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# Investigation of the Penultimate Unit Effect in Halogen Atom Chain Transfer in Free Radical Copolymerization

**Simon Harrisson, Heidi Kapfenstein-Doak, and Thomas P. Davis***

*Centre for Advanced Macromolecular Design, School of Chemical Engineering and Industrial Chemistry, The University of New South Wales, Sydney, NSW 2052, Australia*

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ABSTRACT: Chain transfer constants to carbon tetrachloride ($CCl_4$) and carbon tetrabromide ($CBr_4$) were measured for the STY−MMA copolymerization system at 40, 50, and 60 °C, and Arrhenius parameters were determined across this range of temperatures. A value for $C_S$ of $CBr_4$ in STY ($2.8 \times 10^2$) was determined using Bamford's moderated copolymerization method. The chain transfer constants obtained were fitted to a terminal model and a penultimate unit effect (PUE) model, of which only the PUE model provided a realistic fit to the data. The chain transfer reaction of STY−STY-terminated radicals to $CCl_4$ at 60 °C was found to be 3.3 times faster than that of MMA−STY-terminated radicals. With $CBr_4$ at the same temperature, STY−STY-terminated radicals reacted 9.4 times faster than MMA−STY-terminated radicals. Subsequently, the effect of temperature on the PUE was quantified. Additional experiments on $CCl_4$ were performed using dimethylformamide (DMF) as solvent. These experiments showed an increase in the magnitude of both the chain transfer constants and the PUE in DMF compared to the bulk experiments (from a factor of 3.3−7.2 times faster), suggesting the involvement of a polar transition state in transfer to $CCl_4$ and a polar contribution to the penultimate unit effect. We also discuss the effect that polar stabilization may have in atom transfer radical polymerization.

## Introduction

Much work[1−15] has been carried out to investigate the existence and nature of penultimate unit effects (PUEs) in copolymerization. Most of this work has focused on the PUE in the propagation step. Bamford and coworkers[1−5] investigated chain transfer in copolymer systems using a technique they termed "moderated copolymerization". From experiments with $CBr_4$, a PUE in the chain transfer step of styrene-terminated radicals in methyl methacrylate (MMA)/styrene (STY) copolymerization was proposed. This was assumed to be caused mainly by entropic effects due to steric interactions between the incoming $CBr_4$ molecule and the $\gamma$-methyl group (from the penultimate MMA unit). More recently, chain transfer to 1-dodecanethiol in butyl acrylate−methyl methacrylate copolymerization has been investigated, with uncertain results.[6]

In recent times, the cause of the PUE has been the subject of much debate. Fukuda and co-workers[7−9] initially proposed that radical stabilization was the origin of the PUE and that the penultimate unit affected the reactivity but not the selectivity of the radical. In other words, the PUE was independent of the type of incoming monomer unit and depended only on the radical chain end type. This idea was used to explain the ability of the terminal model equations to describe the copolymer composition but not the propagation rate.

Bamford[5] disagreed with this idea, claiming that the moderated copolymerization experiments indicated that the PUE had steric origins, and thus both the radical chain end type and the incoming monomer contributed to the effect.

Coote and co-workers[10−15] have recently demonstrated that polar effects may play an important role in the PUE. If true, this would also suggest that both the radical chain end and the incoming monomer are important in determining the extent of the PUE.

Bamford's work with carbon tetrabromide was hampered by several factors. First, the equipment available for measuring molecular weights was significantly less advanced than that available today, with the advent of reliable gel permeation chromatography. Second, the use of carbon tetrabromide as a chain transfer agent is problematic due to its very high rate of transfer to styrene and the consequent difficulties in obtaining an accurate value for the chain transfer constant. Finally, at the time the experiments were carried out, it was assumed that the terminal model was an adequate representation of $\langle k_p \rangle$ in copolymerization. It is now evident that this is not correct and therefore that the PUE on transfer reactions as measured by Bamford necessarily requires amendment.

Further investigations into the PUE in halogen atom transfers would be useful, however, in light of the recent discovery of atom transfer radical polymerization (ATRP).[16] Halogen atom transfer reactions are a fundamental feature of this technique; hence, a deeper understanding of the processes involved will be essential in order to apply ATRP effectively to copolymerizations.

The effect of a chain transfer agent on the molecular weight of a polymer is quantitatively determined by the Mayo equation (eq 1),[17,18] which expresses the reciprocal of the number-average degree of polymerization ($DP_n$) as a function of the rates of chain propagation and termination:

$$\frac{1}{DP_n} = \frac{(1+\lambda)\langle k_t \rangle [R^\bullet]}{k_p[M]} + C_M + C_S\frac{[S]}{[M]} \qquad (1)$$

In this equation, $\lambda$ is the fraction of termination by disproportionation, $\langle k_t \rangle$ the average termination rate coefficient, $[R^\bullet]$ the overall radical concentration, [M] the monomer concentration, and [S] the concentration of chain transfer agent. $C_S$ and $C_M$ represent the ratio of the chain transfer and propagation rate coefficients ($k_{tr}/k_p$) to chain transfer agent, S, and monomer, M, respectively. Hence, $C_S$ may be determined from a plot of $DP_n^{-1}$ vs [S]/[M], known as a Mayo plot.

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The Mayo equation can be extended to the case of copolymerization in a similar manner. If terminal kinetics are assumed (i.e., penultimate and antepenultimate units have no effect on the kinetics of either propagation or transfer), eq 2 is obtained:[1]

$$\frac{1}{\mathrm{DP_n}} = \frac{1}{\mathrm{DP_n^0}} + \frac{[\mathrm{S}]}{[\mathrm{A+B}]}\,\frac{r_\mathrm{A}C_\mathrm{S}^\mathrm{A}f_\mathrm{A} + r_\mathrm{B}C_\mathrm{S}^\mathrm{B}f_\mathrm{B}}{r_\mathrm{A}f_\mathrm{A}^{\,2} + 2f_\mathrm{A}f_\mathrm{B} + r_\mathrm{B}f_\mathrm{B}^{\,2}} \qquad (2)$$

In this equation, $\mathrm{DP_n^0}$ represents the degree of polymerization obtained in the absence of additional chain transfer agent, S. This term is equivalent to the sum of the first two terms on the right-hand side of eq 1. $C_\mathrm{S}^\mathrm{A}$, $C_\mathrm{S}^\mathrm{B}$, $r_\mathrm{A}$, $r_\mathrm{B}$, $f_\mathrm{A}$, and $f_\mathrm{B}$ represent the chain transfer coefficients (to S), reactivity ratios, and mole fractions of the comonomers A and B, respectively. The total monomer concentration is denoted by [A + B]. At any constant comonomer composition, an apparent chain transfer constant, $\langle C_\mathrm{S}\rangle$, may be determined from a plot of $\mathrm{DP_n}^{-1}$ vs [S]/[A + B], given by eq 3 (assuming terminal kinetics):

$$\langle C_\mathrm{S}\rangle = \frac{r_\mathrm{A}C_\mathrm{S}^\mathrm{A}f_\mathrm{A} + r_\mathrm{B}C_\mathrm{S}^\mathrm{B}f_\mathrm{B}}{r_\mathrm{A}f_\mathrm{A}^{\,2} + 2f_\mathrm{A}f_\mathrm{B} + r_\mathrm{B}f_\mathrm{B}^{\,2}} \qquad (3)$$

