA.

4. Conclusions

The results presented in this paper further substantiate the hypothesis that the catalytic chain transfer reaction in methacrylates is diffusion-controlled. In accordance with the increasing viscosities for the methacrylate series ($\eta_{\text{MMA}} < \eta_{\text{EMA}} < \eta_{\text{BMA}} \ll \eta_{\text{POEMA}}$) we find the reverse order in the chain transfer constants of COPhBF in these monomers ($C_{\text{Co,MMA}} > C_{\text{Co,EMA}} > C_{\text{Co,BMA}} > C_{\text{Co,POEMA}}$). The absence of any significant difference in the chain transfer constants of *n*-dodecanethiol in POEMA and in MMA indicates that the experimental results with COPhBF cannot be attributed to unusual solvent effects.

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