Chain Transfer Activity of ω-Unsaturated Methyl Methacrylate Oligomers

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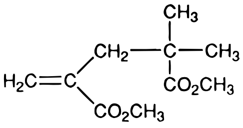
ABSTRACT: The chain transfer activities of a series of ω-unsaturated methyl methacrylate oligomers [(dimer (**1**), trimer (**2**), tetramer (**3**), and a methyl methacrylate macromonomer with average chain length of 24 units (**4**)] have been evaluated in methyl methacrylate polymerizations over the temperature range 45−100 °C. Transfer constants were determined by analysis of the ln chain length distributions. The dimer (**1**) was found to be substantially less effective as a chain transfer agent than the trimer (**2**) or the higher macromonomers (**3**, **4**) [C_T(60 °C) **1**, 0.013; **2**, 0.19; **3**, 0.31; **4**, 0.21]. The transfer constants show only a small temperature dependence and no variation with conversion. No discernible retardation was observed in these polymerizations. A reduced yield of polymer observed at conversions >10% in bulk polymerizations of MMA carried out in the presence of **1**−**4** can be attributed to the absence of the gel (Trommsdorff) effect. The results are interpreted in terms of the addition−fragmentation mechanism for chain transfer.

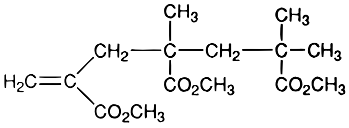
Introduction

Methyl methacrylate macromonomers of general structure (**4**) have recently become of importance as precursors to block[1−3] and graft copolymers[4−10] and as chain transfer agents.[2,11,12]

However, there are currently few quantitative data available on the chain transfer constants of macromonomers (**4**) in methyl methacrylate (MMA)[12−14] or other polymerizations or on the dependence of these parameters on macromonomer molecular weight or reaction temperature. In this work, we redress this deficiency by evaluating the chain transfer activities of dimer (**1**), trimer (**2**), tetramer (**3**), and a macromonomer (**4**, average $n = 23$) in MMA polymerization over a range of temperatures between 45 and 100 °C and develop further insights into the mechanism of addition−fragmentation chain transfer.



(**1**)



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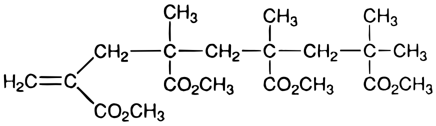

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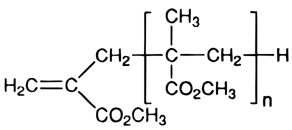

(**4**)

Experimental Section

Materials. MMA Dimer, Trimer, and Tetramer. Low molecular weight MMA oligomers were prepared by polymerizing MMA (1.5 L) in acetone (1.5 L), with 2,2′-azobisisobutyronitrile (AIBN) (1.50 g) as the initiator and (iPr)(H_2O)Co^{III}(DMG-BF$_2$)$_2$[15] (0.22 g) as the catalytic chain transfer agent.[16] The reaction was carried out at 72 °C for 4 h under nitrogen. The conversion of monomer was *ca.* 25%. Under these reaction conditions, it is necessary to keep conversion below 30% to avoid the formation of small amounts of an isomeric trimer with an internal double bond. Solvent and unreacted monomer were removed (rotary evaporator); pure MMA dimer and MMA trimer and a tetramer-rich fraction were isolated by fractional distillation under reduced pressure (0.03 mmHg). The pure *racemic* MMA tetramer was isolated from the tetramer fraction by chromatography on a silica gel column with petroleum ether (bp 30−40 °C):ethyl acetate (4:1) as eluent.

MMA Dimer (2,4-bis(methoxycarbonyl)-4-methylpent-1-ene)) (1): 156 g; bp 45−46 °C (0.03 mmHg); ^{1}H NMR (CDCl$_3$) δ 1.17, s, 6H, 2 × CH$_3$; 2.61, d, 2H, CH$_2$; 3.65, s, 3H, OCH$_3$; 3.73, s, 3H, OCH$_3$; 5.52, dd, 1H, and 6.22, dd, 1H, olefinic protons.

MMA Trimer (2,4,6-tris(methoxycarbonyl)-4,6-dimethylhept-1-ene) (2): 66 g; bp 100−102 °C (0.03 mmHg); ^{1}H NMR (CDCl$_3$) δ 1.00, s, 3H, 1.06, s, 3H, 1.18, s, 3H, 3 × CH$_3$; 2.09, dd, 2H, CH$_2$; 2.55, s, 2H, CH$_2$C=; 3.61, s, 3H, 3.65, s, 3H, 3.73, s, 3H, 3 × OCH$_3$; 5.50, dd, 1H, and 6.20, dd, 1H, olefinic protons.

Racemic MMA Tetramer (2,4,6,8-tetrakis(methoxycarbonyl)-4,6,8-trimethylnon-1-ene) (3): mp 51−55 °C; ^{1}H NMR (CDCl$_3$) δ 0.94, s, 3H, 0.97, s, 3H, 1.06, s, 3H, 1.15, s, 3H, 4 × CH$_3$; 1.90−2.20, m, 4H, 2 × CH$_2$; 2.51, s, 2H, CH$_2$C=; 3.60, s, 3H, 3.62, s, 3H, 3.64, s, 3H, 3.72, s, 3H, 4 × OCH$_3$; 5.48, 1H, and 6.20, 1H, olefinic protons.

MMA Macromonomer (4). MMA macromonomer was prepared by emulsion polymerization of MMA in the presence of a catalytic chain transfer agent, (Me)(H_2O)Co^{III}(DEG-BF$_2$)$_2$.[15,17]

A solution of 4,4′-azobis(cyanopentanoic acid) (280 mg) and sodium dodecyl sulfate (6 g of 10 wt % aqueous solution) in water (150 g) was degassed over 20 min and heated to 80 °C under nitrogen when a solution of (Me)(H_2O)Co^{III}(DEG-BF$_2$)$_2$ (7 mg) in MMA (7 g) was added in one shot. Further cobalt complex (3 mg) dissolved in MMA (63.4 g) was added over 90 min by syringe pump. The reaction temperature was then increased to 85 °C, and heating and stirring were continued for a further 90 min. The conversion of monomer was >90%. The resulting latex was freeze-dried and precipitated from chloroform into pentane, yielding a MMA macromonomer with $\bar{M}_n$ 2400 and $\bar{M}_w/\bar{M}_n$ 1.3. Dimer and trimer were not detectable in this sample by gel permeation chromatography (GPC) or NMR analysis.