An identical equation is obtained if an implicit penultimate unit effect is assumed, as in such a case the stabilization afforded by the penultimate unit is independent of the coreagent. This means that the penultimate unit effect will be identical on both propagation and transfer reactions. Thus,

$$C_\mathrm{S}^\mathrm{AA} = \frac{k_\mathrm{AA,S}}{k_\mathrm{AAA}} = \frac{\alpha k_\mathrm{BA,S}}{\alpha k_\mathrm{BAA}} = C_\mathrm{S}^\mathrm{BA} = C_\mathrm{S}^\mathrm{A} \qquad (4)$$

where $k_\mathrm{XX,S}$ (X = A, B) represents the rate coefficient of transfer from a radical with terminal units XX, $k_\mathrm{XXX}$ represents that radical's rate coefficient of propagation, and $\alpha = 1/s_\mathrm{A}$, the reciprocal of the radical reactivity ratio:

$$\alpha = 1/s_\mathrm{A} = \frac{k_\mathrm{AAA}}{k_\mathrm{BAA}} \qquad (5)$$

Hence, if the theoretical foundation of the implicit PUE model is justified, eq 3 should accurately describe the variation of the apparent chain transfer constant, $\langle C_\mathrm{S}\rangle$, with the comonomer composition.

When chain termination occurs exclusively by chain transfer or disproportionation, the length of the dead polymer will coincide with the length of the growing radicals at the time of their termination. This produces a "most probable" distribution of molecular weights, with $M_\mathrm{w}/M_\mathrm{n}$ equal to 2.[21] For this reason, in a polymerization in which chain termination is dominated by transfer, $2\mathrm{DP_w}^{-1}$ (where $\mathrm{DP_w}$, the weight-average degree of polymerization, is equal to $M_\mathrm{w}/m_0$, $m_0$ being the molecular weight of the polymer repeat unit) may be substituted for $\mathrm{DP_n}^{-1}$ in eqs 1 and 2. This has been shown[22] to improve the accuracy of $C_\mathrm{S}$ determinations, as $M_\mathrm{w}$ is much less sensitive to errors in analysis of the size exclusion chromatogram than $M_\mathrm{n}$.

A further refinement may be made to the Mayo equation in cases where rapid consumption of the chain transfer agent must be taken into account. In such cases, eq 6 may be used to compensate for the changing chain transfer agent concentration:[2]

$$C_\mathrm{S} = \ln\left[1 - \frac{\Delta(\mathrm{A+B})}{[\mathrm{S}]_0}\left(\frac{2}{\mathrm{DP_w}} - \frac{2}{\mathrm{DP_w^0}}\right)\right] \qquad (6)$$

In this equation, Δ(A + B) represents the total change in monomer concentration, and $[\mathrm{S}]_0$ is the initial concentration of chain transfer agent.

This work was inspired by the investigations into copolymerizations carried out many years ago by Bamford and co-workers.[1-5] In the intervening years there has been a paradigm shift in our understanding of copolymerization kinetics. This has come from the work of Fukuda[7-9] and Davis et al.[10-15] It is now evident that PUEs play a major role in copolymerization propagation reactions and that both entropic and enthalpic factors are important in determining the magnitude of these effects. It is highly likely that there is a PUE on chain transfer, and it is now possible (for the first time) to separate this from the effect on the propagation reaction, since accurate $\langle k_\mathrm{p}\rangle$ data are readily available from the pulsed laser polymerization technique.[19]

The MMA−STY−$\mathrm{CX_4}$ (X = Cl, Br) systems are ideal subjects for these experiments, as there are abundant data on the reactivity ratios and $\langle k_\mathrm{p}\rangle$ values of MMA−STY, the "fruit fly" of copolymerizations. STY-terminated radicals are far more reactive than MMA-terminated radicals toward both carbon tetrahalides, which means that in almost all cases reactions of MMA-terminated radicals with $\mathrm{CX_4}$ have a negligible effect on the kinetics. This causes a substantial reduction in the number of parameters necessary to model the system and allows the determination of penultimate unit effects on STY-terminated radicals without interference from effects by radicals with MMA end groups. In addition, any polar effects on the PUE on transfer should be easier to observe, due to the strong electron-withdrawing character of the $\mathrm{CX_3}$ moiety (X = Cl, Br).

Thus, the goals of this paper are to probe the origin of the PUE using the MMA−STY−$\mathrm{CX_4}$ systems and thereby investigate the validity of the assumption of substrate independence inherent in the implicit PUE model.

## Experimental Procedures

**Materials.** MMA (Aldrich, 99%) and STY (Aldrich, 99%) were passed through a column of basic alumina to remove the inhibitor (10−100 ppm hydroquinone monomethyl ether) before use. AIBN was recrystallized from methanol. $\mathrm{CCl_4}$ (Aldrich, 99%) and $\mathrm{CBr_4}$ (Aldrich, 99%) were used as received.

**Equipment.** Molecular weight distributions were determined by size exclusion chromatography using a GBC Instruments LC1120 HPLC pump, a Shimadzu SIL-10A autoinjector, a column set consisting of a Polymer Laboratories 3.0 μm bead-size guard column (50 × 7.5 mm) followed by four linear PL columns ($10^6$, $10^5$, $10^4$, and $10^3$), and a VISCOTEK dual detector model 250 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) (Polymer Laboratories, molecular weight range 200−1.6 × $10^6$ g $\mathrm{mol^{-1}}$) and polystyrene standards (Polymer Laboratories, range 1250−9.8 × $10^5$ g $\mathrm{mol^{-1}}$). Molecular weight distribution analysis of the samples was performed using PL software. $^1$H NMR spectra were obtained using a Bruker 200 MHz spectrometer with $\mathrm{CDCl_3}$ as solvent at room temperature.

**Polymerizations with $\mathrm{CCl_4}$ as the Chain Transfer Agent. Typical Example.** A stock solution of MMA (30.0 g,

**Table 1. Experimental Details, Transfer to $CCl_4$ in STY−MMA Copolymerization, $f_{STY} = 0.662$**

| stock soln (g) | AIBN (mg) | $CCl_4$ (g) | $[CCl_4]$/[M] | time (min) | conv (%) | $M_n$ ($\times 10^3$) | $M_w$ ($\times 10^3$) | PDI |
|---|---|---|---|---|---|---|---|---|
| 9.042 | 9.6 | 0.000 | 0.00 | 120 | 3.91 | 110.8 | 214.9 | 1.94 |
| 8.023 | 9.8 | 2.097 | 0.17 | 120 | 3.97 | 65.0 | 121.8 | 1.88 |
| 7.043 | 9.1 | 3.035 | 0.29 | 120 | 3.87 | 51.7 | 101.2 | 1.96 |
| 6.007 | 8.8 | 4.046 | 0.45 | 120 | 3.78 | 30.9 | 73.4 | 2.37 |
| 5.050 | 8.2 | 5.003 | 0.66 | 120 | 3.68 | 28.1 | 60.8 | 2.16 |
| 9.021 | 9.4 | 0.000 | 0.00 | 120 | 3.87 | 116.5 | 221.6 | 1.90 |
| 8.058 | 10.0 | 2.058 | 0.17 | 120 | 4.05 | 53.0 | 124.1 | 2.34 |
| 7.026 | 9.3 | 3.046 | 0.29 | 120 | 3.99 | 39.9 | 98.3 | 2.46 |
| 6.018 | 9.0 | 4.117 | 0.46 | 120 | 3.94 | 34.6 | 71.0 | 2.05 |
| 5.030 | 8.2 | 5.044 | 0.67 | 120 | 3.70 | 26.7 | 57.7 | 2.16 |

**Table 2. Experimental Details, Transfer to $CBr_4$ in STY−MMA Copolymerization, $f_{STY} = 0.103$**

| stock soln (g) | $CBr_4$ (mg) | $[CBr_4]$/[M] ($\times 10^3$) | time (min) | conv (%) | $M_n$ ($\times 10^3$) | $M_w$ ($\times 10^3$) | PDI |
|---|---|---|---|---|---|---|---|
| 8.417 | 0.0 | 0.00 | 60 | 2.05 | 590.5 | 772.1 | 1.31 |
| 8.656 | 0.0 | 0.00 | 60 | 2.10 | 650.4 | 761.1 | 1.17 |
| 8.404 | 1.6 | 0.06 | 60 | 1.87 | 185.9 | 272.0 | 1.46 |
| 8.410 | 1.4 | 0.05 | 60 | 1.99 | 188.3 | 281.3 | 1.49 |
| 8.403 | 3.6 | 0.13 | 60 | 1.85 | 99.8 | 147.0 | 1.47 |
| 8.378 | 3.2 | 0.12 | 60 | 1.94 | 108.5 | 156.4 | 1.44 |
| 8.427 | 4.3 | 0.15 | 60 | 1.93 | 84.6 | 123.3 | 1.46 |
| 8.333 | 4.2 | 0.15 | 60 | 1.84 | 98.8 | 136.9 | 1.39 |
| 8.352 | 5.6 | 0.20 | 60 | 1.85 | 68.0 | 98.9 | 1.46 |
| 7.772 | 6.0 | 0.23 | 60 | 1.85 | 59.3 | 87.3 | 1.47 |

**Table 3. Experimental Details, Transfer to $CCl_4$ in STY−MMA Copolymerization, $f_{STY} = 0.390$, Solution in DMF**

| stock soln (g) | AIBN (mg) | $CCl_4$ (g) | total vol (mL) | $[CCl_4]$/[M] | time (min) | conv (%) | $M_n$ ($\times 10^3$) | $M_w$ ($\times 10^3$) | PDI |
|---|---|---|---|---|---|---|---|---|---|
| 0.500 | 6.8 | 4.512 | 25 | 5.96 | 200 | 2.05 | 590.5 | 772.1 | 1.31 |
| 0.756 | 6.9 | 4.276 | 25 | 3.74 | 200 | 2.10 | 650.4 | 761.1 | 1.17 |
| 1.008 | 7.3 | 3.998 | 25 | 2.62 | 200 | 1.87 | 185.9 | 272.0 | 1.46 |
| 1.497 | 6.7 | 3.565 | 25 | 1.57 | 120 | 1.99 | 188.3 | 281.3 | 1.49 |
| 4.999 | 11.4 | 0.000 | 25 | 0.00 | 32 | 1.85 | 99.8 | 147.0 | 1.47 |
| 0.539 | 6.9 | 4.442 | 25 | 5.45 | 200 | 1.94 | 108.5 | 156.4 | 1.44 |
| 0.751 | 6.6 | 4.246 | 25 | 3.74 | 200 | 1.93 | 84.6 | 123.3 | 1.46 |
| 1.024 | 7.7 | 4.016 | 25 | 2.59 | 200 | 1.84 | 98.8 | 136.9 | 1.39 |
| 1.515 | 6.8 | 3.487 | 25 | 1.52 | 120 | 1.85 | 68.0 | 98.9 | 1.46 |
| 5.015 | 11.7 | 0.000 | 25 | 0.00 | 32 | 1.85 | 59.3 | 87.3 | 1.47 |

**Table 4. Experimental Details of Determination of STY−MMA Copolymer Compositions (Solution in DMF), $T = 60$ °C**

| MMA (g) | STY (g) | DMF (g) | AIBN (mg) | time (min) | conv (%) | $f_{STY}$ | $F_{STY}$[a] |
|---|---|---|---|---|---|---|---|
| 0.908 | 0.103 | 4.022 | 1.8 | 40 | 1.31 | 0.099 | 0.187 |
| 0.813 | 0.208 | 4.040 | 2.7 | 240 | 5.02 | 0.198 | 0.289 |
| 0.607 | 0.414 | 3.997 | 2.3 | 180 | 0.63 | 0.396 | 0.407 |
| 0.414 | 0.599 | 4.035 | 1.9 | 90 | 0.61 | 0.582 | 0.587 |
| 0.418 | 0.618 | 4.043 | 2.4 | 90 | 0.81 | 0.587 | 0.557 |
| 0.193 | 0.806 | 4.051 | 1.9 | 60 | 0.75 | 0.800 | 0.717 |
| 0.205 | 0.879 | 4.023 | 2.5 | 60 | 0.99 | 0.805 | 0.718 |
| 0.105 | 0.905 | 4.008 | 3.3 | 300 | 2.31 | 0.893 | 0.778 |

[a] Determined by $^1$H NMR analysis: $F_{STY} = A_{STY}/(A_{STY} + A_{MMA} \times {}^5/_3)$, where $A_{STY}$ and $A_{MMA}$ are the areas of the STY aromatic and MMA $OCH_3$ resonances, respectively.

0.300 mol) and STY (60.0 g, 0.576 mol, $f_{STY} = 0.662$) was made up and charged to a series of 10 glass bottles, to each of which was added AIBN (approximately 10 mg) and varying amounts of $CCl_4$. Each sample was run in duplicate. The samples were degassed by purging with $N_2$, sealed, and immersed in a 60 °C thermostated water bath. Full experimental details for this example are shown in Table 1.

After reaction, the mixtures were poured into aluminum pans containing a small amount of hydroquinone. The unreacted monomer and $CCl_4$ was allowed to evaporate, and the polymers were dried under reduced pressure until constant weights were obtained. Conversions were measured gravimetrically (average: 3.88%; $\sigma$: 0.12%).

Complete experimental details for all $CCl_4$ polymerizations (at 40, 50, and 60 °C) are included in the Supporting Information, Tables S1−S3.

**Polymerizations with $CBr_4$ as the Chain Transfer Agent. Typical Example.** A stock solution of MMA (75.0 g, 0.749 mol), STY (8.98 g, 0.0862 mol, $f_{STY} = 0.103$), and AIBN (13.6 mg, 0.083 mmol) was made up and charged to 10 glass bottles. Varying amounts of $CBr_4$ were added to each bottle (full details in Table 2). Each sample was run in duplicate. After purging with $N_2$ and sealing, the bottles were immersed in a 60 °C thermostated water bath for 1 h. The mixtures were then poured into aluminum pans containing a small amount of hydroquinone. The unreacted monomer was allowed to evaporate, and the polymers were dried under reduced pressure until constant weights were obtained. Conversions were measured gravimetrically (average: 1.93%; $\sigma$: 0.09%).