Bulk Polymerizations. Sample Polymerization. Aliquots (1 mL) of a stock solution of AIBN in freshly distilled

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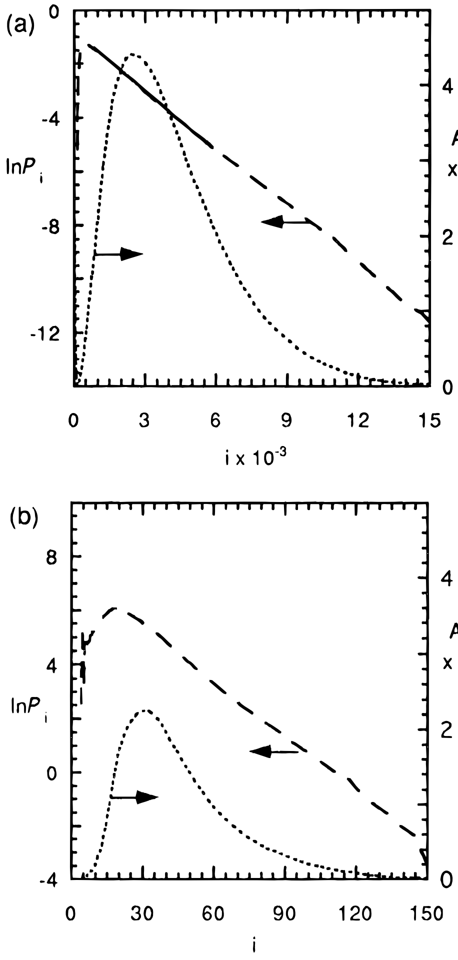


Figure 1. (a) GPC distribution (···) and ln chain length distribution (- - -) for MMA polymerization with [**4**] = 0.0259 M, [2,2′-azobis(2,4-dimethylpentanenitrile)] = 1.88 × 10^{-3} M at 45 °C (14% conversion). The solid line (—) denotes region over which ln CLD was fitted. (b) Expanded low molecular weight region (macromonomer peak).

Table 1. Chain Transfer Constants (C_T) for MMA Oligomers in Polymerizations of MMA Determined from the ln Chain Length Distribution[a]

temp (°C)	dimer	trimer	tetramer	macromonomer[b]
45	0.0124 ± 0.0007	0.168 ± 0.004	0.260 ± 0.005	0.185 ± 0.003
60	0.0125 ± 0.0011	0.188 ± 0.006	0.314 ± 0.036	0.207 ± 0.016
70			0.272 ± 0.019	
80	0.0157 ± 0.0003	0.188 ± 0.023	0.264 ± 0.018	0.218 ± 0.013
100	0.0182 ± 0.0020	0.187 ± 0.006	0.281 ± 0.013	0.248 ± 0.010

[a] Error ranges are 95% confidence intervals (2 × standard deviation of slope) [b] Fractionated oligomer, $\bar{M}_n$ 2400, $\bar{M}_w/\bar{M}_n$ 1.3

MMA (10.5 mg/10.00 mL) were added to preweighed quantities of transfer agent. After dissolution, the solutions were transferred to ampules, degassed using three freeze−pump−thaw cycles, and sealed under vacuum (<10^{-3} mmHg). The solutions were polymerized at 60 °C for 45 min. Samples of the monomer/polymer mixtures were diluted with tetrahydrofuran or chloroform-d_1 (for GPC or NMR analysis, respectively).

The initiator was selected according to the polymerization temperature (45 °C, 2,2′-azobis(2,4-dimethylpentanenitrile); 60−80 °C, AIBN; 100 °C, *tert*-butyl peroxybenzoate). Initiator concentrations [(0.1 − 5) × 10^{-3} mol/L] and polymerization times (30−180 min) were selected such that conversion of monomer to polymer was less than 10% and to allow adequate time for temperature equilibration. In these experiments, low conversions ensure that the results are not confused by the further reaction of the macromonomer formed by chain transfer.

^{1}H NMR spectra (Bruker AC200, 200 MHz) were obtained on the final reaction mixtures diluted with $CDCl_3$. The conversions were estimated from the relative intensities of the OCH_3 resonances for monomer and polymer (δ 3.7 and 3.5, respectively).

Molecular weight data were obtained by GPC (Waters Associates liquid chromatograph) equipped with differential refractometer and 10^6, 10^5, 10^4, 10^3, 500, and 100 Å Ultrastyragel columns. Tetrahydrofuran (flow rate of 1.0 mL/min) was used as eluent. The GPC was calibrated with narrow polydispersity poly(methyl methacrylate) standards. A third-order polynomial was used to fit the log *M vs* time calibration curve, which was linear across the molecular weight range from 2 × 10^2 to 2 × 10^6. Number molecular weight distributions were derived from the intensity-retention time data[18−20] which were processed using KaleidaGraph software on a Macintosh computer. A sample ln chain length distribution for a polymerization carried out with macromonomer **4** is shown in Figure 1.

Values of transfer constants were determined by analysis of the ln chain length distributions (ln CLD method, discussed below) and the conventional Mayo method are presented in Tables 1 and 2, respectively. Sample conversion and molecular weight and data are shown in Table 3. Complete data on conversion and molecular weight for polymerizations carried out in the presence of **1**−**4** over a range of concentrations and polymerization temperatures (45, 60, 70, 80, 100 °C) are available as Supporting Information (Tables 7−10). Polydispersities ($\bar{M}_w/\bar{M}_n$) as measured by conventional GPC analysis were typically in the range 1.7−1.9. In some sample sets a slight trend for narrowing of polydispersity with increasing transfer agent concentration was observed. This phenomenon has also been observed by other workers (*e.g.* in chain transfer studies of methyl α-substituted acrylates[21−23]) and might in part be attributed to problems associated with baseline definition during measurement of $\bar{M}_n$ by GPC.[20,24]

Molecular Orbital Calculations. Semiempirical molecular orbital calculations were performed using MNDO93 as implemented as part of the Unichem package (Cray Research, version 3.0.1) and the CSIRO Cray YMP-4E. The merits of using this methodology for calculations on free radical reactions have been discussed in an earlier paper.[25]

Results and Discussion

Determination of Chain Transfer Constants. In free-radical polymerization, chain transfer occurs in competition with normal monomer propagation. The proposed mechanism whereby methacrylate macromonomers (**4**) give chain transfer involves an addition−fragmentation sequence as shown in Scheme 1. According to this mechanism, the transfer constant depends

Table 2. Chain Transfer Constants (C_T) for MMA Oligomers in Polymerizations of MMA Determined by Use of a Traditional Mayo Plot[a,b]

temp (°C)	dimer	trimer	tetramer	macromonomer[c]
45	0.011 ± 0.001 (0.012)	0.14 ± 0.01 (0.17)	0.22 ± 0.01 (0.26)	0.15 ± 0.03 (0.18)
60	0.008 ± 0.002 (0.015)	0.20 ± 0.03 (0.19)	0.34 ± 0.03 (0.31)	0.14 ± 0.03 (0.20)
70			0.20 ± 0.02 (0.27)	
80	0.014 ± 0.002 (0.017)	0.17 ± 0.03 (0.18)	0.25 ± 0.01 (0.28)	0.16 ± 0.02 (0.23)
100	0.018 ± 0.002 (0.018)	0.16 ± 0.01 (0.19)	0.26 ± 0.01 (0.28)	0.20 ± 0.02 (0.25)