Complete experimental details for all $CBr_4$ polymerizations are included in the Supporting Information, Tables S4−S6

**Polymerizations in Dimethylformamide (DMF). Typical Example.** A stock solution of MMA (12.02 g) and STY (8.00 g) was divided between 10 25 mL volumetric flasks. AIBN (approximately 2 mg) and varying amounts of $CCl_4$ were added to each sample to make a total volume of 5 mL, which was then made up to 25 mL with DMF. The samples were transferred to glass bottles, degassed by purging with $N_2$, sealed with rubber septa, and immersed in a 60 °C thermostated water bath. Full experimental details for this example are shown in Table 3. After the reaction was complete, the mixtures were washed with water to remove most of the DMF and then poured into preweighed aluminum containers, which contained a small amount of hydroquinone to inhibit further polymerization. Residual monomer, $CCl_4$, and solvent were allowed to evaporate, and the polymers were dried under reduced pressure until constant weights were obtained. Conversion was determined gravimetrically (average: 3.85%; $\sigma$ 1.83%).

Complete experimental details for all $CCl_4$ polymerizations in solution in DMF may be found in the Supporting Information, Table S7.

**Copolymer Composition, STY−MMA (Solution in DMF).** A separate set of experiments was carried out to determine the copolymer composition curve of MMA−STY in solution in DMF. Each sample contained 1 g of a mixture of MMA and STY ($f_{MMA}$ = 20, 40, 60, 80, and 90%), made up to 5 mL with DMF. The resulting solutions were degassed by sparging with $N_2$, sealed, and immersed in a 60 °C thermostated water bath for 60−300 min (depending on the relative amounts of MMA and STY). Full details of these experiments are shown in Table 4. The polymers were isolated by precipitation from methanol. Composition was measured by $^1$H NMR analysis of the relative areas of the aromatic resonances from STY repeat units ($\delta$ 5−7 ppm, 5H) and the $OCH_3$ resonance of the MMA repeat units ($\delta$ 3.5 ppm, 3H).

**Pulsed Laser Polymerizations (PLP).** The pulsed laser polymerization technique[19] has been described in detail in other publications by this group.[10,20] It consists of a Spectra Physics Quanta-Ray DCR-11 pulsed Nd:YAG laser with a HG-2 harmonic generator, which is used to generate 355 nm UV laser radiation. Samples for PLP were made up using a total of 1 g of monomers (STY and MMA) and 4 g of DMF and degassed by sparging with $N_2$. They were then sealed and placed in a thermostated copper sample cell (60 °C), where they were allowed to equilibrate for several minutes before laser irradiation began. After irradiation was complete, the polymers were isolated by precipitation from methanol (20 mL) and dried under vacuum. Conversions were measured gravimetrically. Experimental details for the PLP experiments are shown in Table 5.

## Results and Discussion

Measurement of chain transfer constants involves the measurement of an average molecular weight of the

**Table 5. $k_p$ Data and Corresponding Experimental Conditions for MMA−STY in Solution in DMF at 60 °C**

| MMA (g) | STY (g) | DMF (g) | $f_{STY}$ | $[M]_{total}$ (M) | initiator (mg) | [I] (mM) | pulse energy (mJ) | $t_f$ (s) | time (min) | conv (%) | $\nu^a$ | $k_p$ (L mol$^{-1}$ s$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.000 | 1.008 | 4.022 | 1.000 | 1.80 | $0.9^b$ | 5.48 | 10 | 0.1 | 45 | 1.84 | 46.5 | 258 |
| 0.000 | 1.008 | 3.999 | 1.000 | 1.81 | $0.6^b$ | 3.65 | 10 | 0.2 | 45 | 1.21 | 85.6 | 236 |
| 0.196 | 0.839 | 4.032 | 0.904 | 1.85 | $0.8^b$ | 4.87 | 14 | 0.1 | 30 | 1.03 | 100.0 | 270 |
| 0.206 | 0.822 | 4.003 | 0.793 | 1.86 | $10.9^c$ | 51.4 | 11 | 0.2 | 60 | 0.47 | 110 | 296 |
| 0.407 | 0.614 | 4.020 | 0.592 | 1.86 | $10.7^c$ | 50.4 | 11 | 0.5 | 90 | 1.51 | 321 | 346 |
| 0.405 | 0.593 | 4.008 | 0.585 | 1.83 | $1.7^b$ | 10.4 | 15 | 0.05 | 30 | 0.27 | 64.4 | 352 |
| 0.647 | 0.472 | 4.028 | 0.412 | 2.01 | $13.8^c$ | 65.0 | 11 | 0.2 | 45 | 0.45 | 167 | 415 |
| 0.803 | 0.241 | 4.003 | 0.224 | 1.93 | $1.4^b$ | 8.53 | 15 | 0.05 | 20 | 0.99 | 54.0 | 561 |
| 0.832 | 0.238 | 4.003 | 0.215 | 1.97 | $4.9^b$ | 29.8 | 14 | 0.1 | 20 | 0.26 | 111 | 564 |
| 0.805 | 0.204 | 4.095 | 0.196 | 1.84 | $5.3^b$ | 32.3 | 10 | 0.2 | 60 | 0.93 | 211 | 573 |
| 1.004 | 0.000 | 4.019 | 0.000 | 1.88 | $1.6^b$ | 9.74 | 15 | 0.05 | 5 | 0.56 | 215 | 1141 |
| 1.022 | 0.000 | 4.005 | 0.000 | 1.91 | $1.9^b$ | 11.6 | 15 | 0.05 | 10 | 3.34 | 213 | 1113 |
| 1.009 | 0.000 | 4.006 | 0.000 | 1.89 | $4.7^b$ | 28.6 | 10 | 0.1 | 20 | 7.62 | 198 | 1045 |
| 1.004 | 0.000 | 4.004 | 0.000 | 1.89 | $4.2^b$ | 25.6 | 10 | 0.2 | 40 | 5.82 | 363 | 963 |

[a] The degree of polymerization at the low molecular-weight point of inflection. [b] AIBN. [c] Benzoin.