[a] Error ranges are 95% confidence intervals (2 × standard deviation of slope). [b] Numbers in parentheses are based on weight average molecular weights and an assumed polydispersity of 2.0.[24] [c] Fractionated oligomer, $\bar{M}_n$ = 2400, $\bar{M}_w/\bar{M}_n$ = 1.3

Scheme 1

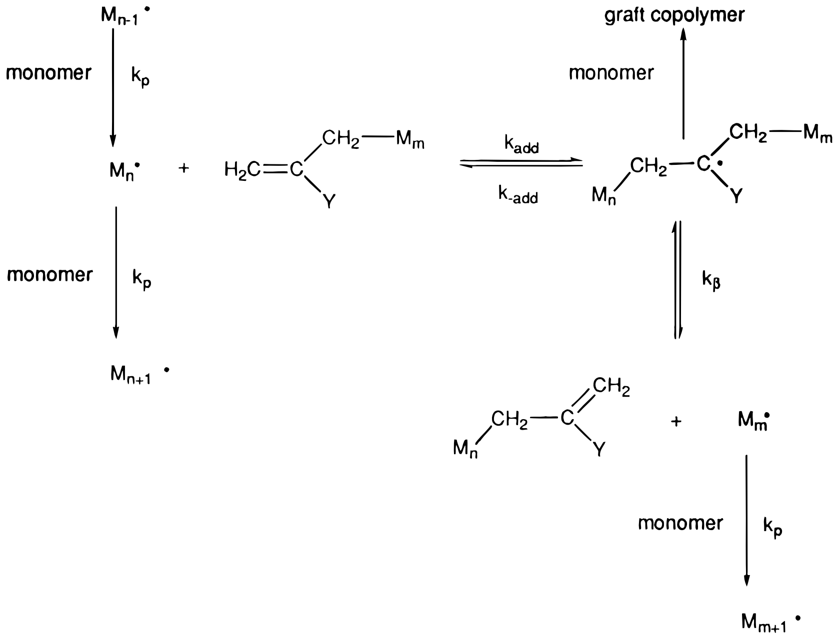


Table 3. Effect of Transfer Agent 2 (MMA Trimer) Concentration on Polymerization of MMA at 60 °C: Molecular Weights, Conversions, and Transfer Constants Calculated Therefrom

[T]/[M] ($\times 10^{3}$)	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$	−Slope[b] ($\times 10^3$)	conv (%)	C_T[c,d]	C_T[e]
0	415 600	1.87_4	0.262 ± 0.001	6.5	0.20_1	0.18_9
0	404 020	2.18_9	0.249 ± 0.001	6.6	(0.18_9)	
3.82	103 850	1.84_7	1.040 ± 0.011	6.8		
5.06	95 460	1.78_6	1.191 ± 0.013	4.9		
13.18	45 000	1.78_6	2.684 ± 0.022	5.3		
15.73	33 760	1.81_4	3.328 ± 0.017	7.4		
22.91	19 470	2.24_1	4.533 ± 0.030	4.9		

[a] Determined by GPC, calibrated with PMMA standards. Estimated error in $\bar{M}_n$ is ±5%. [b] Value of $-\mathrm{d}(\ln P_i)\mathrm{d}i$. Error ranges are 95% confidence intervals (2 × standard deviation of slope). [c] From traditional Mayo plot. [d] Numbers in parentheses are based on weight average molecular weights and an assumed polydispersity of 2.0.[24] [e] From ln chain length distribution plot.

on (a) the reactivity of the double bond and (b) the partitioning of the intermediate between products and starting materials. The effective rate constant for chain transfer (k_{tr}) is then given by the following expression (eq 1):

$$k_{tr} = k_{add}\frac{k_\beta}{k_{-add} + k_\beta} \tag{1}$$

where k_{add}, k_{-add}, and k_β are defined in Scheme 1.

The activity of transfer agents is usually defined in terms of their chain transfer constants ($C_T = k_{tr}/k_p$). Traditionally, chain transfer constants have been evaluated by applying the Mayo equation (eq 2).[26]

$$\frac{1}{\bar{X}_n} = C_T\frac{[T]}{[M]} + \frac{1}{\bar{X}_{n\o}} \tag{2}$$

where $\bar{X}_n$ is the number-average degree of polymerization, [T] and [M] are the concentrations of transfer agent and monomer, respectively, and $\bar{X}_{n\phi}$ is the number-average degree of polymerization obtained in the absence of added transfer agent.

Values of $\bar{X}_n$ are usually obtained by GPC analysis. We have shown that conventional GPC analysis is extremely sensitive even to minor baseline fluctuations (and any low molecular weight impurities). Moreover, it cannot be applied readily if the molecular weight distributions of the formed polymer and the chain transfer agent overlap.[20] This was envisioned as a potential problem in measuring transfer constants of higher molecular weight oligomers (**4**).

These problems led us to consider other methods for transfer constant measurement. Recently, Gilbert and co-workers[19,27−29] have advocated analysis of the ln chain length distribution in this context (ln CLD method), an approach also adopted by Hutchinson.[30] The chain length distribution can be easily obtained from the regular GPC distribution (as obtained with a differential refractometer).[18,31,32]

The method[19,27−29,33] is based on the use of eqs 3 and 4 for the measurement of chain transfer constants.

$$\lim_{i\to\infty,[I]\to 0} P_i \propto \exp\left\{-\frac{k_{tr,M}[M] + k_{tr,T}[T]}{k_p[M]}\right\}i \tag{3}$$

where P_i is the chain length distribution, $k_{tr,M}$ and $k_{tr,T}$ are the rate constants for chain transfer to monomer and transfer agent respectively, k_p is the propagation rate constant, and i is the chain length.

Under these limiting conditions,

$$\frac{\mathrm{d}\,(\ln P_i)}{\mathrm{d}i} = -\left\{C_M + C_T\frac{[T]}{[M]}\right\} \tag{4}$$

Equation 4 is similar in form to the Mayo equation (eq 2). As long as chain transfer to monomer ($C_M = k_{tr,M}/k_p$) is negligible, C_T can be evaluated from a plot of d(ln P_i)di (the slope of the ln chain length distribution) *vs* [T]/[M].

We have shown[20] that this approximation (eq 4) should hold for all i as long as termination is largely by disproportionation or chain transfer. Moreover, it was established that, if the value of d(ln P_i)di is taken over the region coinciding with the peak of the untransformed GPC distribution, the proportionality between

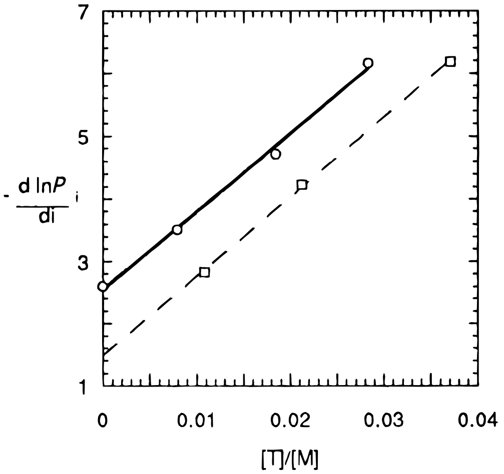


Figure 2. Plots of $-d(\ln P_i)di$ *vs* [T]/[M] for experiments carried out with MMA dimer (**1**) as transfer agent (T) at 60 °C and with [AIBN] = 6.4×10^{-3} (circles, —) and 0.63×10^{-3} M (squares, - - -) as initiator.

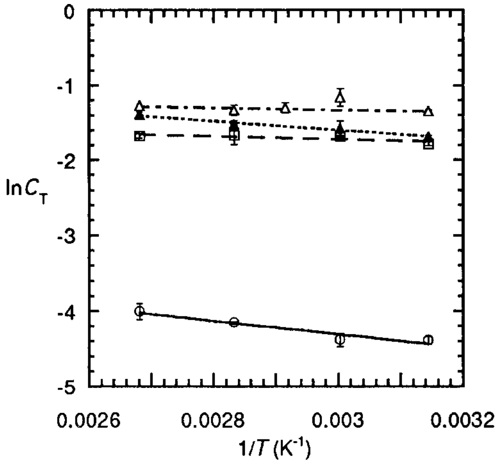


Figure 3. "Arrhenius plot" for transfer constants of MMA oligomers in MMA polymerizations: MMA dimer (**1**) (open circles, —), MMA trimer (**2**) (open squares, — — —), MMA tetramer (**3**) (open triangles, — • —), and MMA macromonomer (**4**) (closed triangles, - - -). Transfer constants were determined using the ln CLD method.

$d(\ln P_i)di$ and [T]/[M] is maintained even if termination in the absence of transfer agent is substantially by combination or baseline selection is imperfect (the latter two factors can give rise to curvature in the ln chain length distribution).[20] This also corresponds to the region of maximum signal-to-noise ratio. This modification to the original method is desirable for maximum accuracy and precision.[20]

In the present work, slopes of the chain length distribution were obtained by least squares regression analysis for the region corresponding to the top 80% of the GPC trace. The 95% confidence regions (two standard deviations) are typically less than ±0.5%, and always less than ±1% of the measured slope (see, for example, Table 3). This contrasts with a 95% confidence region in excess of ±5% for $\bar{X}_n$ values obtained by direct integration of GPC traces. Thus, unlike conventional methods of analysis, the accuracy of transfer constants is not limited by the precision of the molecular weight determination. The precision of the slopes ($d(\ln P_i)di$) is high compared with the small errors likely to be introduced through factors such as minor calibration drift, inaccuracies in making up solutions, and nonzero conversions. These factors are common to all methods of analysis.

Values of the transfer constants for **1**−**4** in MMA polymerizations obtained by applying the above-mentioned methods (the modified ln CLD method and the traditional Mayo plot) are shown in Tables 1 and 2. While discrepancies between values obtained by the two methods are small when considered in relation to the errors usually associated with transfer constant data, it is immediately evident, from the reduced scatter, that the data obtained by the ln CLD method (Table 1) are of higher precision. The scatter in the Mayo-plot data is such that the small temperature dependence of C_T (see below) cannot be reliably determined. Although repeated determinations of the molecular weights may reduce the scatter of the Mayo-plot data, this will not resolve the inaccuracies inherent with the use of GPC for $\bar{M}_n$ determination.[24] Such problems are demonstrably of lesser importance in the ln CLD method, which offers high-quality data without the need for further experiments.[20]

As a further check on the ln CLD method, one set of experiments (for dimer (**1**) at 60 °C) was carried out with two different concentrations of initiator ([AIBN] = 6.4×10^{-3} and 0.63×10^{-3} M). The results are summarized in Figure 2 (full details appear in Supporting Information, Table 7). It is clear that the value of the transfer constant is independent of the initiator concentration. These experiments serve to illustrate several points: (a) that transfer to initiator is not important under these experimental conditions (as is expected for AIBN) and (b) that the measured transfer constant is independent of the control molecular weight. The latter finding is in accord with the proposal that chain length-dependence of termination should not affect the application of the method (see the accompanying paper[20] for relevant discussion).

An "Arrhenius" plot of the transfer constants derived by use of the ln CLD method is shown in Figure 3. The transfer constant (C_T) for MMA dimer (**1**) has a small temperature dependence while those for the trimer (**2**) and tetramer (**3**) are independent of temperature. The transfer constant for the fractionated macromonomer (**4**) shows a small temperature dependence.

The Arrhenius relationships for the transfer constants are as follows (the errors quoted are two standard deviations):

$$C_T(\text{dimer}) = 10^{\{-0.71\pm0.45\}}\exp\left\{\frac{-7.41 \pm 2.94\ \text{kJ}\cdot\text{mol}^{-1}}{RT}\right\}$$

$$C_T(\text{trimer}) = 10^{\{-0.48\pm0.15\}}\exp\left\{\frac{-1.74 \pm 1.95\ \text{kJ}\cdot\text{mol}^{-1}}{RT}\right\}$$

$$C_T(\text{tetramer}) = 10^{\{-0.39\pm0.09\}}\exp\left\{\frac{-1.22 \pm 1.18\ \text{kJ}\cdot\text{mol}^{-1}}{RT}\right\}$$

$$C_T(\text{macromonomer}) = 10^{\{0.080\pm0.096\}}\exp\left\{\frac{-4.93 \pm 1.26\ \text{kJ}\cdot\text{mol}^{-1}}{RT}\right\}$$

The transfer constant for MMA dimer **1** at 60 °C (C_T = 0.013) is similar to that previously reported by Tanaka *et al.*[14] for an impure sample of MMA dimer (C_T = 0.01). The absolute value for C_T (macromonomer) is dependent on the precision of the molecular weight measurement (±5%).

The determination of $k_{tr}(=C_Tk_p)$ requires knowledge of k_p. The magnitude and temperature dependence of k_p for MMA polymerizations have been determined by a number of workers.[34−39] In this work, we have adopted the recently revised relationship proposed by Hutchinson *et al.*,[39] since that study covers a wide temperature range and is based on a relatively large number of data points:

$$k_p = 10^{\{6.380\pm0.048\}}\ \mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}} \times \exp\left\{\frac{-22.19 \pm 0.28\ \mathrm{kJ{\cdot}mol^{-1}}}{RT}\right\}$$

This leads to the derived Arrhenius relationships:

$$k_{tr}(\mathrm{dimer}) = 10^{\{5.557\pm0.448\}}\ \mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}} \times \exp\left\{\frac{-28.72 \pm 2.94\ \mathrm{kJ{\cdot}mol^{-1}}}{RT}\right\}$$

$$k_{tr}(\mathrm{trimer}) = 10^{\{5.792\pm0.297\}}\ \mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}} \times \exp\left\{\frac{-23.05 \pm 1.94\ \mathrm{kJ{\cdot}mol^{-1}}}{RT}\right\}$$

$$k_{tr}(\mathrm{tetramer}) = 10^{\{5.881\pm0.179\}}\ \mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}} \times \exp\left\{\frac{-22.53 \pm 1.18\ \mathrm{kJ{\cdot}mol^{-1}}}{RT}\right\}$$