**Table 6. $\langle C_{CCl_4}\rangle \times 10^4$ at 40, 50, and 60 °C and Corresponding Arrhenius Parameters in MMA−STY Copolymerizations**

| $f_{STY}$ | $[CCl_4]$ (M) | 40 °C | 50 °C | 60 °C | ln(*A*) | $E_A$ |
|---|---|---|---|---|---|---|
| 0.00 | 0−8.5 | 0.83 | 1.6 | 2.6 | 9.8 ± 1.6 | 50.0 ± 4.2 |
| 0.01 | 0−8.5 | 0.97 | 1.7 | 3.1 | 9.9 ± 0.8 | 49.8 ± 2.1 |
| 0.11 | 0−8.5 | 2.6 | 4.6 | 6.3 | 6.7 ± 1.4 | 38.9 ± 3.8 |
| 0.22 | 0−8.5 | 5.3 | 8.0 | 11 | 5.2 ± 2.4 | 33.1 ± 6.4 |
| 0.33 | 0−8.5 | 7.3 | 11 | 15 | 5.2 ± 1.3 | 32.2 ± 3.5 |
| 0.44 | 0−3.7 | 12 | 16 | 23 | 3.7 ± 1.3 | 27.3 ± 3.4 |
| 0.55 | 0−3.7 | 17 | 22 | 31 | 3.6 ± 0.8 | 26.0 ± 2.0 |
| 0.66 | 0−3.7 | 23 | 27 | 39 | 2.8 ± 1.1 | 23.2 ± 3.0 |
| 0.77 | 0−3.7 | 33 | 41 | 51 | 1.4 ± 1.0 | 18.5 ± 2.7 |
| 0.88 | 0−3.7 | 43 | 54 | 66 | 1.9 ± 0.9 | 19.1 ± 2.2 |
| 1.00 | 0−3.7 | 64 | 75 | 88 | 0.2 ± 0.5 | 13.8 ± 1.2 |

MWD ($M_n$ or $M_w$) as a function of the ratio of chain transfer agent to monomer (i.e., [S]/[M]). In all cases, a linear relationship was observed in this work between $2DP_w^{-1}$ (and $DP_n^{-1}$) and [S]/[M]. The weight-average degree of polymerization, $DP_w$, was used to determine the chain transfer constant on account of its lower sensitivity to errors in baseline selection.[22]

**A. Results for Polymerizations Carried Out in the Presence of $CCl_4$.** The values of the apparent chain transfer constants to $CCl_4$ ($\langle C_{CCl_4}\rangle$) were calculated from $M_w$ data using eq 2 and are shown in Table 6. A sample Mayo plot is shown in Figure 1.

The samples used for the determination of $\langle C_{CCl_4}\rangle$ contain varying monomer concentrations. This was necessary because large amounts of $CCl_4$ were needed to produce significant changes in the MWD, because of its low chain transfer constant (vide supra). It may seem that the Mayo method is not appropriate to determine the $\langle C_S\rangle$ values because the first term on the right-hand side of eq 1 is not constant for each point on the plot. It has been suggested,[21,22] however, that the first term on the right-hand side of the equation is *in general* not constant, as chain length dependence in the termination rate, $\langle k_t\rangle[R^\bullet]$, will cause it to vary with the ratio [S]/[M] as the average degree of polymerization varies. Hence, even when [M] is constant, the frequency of bimolecular termination will vary.

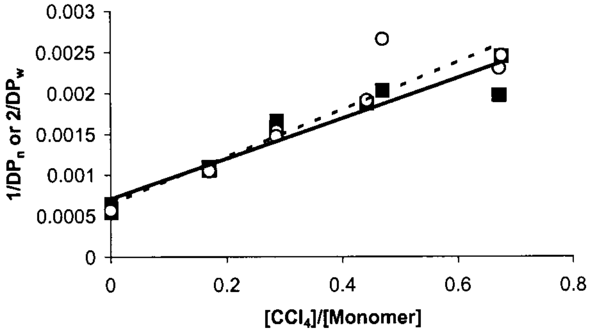


**Figure 1.** A sample Mayo plot ($1/DP_n$ or $2/DP_w$ vs $[CCl_4]/[M]$) for $CCl_4$ data at 50 °C, $f_{STY} = 0.66$ (■) $1/DP_n$ and (○) $2/DP_w$, and the corresponding lines of best fit (—) $1/DP_n$ and (- - -) $2/DP_w$.

Mayo plots, both in this work and generally, are linear; this indicates that first term in eq 1 makes a negligible experimental contribution to $DP_n^{-1}$ and thus is unlikely to introduce a large error into the calculation of $\langle C_S\rangle$. The chain transfer constants obtained in this work for the two homopolymerizations fall within the range of literature values.[24]

It can be seen that the $\langle C_{CCl_4}\rangle$ values show an increase with increasing temperature and increasing STY concentration in the feed solution, as expected (Table 6).

**1. Arrhenius Parameters ($CCl_4$).** From these values of the chain transfer constants at different temperatures the Arrhenius parameters for $CCl_4$ for each MMA:STY ratio were calculated. A sample Arrhenius plot is shown in Figure 2, and the values of the Arrhenius parameters for $\langle C_{CCl_4}\rangle$ are given in Table 6.

The Arrhenius parameters calculated from the $\langle C_S\rangle$ values follow a clear pattern. The values of the preexponential factor, ln(*A*), and the activation energy, $E_A$, initially decrease rapidly with the addition of STY to the feed solution and then more slowly after $f_{STY}$ reaches 0.22. The rapid initial decrease reflects the dominant role of STY-terminated radicals in transfer to $CCl_4$ in MMA−STY copolymerizations.

**2. Model Fitting ($CCl_4$).** The variation in $\langle C_S\rangle$ with $f_{STY}$ was fitted to two different models, shown in Figure 3. The simplest of these models, in which the PUE on

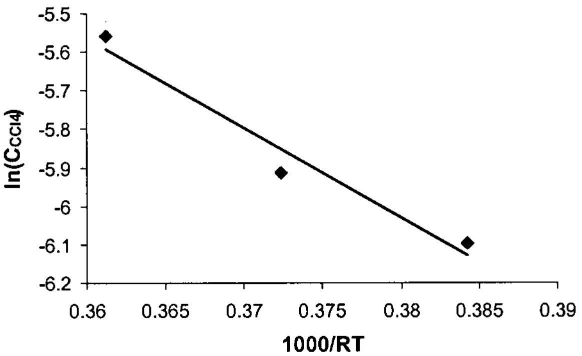


**Figure 2.** Arrhenius plot of $\langle C_{CCl_4}\rangle$ data, $f_{STY} = 0.66$.

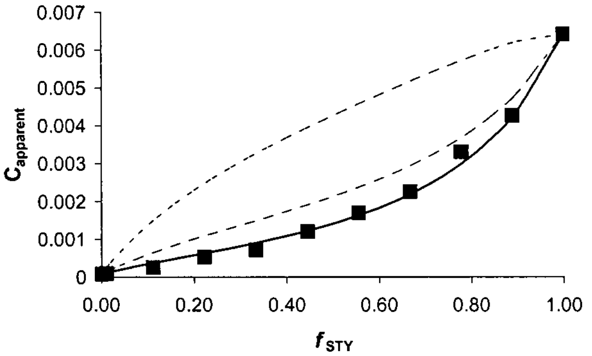


**Figure 3.** $CCl_4$ polymerization experimental data at 40 °C compared to the predictions of (- - -) a model with no PUE in transfer (but a PUE in propagation), (— — —) the terminal model, and (—) a model incorporating a PUE on transfer.