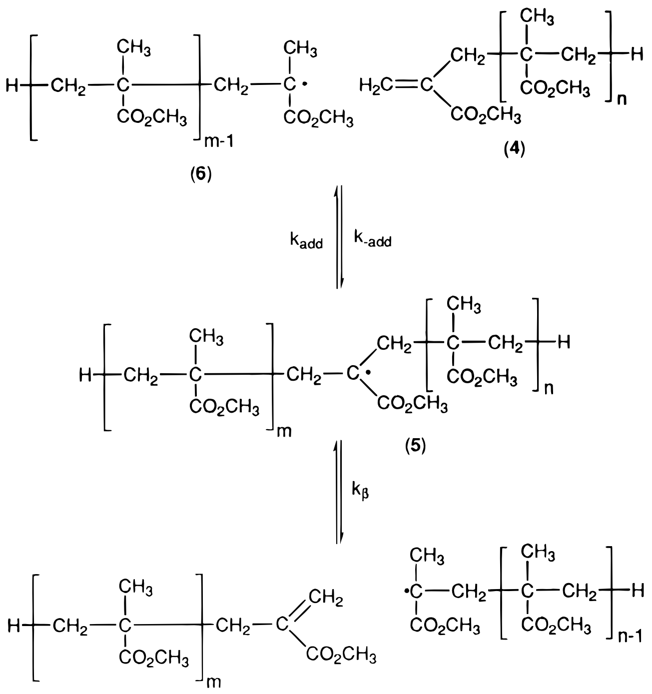
$$k_{tr}(\mathrm{macromonomer}) = 10^{\{6.347\pm0.192\}}\ \mathrm{L{\cdot}mol^{-1}{\cdot}s^{-1}} \times \exp\left\{\frac{-26.24 \pm 1.26\ \mathrm{kJ{\cdot}mol^{-1}}}{RT}\right\}$$

The value of the Arrhenius pre-exponential factor, *A*, for k_{tr}, shows a small increase with increasing size of the MMA macromonomer. The activation energies for k_{tr} with trimer (**2**) and tetramer (**3**) are close to that for k_p. Those for dimer and macromonomer are slightly higher. However, it must be emphasized that, since chain transfer occurs by an addition−fragmentation mechanism (Scheme 2), k_{tr} is a composite term (eq 1). The significance of these values is discussed further below.

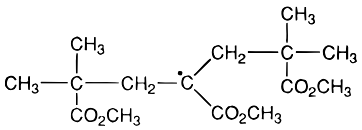
Transfer Efficiency, Retardation, Effects of Conversion. For efficient chain transfer, it is important that the lifetime of the intermediate (**5**; see Scheme 2) is short with respect to the lifetime of a MMA-propagating species (**6**) and that it does not undergo side reactions. Possible side reactions include reaction with monomer (copolymerization of macromonomer, see Scheme 1) and radical−radical reaction. Earlier work demonstrated that, while copolymerization of macromonomer is important with monosubstituted monomers, it does not occur in the case of methacrylate monomers and macromonomers (**4**).[5,6,9] This discovery has led to the chemistry shown in Scheme 1 being used as the basis of a new synthesis of narrow polydispersity block copolymers.[1]

Many workers have observed apparent retardation of polymerization when a chain transfer agent is added to a polymerizing medium.[40,41] This is manifested in a decreased conversion for a given polymerization time. Often this can be attributed to degradative chain transfer, resulting from the low reactivity toward reinitiation of a radical formed in the transfer step.[42,43] In the case of the MMA macromonomer transfer agents (**4**), where the product radical is a MMA-propagating species (**6**), there should be no retardation of this nature. Retardation may arise in addition−fragmentation chain transfer if the rate of fragmentation of the intermediate (*e.g.* **5**) is slow relative to the lifetime of a typical propagating species.

Scheme 2



In this context, it is noteworthy that Tanaka *et al.*[14,44] have described the radical (**7**) formed by addition of 2-carbomethoxy-2-propyl radicals to dimer (**1**) as persistent. A similar finding was made by Harrison,[12] who examined the reaction of 2-carbobutoxy-2-propyl radicals with dimer (**1**) by ESR spectroscopy. It appears that the 2-carboalkoxy-2-propyl radical is a relatively poor free radical leaving group with respect to corresponding oligomeric radicals.



(**7**)

The analogous intermediates (**5**) formed between propagating species and the dimer (**1**) are clearly not persistent. If this were the case, there would be retardation of polymerization, and this is not observed (see below). Nonetheless, the observation that the 2-carboalkoxy-2-propyl radical is a relatively poor free radical leaving group is consistent with the finding that the dimer (**1**) has a low transfer constant because the adduct formed (**5**) partitions preferentially to starting materials.

Degrees of conversion obtained in the transfer constant measurement experiments were determined from ^{1}H NMR analysis of the reaction mixtures. A representative set of conversion data, for the polymerization of MMA at 60 °C in the presence of various concentrations of MMA trimer (**3**), is presented in Table 3. Inspection of the conversion data reveals that the conversions of monomer to polymer (in the range

Table 4. Effect of Conversion on Molecular Weight and Apparent Chain Transfer Constant (Mayo Equation) for MMA Polymerizations at 60 °C with and without Transfer Agent 2 (MMA trimer)

time (min)	control			[trimer] = 0.167 M				
	$\bar{M}_n{}^c$	$\bar{M}_w/\bar{M}_n$	% conv	$\bar{M}_n{}^c$	$\bar{M}_w/\bar{M}_n$	% conv	$C_T{}^a$	$C_T{}^b$
45	364 740	1.91_9	5.9	28670	1.60_8	5.0	0.19	0.18
90	340 510	1.87_7	11.9	26400	1.82_5	10.2	0.20	0.19
135	391 310	1.97_8	23.5	25700	1.82_7	16.2	0.21	0.19
180	450 150	2.35_4	39.0	25340	1.81_4	18.8	0.22	0.19

[a] Transfer constant calculated using the Mayo equation (eq 2). [b] Transfer constant corrected for conversion using eq 5 (see the text and Appendix). [c] $\bar{M}_n$ determined from GPC calibrated with polystyrene standards.

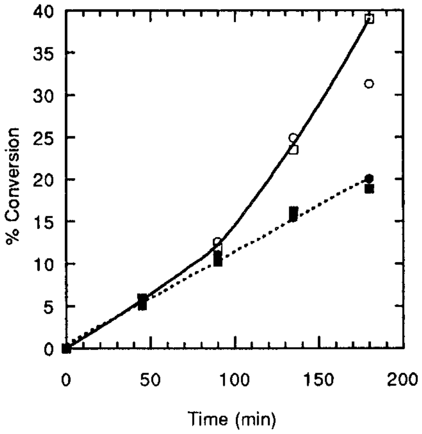


Figure 4. Conversion−time relationships for the polymerization of MMA at 60 °C showing the apparent "retardation" of polymerization in the presence of MMA dimer (**1**, squares) or MMA trimer (**2**, circles) as transfer agent. Polymerization in absence of transfer agent (open symbols, —); Polymerizations with transfer agent (closed symbols, - - -). [AIBN] = 6.40 × 10^{-3} M, [**1**] = 0.247 M, [**2**] 0.163 M.

5−10%, depending on the particular initiator concentration and reaction temperature) show no significant dependence on the concentration or molecular weight of the macromonomer chain transfer agent (**1**−**4**).

In order to more fully investigate the effect of transfer agent on conversion, a series of MMA polymerizations were carried out at 60 °C with the same initial concentration of transfer agent and varying reaction times. While the control experiments (without added transfer agent) show a conversion−time curve typical of bulk MMA polymerization,[45−47] the polymerizations with transfer agent [whether MMA dimer (**1**) or MMA trimer (**2**)] show a linear rate of polymerization with no acceleration over the conversion range examined. For low conversions (≤10%) the rates of polymerization (R_p) for samples with and without transfer agent are identical (see Table 4 and Figure 4).

It is clear that the reduced conversions for reaction times >90 min are not due to retardation. Rather, they are a consequence of the polymerization rate not accelerating. For bulk polymerizations of MMA, the existence of the Trommsdorff (or gel) effect is well-known.[48,49] Autoacceleration sets in at about 10−15% conversion (dependent on initiator concentration) and is accompanied by an increase in sample viscosity and instantaneous molecular weight, and there are corresponding changes in the molecular weight distribution.[45] The effect is attributed to a reduced rate of radical−radical termination. On the other hand, in the presence of chain transfer agent, autoacceleration is reduced or (as in the present example) eliminated, due to the reduction in molecular weight of the polymer formed (and sample viscosity).[50] The dominant termination mechanism is chain transfer.

Transfer constants obtained by direct application of the Mayo equation (eq 2) suggest that there is an increase in transfer constant with conversion (see Table 4). However, transfer constants determined in this way will be distorted by the variation in the relative concentrations of transfer agent and monomer with conversion. To overcome this problem, and investigate the possible conversion dependence of the transfer constant, it is necessary to use an integrated from of the Mayo equation.

Several workers have reported integrated forms of the Mayo equation suitable for calculating transfer constants at nonzero conversions.[41,51−56] Some of these are only applicable when the transfer agent is in vast excess or the transfer constant is small so that consumption of transfer agent can be neglected. The following integrated form of the Mayo equation (eq 5) is based on a treatment reported by Bamford for chain transfer in binary copolymerization.[57] The use of this expression has also been proposed by Harwood.[54] A derivation of this expression (not previously published) is presented in the Appendix.

$$\ln\left(1 - \frac{[\mathrm{M}]_\phi x}{[\mathrm{T}]_\phi}\left(\frac{1}{\bar{X}_\mathrm{n}} - \frac{1}{\bar{X}_{\mathrm{n}\phi}}\right)\right) = C_\mathrm{T} \ln(1 - x) \qquad (5)$$

where x is the fractional conversion of monomer to polymer.

Thus a plot of

$$\ln\left(1 - \frac{[\mathrm{M}]_\phi x}{[\mathrm{T}]_\phi}\left(\frac{1}{\bar{X}_\mathrm{n}} - \frac{1}{\bar{X}_{\mathrm{n}\phi}}\right)\right)$$

vs $\ln(1 - x)$ will yield C_T.

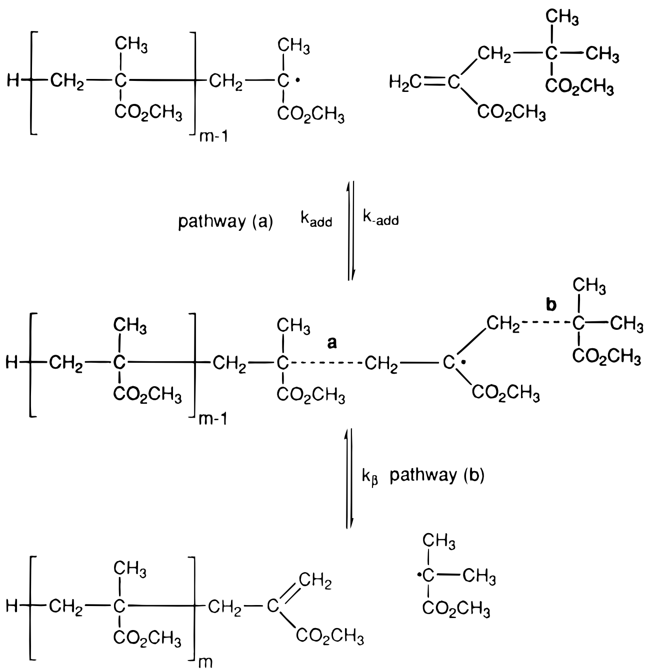
Application of this expression shows that the transfer constant remains constant with conversion for MMA trimer (see Table 4).

Kinetics and Mechanism of Chain Transfer. According to the proposed mechanism for chain transfer of methacrylate macromonomers by addition−fragmentation (Scheme 2), the rate constant for chain transfer is actually a composite term, comprised of several rate constants (k_{add}, k_β, and k_{-add}; see eq 1). The value of k_{tr} is thus determined both by the reactivity of the double bond and the partitioning of the radical intermediate **5**. On the basis of the finding that there is no retardation in polymerizations carried out in the presence of the macromonomer transfer agents (**1**−**4**, see above), we conclude that fragmentation is fast relative to addition (*i.e.* addition to the double bond is the rate-determining step in the transfer process).

Rate constants for addition of radicals to double bonds are controlled by a combination of steric, polar, and resonance terms.[58,59] Since differences between the oligomers are remote from the double bond, for the case of a MMA-propagating radical adding to a MMA macromonomer (**1**−**4**), the reactivity of the double bond for chain lengths greater than or equal to the dimer (**1**) might be anticipated to be largely independent of the macromonomer chain length.

Consistent with this hypothesis, it has been found[6,12] that the double bonds of dimer and trimer have approximately the same reactivity toward *tert*-butoxy radicals and are only *ca.* 2-fold less reactive than MMA monomer (relative reactivity of monomer:**1**:**2** = 1.0:0.6$_3$:

Scheme 3



0.5_6). The lesser reactivity of the macromonomers with respect to MMA monomer was attributed to the influence of steric factors. This trend in reactivity is also evident from the results of molecular orbital calculations (see below).

On the basis of these considerations, the MMA dimer (**1**) might be anticipated to have the same or even slightly greater reactivity (k_{add}) than the higher oligomers (**2**−**4**). However, MMA dimer (**1**) has a substantially lower transfer constant in MMA polymerization (see Table 1)!

The low transfer constant for dimer (**1**) with respect to higher oligomers (**2**−**4**) is therefore attributed to the radical intermediate (**5**) partitioning preferentially toward starting materials (see Scheme 3). The transfer constants can then be understood in terms of the influence of steric factors on the position of the equilibria involved.