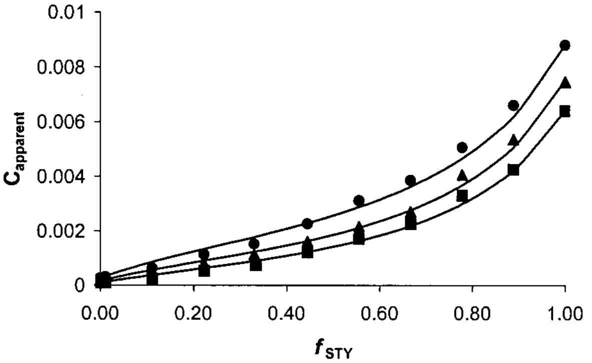


**Figure 4.** A plot of $\langle C_{CCl_4} \rangle$ experimental data vs $f_{STY}$ at 40 (■), 50 (▲), and 60 °C (○). Lines are fits using the PUE model described in the text.

chain transfer is equal to that on propagation (equivalent to the implicit PUE and terminal models), clearly does not fit the experimental data. A model assuming the occurrence of an explicit PUE in the chain transfer step was therefore investigated to see whether it would provide an adequate fit to the results. In both cases, the reactivity ratios were assumed to be constant from 40 to 60 °C.[10]

**3. PUE in Chain Transfer.** An alternative to the terminal and implicit PUE models is a model with a PUE on the chain transfer step that is not exactly equal to the PUE on propagation. In this model, four new chain transfer constants, $C_S^A$, $C_S^B$, $C_S^{A'}$, and $C_S^{B'}$, are defined:

$$C_S^A = \frac{k_{AA,S}}{k_{AAA}} \tag{7}$$

and

$$C_S^{A'} = \frac{k_{BA,S}}{k_{BAA}} = \frac{1}{\tau_A s_A} C_S^A \tag{8}$$

where $s_A$ is the radical reactivity ratio (defined in eq 5), and

$$\tau_A = \frac{k_{AA,S}}{k_{BA,S}} \tag{9}$$

where $\tau_A$ is the reactivity ratio of transfer from A to S.

The extent of the penultimate unit effect on transfer is thus described by the transfer reactivity ratios $\tau_A$ and $\tau_B$, in the same way that the radical reactivity ratios $s_A$ and $s_B$ (eq 5) denote the extent of the penultimate unit effect on propagation.

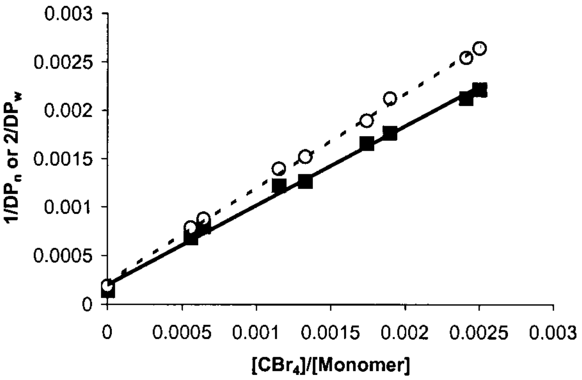


**Figure 5.** A sample Mayo plot ($1/DP_n$ or $2/DP_w$ vs $[CBr_4]/[M]$) for $CBr_4$ data at 50 °C, $f_{STY} = 0.01$ (■) $1/DP_n$ and (○) $2/DP_w$, and the lines of best fit (—) $1/DP_n$ data and (- - -) $2/DP_w$.

Substituting these terms into the Mayo equation, we have

$$\frac{2}{DP_w} - \frac{2}{DP_w^0} = [S]\,\frac{r_A C_S^A[A]\left(1 + \dfrac{\left(\dfrac{r'_A}{r_A s_A \tau_A} - 1\right)[B]}{[B] + r'_A[A]}\right) + r_B C_S^B[B]\left(1 + \dfrac{\left(\dfrac{r'_B}{r_B s_B \tau_B} - 1\right)[A]}{[A] + r'_B[B]}\right)}{r_A[A]^2 + 2[A][B] + r_B[B]^2} \tag{10}$$

For an implicit PUE, $r_X = r_X'$, and eq 10 reduces to

$$\frac{2}{DP_w} - \frac{2}{DP_w^0} = [S]\,\frac{r_A C_S^A[A]\left(\dfrac{r_A[A] + \dfrac{[B]}{s_A \tau_A}}{[B] + r_A[A]}\right) + r_B C_S^B[B]\left(\dfrac{r_B[B] + \dfrac{[A]}{s_B \tau_B}}{[A] + r_B[B]}\right)}{r_A[A]^2 + 2[A][B] + r_B[B]^2} \tag{11}$$

In STY–MMA copolymerizations in the presence of carbon tetrahalides, the chain transfer constant from STY-terminated radicals ($C_{CX_4}^{STY}$) is so much larger than that from MMA-terminated radicals ($C_{CX_4}^{MMA}$) that any PUE on chain transfer from MMA-terminated radicals can safely be neglected (i.e., $\tau_{MMA}$ can be set to 1). The only fit parameter for this model is then $\tau_{STY}$, since all other constants can be determined from separate experiments.

The model incorporating the PUE in the chain transfer step could be fitted to the data with reasonable values of the fit parameter, $\tau_{STY}$. A discussion of the significance of $\tau$ is given below. This model was then fitted to the $CCl_4$ data at the other polymerization temperatures with the same degree of success (Figures 3 and 4).

In the derivation of the model above, an implicit PUE on the kinetics of propagation was assumed (i.e., $r_X = r'_X$). This assumption appears to be empirically valid, as the implicit PUE model describes adequately the composition, sequence distribution, and kinetics of the STY–MMA system.[7,8,23] However, the need for a further parameter, $\tau$ ($\neq 1/s$), to achieve a good fit to the data indicates that an implicit PUE cannot describe the chain

**Table 7. $\langle C_{\mathrm{CBr_4}} \rangle$ at 40, 50, and 60 °C and Corresponding Arrhenius Parameters in MMA/STY Copolymerizations**

| $f_{\mathrm{STY}}$ | $[\mathrm{CBr_4}]$ (mM) | 40 °C | 50 °C | 60 °C | ln($A$) | $E_{\mathrm{A}}$ |
|---|---|---|---|---|---|---|
| 0.00 | 0−81 | 0.16 | 0.20 | 0.23 | 3.99 ± 0.01 | 15.11 ± 0.02 |
| 0.01 | 0−21 | 0.98 | 1.00 | 1.03 | 0.74 ± 0.16 | 1.98 ± 0.42 |
| 0.11 | 0−2.7 | 8.5 | 8.2 | 7.9 | 0.85 ± 0.03 | −3.38 ± 0.08 |
| 0.22 | 0−1.6 | 16.2 | 14.3 | 14.6 | 1.0 ± 1.3[a] | −4.6 ± 3.6[a] |
| 0.32 | 0−1.2 | 27.5 | 17.4 | 25.5 | 2 ± 8[a] | −4 ± 21[a] |

[a] Arrhenius parameters at $f_{\mathrm{STY}} = 0.22$ and 0.32 are very imprecise due to scatter in the data.

transfer mechanism occurring in this system. The magnitude of the PUE depends on the coreagent, and hence the PUE on chain transfer is explicit in nature.