A variety of factors are known to influence the specificity of radical fragmentation (and the reverse addition reactions).[59−62] These include radical polarity, radical delocalization, stereoelectronic effects, and steric factors. In the present case (see Scheme 3), the first two terms are expected to be more or less evenly balanced. Thus, steric effects are expected to play a dominant role in determining the preferred fragmentation pathway. In the fragmentation process, steric compression is relieved as the β-carbon (the incipient radical center) moves from tetrahedral (sp^3) hybridization to planar (sp^2) hybridization, thus allowing the attached (γ) substituents to move further apart from each other. For the case of an adduct to the dimer (cf. Scheme 3), the steric repulsion between the two methyl groups and the carbomethoxy substituent (pathway a) is less than that among a methyl group, a polymer chain, and a carbomethoxy substituent (pathway b). Hence, pathway b should be favored, as is observed. These effects should be reflected in both the enthalpy (see MO calculations section below) and entropy of activation for the fragmentation reaction. Other experimental studies of rates of fragmentation of radicals[63,64] and neutral molecules[25,65] generally lend support to the view that steric factors are important in determining the selectivity (although rigorous separation of the relative influences of steric, polar, and radical stability terms is not always possible since, in many cases, all operate to favor the same outcome). Steric factors are also of demonstrated importance in the reverse addition process.[59−62,65] They are thought to be largely responsible for the chain length dependence of propagation for the first few addition steps[66,67] and the lower ceiling temperatures and propagation rate constants observed for polymerizations of α-substituted vinyl monomers with respect to those for analogous vinyl monomers.[68−70]

On the basis of these considerations, the adducts to MMA dimer (**1**) are expected to partition heavily in favor of the starting materials. As the molecular size of the macromonomer increases, the difference in bulkiness between the starting and the product radicals diminishes (both are MMA-propagating species) and for longer chain macromonomers (≥tetramer) the partitioning would be expected to be equal. Under these circumstances ($k_{-add} = k_\beta$), the maximum value for the transfer constant to macromonomer is

$$C_T = 0.5k_{add}/k_p \qquad (6)$$

Thus the finding that the transfer constants for **2**−**4** are in the range 0.2−0.3 (see Table 1) suggests that the double bond reactivities of the macromonomers toward the MMA-propagating radical are 40−60% of MMA monomer. This finding indicates that the relative reactivity of the MMA macromonomers toward MMA-propagating radicals is similar to their reactivity toward *tert*-butoxy radicals (see above).

That partitioning of the intermediate is the most important factor in determining the apparent transfer constant of macromonomers (**4**) is also reflected in the temperature dependence of the transfer constant. Only the transfer constant for dimer (**2**) shows any significant temperature dependence. The transfer constant increases from 0.012 at 45 °C to 0.018 at 100 °C (see Table 1). This can be understood in terms of there being less specificity in the way the intermediate (**5**) partitions at higher temperatures. The transfer constants for trimer (**2**) and tetramer (**3**) do not show any significant temperature dependence.

On the basis of the considerations discussed above, the value for k_{add} should show no substantial dependence on chain length. If the values of k_{add} for (**1**−**3**) are assumed to be the same, it is then possible to estimate values of k_{-add} for dimer, trimer, and tetramer as follows.

If k_{-add}(tetramer) = k_β, it follows from eq 1 that

$$\begin{aligned} k_{add} &= 2k_{tr}(\text{tetramer}) \\ &= 10^{6.18}\ \text{L·mol}^{-1}\text{·s}^{-1} \exp\left\{\frac{-22.53\ \text{kJ·mol}^{-1}}{RT}\right\} \end{aligned}$$

Thus, if k_{add} is independent of chain length:

$$k_{-add}(\text{dimer}) = 10^{0.57} \exp\left\{\frac{6.45\ \text{kJ·mol}^{-1}}{RT}\right\} k_\beta$$

$$k_{-add}(\text{trimer}) = 10^{0.17} \exp\left\{\frac{0.80\ \text{kJ·mol}^{-1}}{RT}\right\} k_\beta$$

These rate constants have been used in kinetic simulations of polymerization processes involving methacrylate macromonomers. Since retardation is not

Table 5. Calculated Heats of Formation of 4−6 (kJ mol^{-1})[a]

	ΔH_f			
n or *m*	**4** ($n-1$)	**6** (m)	**5** (n, $m = 1$)	**5** (n, $m = 22$)
1	−320.6	−344.5	−1121.4	−1499.8
2	−714.6	−736.7	−1499.8	−1875.3
3	−1096.3	−1119.0	−1875.7	−2255.0
4	−1476.4	−1499.0	−2256.3	
5	−1854.8	−1877.8		
6	−2234.5	−2257.1		

[a] Results of AM1 calculations.

discernible over the concentration range used in the current experiments, we can place a lower limit on the value of k_β. Values of k_β significantly less than 1×10^3 s^{-1} lead to retarded polymerization rates; thus, for dimer (**1**), $k_\beta \geq 1 \times 10^3$ s^{-1}.

The value of k_{tr}(macromonomer) is slightly less than k_{tr}(tetramer), and k_{tr}(macromonomer) also shows a small temperature dependence. For the high molecular weight species, it seems unlikely that k_{-add}(macromonomer) ≠ k_β. The relative magnitude and temperature dependence of k_{tr}(macromonomer) are therefore attributed to corresponding changes in the value of k_{add}. This may be due to the addition step being limited by diffusion or segmental reorganization. It should be noted that the rate of translational diffusion for the macromonomer transfer agent in dilute solution (low conversion) should be orders of magnitude more rapid than k_{add}.[71]

The observation of a temperature dependence for k_{tr}(macromonomer) suggests that the use of higher polymerization temperatures may be beneficial in syntheses of block and narrow polydispersity polymers based on methacrylate monomers.[1]

Molecular Orbital Calculations. Steric factors may be responsible for the intermediate (**5**) formed by addition to dimer (**1**) partitioning to favor reformation of MMA dimer (by cleavage of bond b; cf. Scheme 3) over formation of a higher macromonomer and a monomeric MMA radical (by cleavage of bond a). In this case, it might be anticipated that this may in part be reflected in differences in the strengths of the two bonds (a and b) and in the heats of reaction for the two pathways.

In order to test this hypothesis, we have carried out semiempirical molecular orbital calculations with the AM1 method (UHF for radical species) to predict the heats of reaction for the two reaction pathways. Calculations were carried out for species with the PMMA chain(s) in a syndiotactic configuration and with the ester group at the radical center staggered with respect to ester groups in the neighboring MMA units. Full geometry minimizations were performed on these structures. The calculated heats of formation for reactants and products are summarized in Table 5.