**B. Results for Polymerizations Carried Out in the Presence of CBr₄. 1. Calculation of Chain Transfer Constants.** Mayo plots were constructed using the weight-average molecular weights to calculate the chain transfer constants. A sample Mayo plot is shown in Figure 5. From these Mayo plots, and using eq 6 to compensate for the consumption of chain transfer agent during reaction, values of the chain transfer constant to $\mathrm{CBr_4}$ were determined. These are shown in Table 7.

An estimate of the chain transfer constant to $\mathrm{CBr_4}$ in STY homopolymerization was made for modeling purposes using the method of Bamford and co-workers.[2]

Bamford's method involves the use of the relation

$$\langle C_{\mathrm{CBr_4}}^{\mathrm{STY}} \rangle = \frac{1}{1 + r_{\mathrm{STY}}[\mathrm{STY}]/[\mathrm{MMA}]}\left\{ C_{\mathrm{CBr_4}}^{\mathrm{STY}'} + C_{\mathrm{CBr_4}}^{\mathrm{STY}} r_{\mathrm{STY}} \frac{[\mathrm{STY}]}{[\mathrm{MMA}]} \right\} \quad (12)$$

in which $\langle C_{\mathrm{CBr_4}}^{\mathrm{STY}} \rangle$ is the apparent transfer constant of STY-terminated radicals according to the terminal model, calculated from eq 3. $C_{\mathrm{CBr_4}}^{\mathrm{STY}'}$ represents the transfer constant of STY-terminated radicals with MMA penultimate units, and $C_{\mathrm{CBr_4}}^{\mathrm{STY}}$ represents the transfer constant of homo-STY radicals. Although Bamford assumed terminal propagation kinetics in his derivation of eq 12, it remains valid in the presence of an implicit penultimate unit effect on propagation. This relation allows the graphical determination of $C_{\mathrm{CBr_4}}^{\mathrm{STY}}$ from the slope of a plot of $\langle C_{\mathrm{CBr_4}}^{\mathrm{STY}} \rangle (1 + r_{\mathrm{STY}}[\mathrm{STY}]/[\mathrm{MMA}])$ against $r_{\mathrm{STY}}[\mathrm{STY}]/[\mathrm{MMA}]$.

Because of the large amount of scatter in the data, it was difficult to determine the $C_{\mathrm{CBr_4}}^{\mathrm{STY}}$ values at each temperature. Therefore, the $\mathrm{CBr_4}$ data were combined to find an average chain transfer constant to $\mathrm{CBr_4}$ in STY homopolymerizations in the temperature range 40−60 °C. Since the value determined at $f_{\mathrm{STY}} = 0.32$, 50 °C, falls well below the trend of the other values, this point was omitted from the calculation. The average $C_{\mathrm{CBr_4}}^{\mathrm{STY}}$ in the temperature range 40−60 °C was found to be $2.8 \times 10^2$, a value that falls well within the range of values found in the literature.[24] The plot that was used to determine this value is shown in Figure 6.

**2. Effect of Temperature (CBr₄).** The apparent $C_{\mathrm{S}}$ values increase with the amount of STY in the feed solution, as expected. They do not show a definite increase with temperature, however, and appear to decrease with temperature at higher STY concentrations. This indicates that the activation energy of transfer is less than that of propagation, resulting in a negative value for the activation energy of the overall chain transfer constant. Similar behavior has been observed for several thiols.[25]

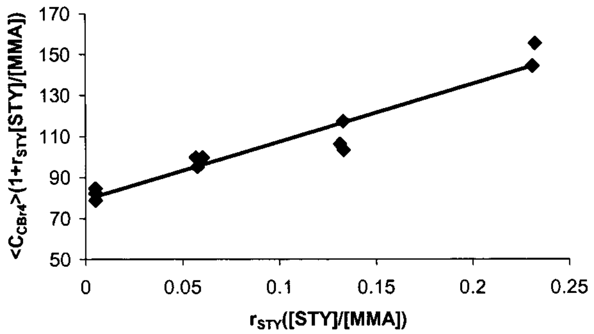


**Figure 6.** Bamford plot[2] using combined data from 40 to 60 °C for the determination of $C_{\mathrm{CBr_4}}^{\mathrm{STY}}$ by the method of moderated copolymerization. The line of best fit has a gradient of $2.8 \times 10^2$, equal to $C_{\mathrm{CBr_4}}^{\mathrm{STY}}$.

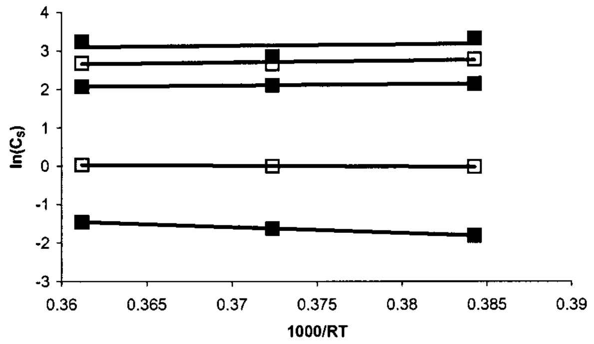


**Figure 7.** Arrhenius plots of $\langle C_{\mathrm{CBr_4}} \rangle$ data, with lines of best fit. From lowest to highest, $f_{\mathrm{STY}} = 0$, 0.01, 0.11, 0.22, and 0.32.

Arrhenius parameters were calculated for the apparent chain transfer constant, $\langle C_{\mathrm{CBr_4}} \rangle$ at each monomer feed ratio. These are given Table 7, and the corresponding Arrhenius plots are shown in Figure 7. Scatter in the data at the two highest STY concentrations ($f_{\mathrm{STY}} = 0.20$ and 0.30) prevented accurate determination of Arrhenius parameters, but it is apparent from Figure 7 that the temperature dependence of $\langle C_{\mathrm{CBr_4}} \rangle$ at these concentrations is small.

The trend is similar to that seen in the Arrhenius parameters for the $\mathrm{CCl_4}$ data. Again, the rapid decrease of the activation energy on the addition of STY to the system indicates that most of the chain transfer reactions are occurring with STY-terminated radicals even when the feed ratio of STY to MMA is low.

**3. Model Fitting.** As for the $\mathrm{CCl_4}$ data, the model that best fits the $\mathrm{CBr_4}$ data has an explicit PUE incorporated into the chain transfer step. This is illustrated in Figure 8. It is not possible to fit the data using the terminal model.

**C. Copolymerizations Performed in DMF.** If the PUE is partly due to polar effects, it should be influenced by the use of a polar solvent. Copolymerizations were carried out at 60 °C with $\mathrm{CCl_4}$ in DMF, a very polar solvent. The values of $\langle C_{\mathrm{CCl_4}} \rangle$ under these conditions are shown in Table 8. As before, the chain transfer constant increases with the amount of STY in the feed.