The heats of reaction for fragmentation of intermediates (**5**) indicate that, for those with either n or $m = 1$ (this corresponds to an adduct of dimer **1**), cleavage to form the higher molecular weight propagating species is favored over formation of monomeric radical by >10 kJ mol^{-1} (see Table 6). For intermediates (**5**) with n and $m \geq 2$ (adducts of trimer and above), the two fragmentation pathways appear to be equally favored (difference in $\Delta H_r < 2$ kJ mol^{-1}).

Heats of reaction for addition of mono-, di-, and trimeric MMA-propagating species to MMA and MMA macromonomers can also be calculated from the heat of formation data presented in Table 5. Such calculations indicate that addition to monomer should be favored over addition to macromonomer, and addition to dimer may be slightly favored over addition to trimer. However, the calculated energy differences are small with respect to the precision of the calculations.

Table 6. Calculated Heats of Reaction for Fragmentation of Adducts (5)[a]

reaction	ΔH_r (kJ mol^{-1})
5 ($n = 1$, $m = 1$) → **1** + **6** ($m = 1$)	−62.4
5 ($n = 1$, $m = 2$) → **1** + **6** ($m = 2$)	−48.6
5 ($n = 1$, $m = 2$) → **2** + **6** ($m = 1$)	−59.0
5 ($n = 1$, $m = 3$) → **1** + **6** ($m = 3$)	−42.3
5 ($n = 1$, $m = 3$) → **3** + **6** ($m = 1$)	−54.8
5 ($n = 2$, $m = 2$) → **2** + **6** ($m = 2$)	−42.3
5 ($n = 1$, $m = 4$) → **1** + **6** ($m = 4$)	−42.7
5 ($n = 1$, $m = 4$) → **4** + **6** ($m = 1$)	−56.9
5 ($n = 2$, $m = 3$) → **2** + **6** ($m = 3$)	−39.8
5 ($n = 2$, $m = 3$) → **3** + **6** ($m = 2$)	−41.9

[a] Calculated from heats of formations given in Table 5.

These results are in accord with the proposal that partitioning of the intermediate (**5**) is the most important factor in determining transfer constants.

Conclusions

Transfer constants for several MMA macromonomers (**1**−**4**) in MMA polymerizations have been determined. It has been established that use of the ln CLD method results in transfer constants that are more consistent and precise than values obtained by conventional Mayo analysis. Arrhenius relationships for the chain transfer process have also been established by examining the temperature dependence of the transfer constants over the temperature range 45−100 °C. The transfer constant for MMA dimer (**1**) shows a significant variation with temperature and has a transfer constant which is an order of magnitude lower than the higher macromonomers (**2**−**4**). The transfer constants for MMA trimer and tetramer show no discernible temperature dependence. The kinetic results have been considered in terms of the addition−fragmentation mechanism for chain transfer. It is proposed that the reactivity of the macromonomer (40−60% that of MMA monomer) is essentially independent of molecular weight and that the partitioning of the intermediate (**5**) between starting material and products is the most important factor in determining the observed differences in the transfer constant values.

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Supporting Information Available: Tables 7−10 containing detailed molecular weight and conversion data, and the transfer constants calculated therefrom, for MMA dimer (**1**), trimer (**2**), tetramer (**3**) and macromonomer (**4**) in MMA polymerizations at temperatures from 45−100 °C are available as supporting material (4 pages). Ordering information is given on any current masthead page.

Appendix

Since the rate of transfer agent and monomer consumption are respectively, $d[T]/dt = k_{tr}[T][P\bullet]$ and $d[M]/dt = k_p[M][P\bullet]$, we can write

$$\frac{d[T]}{d[M]} = \frac{k_{tr}[T]}{k_p[M]} = C_T\frac{[T]}{[M]}$$

where C_T is the transfer constant. This can be rearranged to give 1/[T] dt = C_T[M] d[M] and integrated with respect to the transfer agent and monomer concentrations to yield the following expression:

$$\ln\left(\frac{[T]}{[T]_\phi}\right) = C_T \ln\left(\frac{[M]}{[M]_\phi}\right) \tag{A-1}$$

Thus

$$\frac{[T]}{[T]_\phi} = \left(\frac{[M]}{[M]_\phi}\right)^{C_T} \tag{A-2}$$

which can be rearranged to provide an expression for [T], the transfer agent concentration at time t.

$$[T] = [T]_\phi\left(\frac{[M]}{[M]_\phi}\right)^{C_T} \tag{A-3}$$

i.e.

$$[T] = [T]_\phi(1 - x)^{C_T} \tag{A-4}$$

where x is the fractional conversion of monomer to polymer.

The degree of polymerization can be equated with the number of chain started divided by the amount of monomer used (this assumes termination by disproportionation and no transfer to monomer or species other than the transfer agent):

$$\frac{1}{\bar{X}_n} = \frac{[T]_\phi - [T] + [I]_\phi - [I]}{[M]_\phi - [M]} = \frac{[T]_\phi - [T]}{[M]_\phi - [M]} + \frac{1}{\bar{X}_{n\phi}} \tag{A-5}$$

thus

$$\frac{1}{\bar{X}_n} - \frac{1}{\bar{X}_{n\phi}} = \frac{[T]_\phi - [T]}{[M]_\phi - [M]} \tag{A-6}$$

Substitution for [T] (eq A-4) gives

$$\frac{1}{\bar{X}_n} - \frac{1}{\bar{X}_{n\phi}} = \frac{[T]_\phi - [T]_\phi\left(\frac{[M]}{[M]_\phi}\right)^{C_T}}{[M]_\phi - [M]} \tag{A-7}$$

or

$$\frac{1}{\bar{X}_n} - \frac{1}{\bar{X}_{n\phi}} = \frac{[T]_\phi\left(1 - \left(\frac{[M]}{[M]_\phi}\right)^{C_T}\right)}{[M]_\phi\left(1 - \frac{[M]}{[M]_\phi}\right)} \tag{A-8}$$

substitution of 1-x for $[M]/[M]_\phi$ gives

$$\frac{1}{\bar{X}_n} - \frac{1}{\bar{X}_{n\phi}} = \frac{[T]_\phi\,(1 - (1 - x)^{C_T})}{[M]_\phi x} \tag{A-9}$$

which can be rearranged to

$$1 - \frac{[M]_\phi x}{[T]_\phi}\left(\frac{1}{\bar{X}_n} - \frac{1}{\bar{X}_{n\phi}}\right) = (1 - x)^{C_T} \tag{A-10}$$

or

$$\ln\left(1 - \frac{[M]_\phi x}{[T]_\phi}\left(\frac{1}{\bar{X}_n} - \frac{1}{\bar{X}_{n\phi}}\right)\right) = C_T \ln(1 - x) \tag{A-11}$$

Thus a plot of

$$\ln\left(1 - \frac{[M]_\phi x}{[T]_\phi}\left(\frac{1}{\bar{X}_n} - \frac{1}{\bar{X}_{n\phi}}\right)\right)$$

vs ln (1 − x) should yield a straight line passing through the origin with slope C_T.

This method is highly dependent on the precision of the conversion measurements since errors in conversions are magnified in C_T. Bamford has reported the derivation of a similar equation for copolymerization.[57]

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