In all cases measured, including both homopolymerizations, the addition of DMF to the STY−MMA−$\mathrm{CCl_4}$ mixtures produces significantly higher chain transfer constants (Table 8). In MMA, the presence of DMF

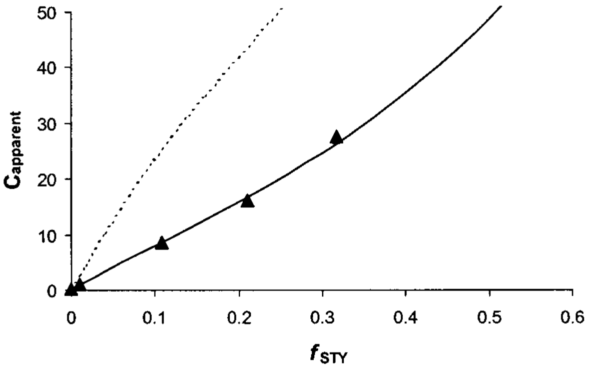


**Figure 8.** $CBr_4$ polymerization experimental data fitted to (– – –) the terminal or implicit PUE models (with no PUE in transfer) and (—) with a PUE, at 40 °C.

produces a 5-fold increase in the chain transfer constant, while in STY, a more than 2-fold increase is observed.

**1. Effect of DMF on the Copolymer Composition of MMA–STY.** To determine the extent of the penultimate unit effect on transfer to $CCl_4$ in the presence of DMF, it was necessary to determine the reactivity ratios of MMA–STY in this solvent. It appears that the presence of DMF has only a small effect on the reactivity ratios. Figure 9 shows the copolymer composition graph of the MMA–STY–DMF system, and the confidence interval obtained for the reactivity ratios. The best fit to the experimental data was obtained using $r_{MMA} = r_{STY} = 0.42$. This compares with the values of $(r_{MMA}, r_{STY}) = (0.4890, 0.4929)$ determined in bulk monomer by Coote et al.[10]

It would be expected that the presence of a polar solvent would have some effect on the copolymer composition, as there is evidence for polar effects in the STY–MMA cross-propagation reaction.[13] This would tend to produce an increase in the tendency toward alternation of the copolymerization, in accordance with the results of this work. However, it has been pointed out[26] that polar effects are unlikely to alter selectivity by a factor of more than 1.5 in this system—a result that is difficult to separate from experimental error.

It can be seen from Figure 9 that the point estimate for the bulk reactivity ratios[10] is contained in the 95% confidence interval for the reactivity ratios determined in DMF. Similarly, the point estimate for the DMF reactivity ratios lies within the confidence interval reported by Coote et al.[10] Hence, it is concluded that there is no statistically significant difference between the reactivity ratios in DMF and bulk. This is not to say that there is no difference between the reactivity ratios, only that any difference is too small to measure reliably with current techniques. For this reason, the reactivity ratios previously reported[10] for bulk MMA–STY, which are derived from a much larger database than that of this work, have been used as parameters in all subsequent modeling of the DMF–MMA–STY system. If the values obtained here in DMF are used, the effect on the results is small, and there is no change to the resulting discussion and conclusions.

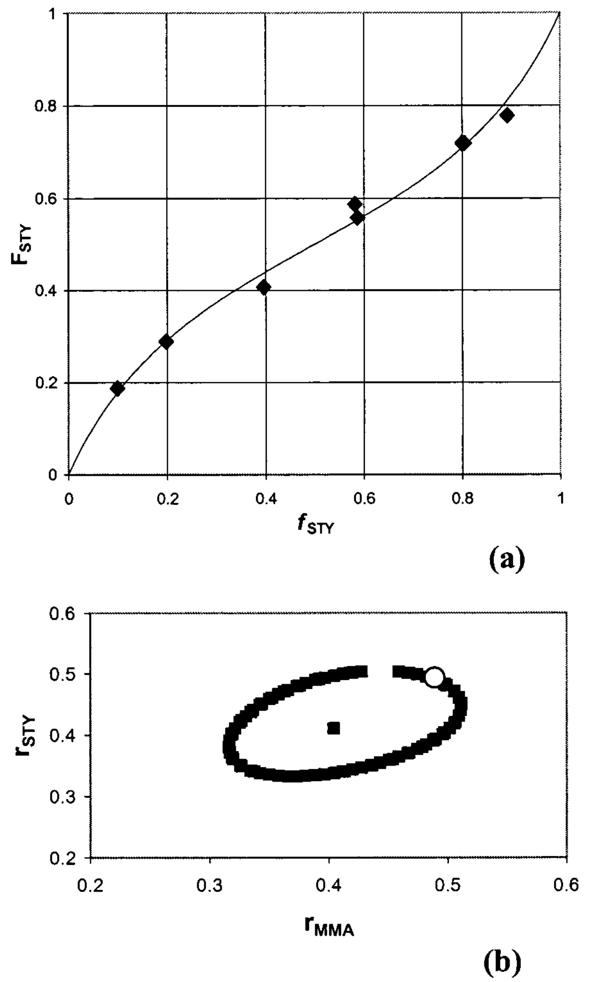


**Figure 9.** (a) Composition data for MMA–STY (20% solution in DMF), fitted to the terminal model with reactivity ratios $r_{MMA} = r_{STY} = 0.42$. (b) 95% confidence interval for reactivity ratios. ○ is Coote's point estimate[10] for the reactivity ratios of bulk MMA–STY.

**2. Effect of DMF on the Average Propagation Rate Constants, $\langle k_p \rangle$, of MMA–STY.** As the chain transfer constant is the ratio of the rate constants of propagation and transfer, the rate of propagation in DMF was measured in order to determine whether the increased $\langle C_{CCl_4} \rangle$ values observed are mainly due to a decrease in the rate of propagation ($k_p$) or an increase in the rate of transfer ($k_{tr}$). The results obtained from these experiments are shown in Table 6 and Figure 10.

**Table 8. Effects of DMF on $\langle C_{CCl_4} \rangle$, $k_p$, and $k_{tr}$**

| | bulk | | | DMF | | | effect of DMF[a] | | |
|---|---|---|---|---|---|---|---|---|---|
| $f_{STY}$ | $\langle C_{CCl_4} \rangle \times 10^4$ | $k_p$[b] (L mol s$^{-1}$) | $k_{tr}$[c] (L mol s$^{-1}$) | $\langle C_{CCl_4} \rangle \times 10^4$ | $k_p$[d] (L mol s$^{-1}$) | $k_{tr}$[c] (L mol s$^{-1}$) | $\langle C_{CCl_4} \rangle \times 10^4$ | $k_p$ (L mol s$^{-1}$) | $k_{tr}$[c] (L mol s$^{-1}$) |
| 0.0 | 2.6 | 756 | 0.20 | 15 | 1065 | 1.6 | 5.77 | 1.41 | 8 |
| 0.2 | 6.9 | 440 | 0.30 | 27 | 565 | 1.5 | 3.91 | 1.28 | 5 |
| 0.4 | 23 | 348 | 0.80 | 44 | 414 | 1.8 | 1.91 | 1.19 | 2.3 |
| 0.6 | 39 | 281 | 1.1 | 58 | 395 | 2.3 | 1.49 | 1.41 | 2.1 |
| 0.8 | 51 | 269 | 1.4 | 97 | 280 | 2.7 | 1.90 | 1.04 | 1.9 |
| 1.0 | 88 | 275 | 2.4 | 217 | 250 | 5.4 | 2.47 | 0.91 | 2.2 |

[a] Effect of DMF = DMF/bulk. [b] Data from Coote et al.[20] [c] Calculated from $k_{tr} = C_S k_p$. [d] This work.

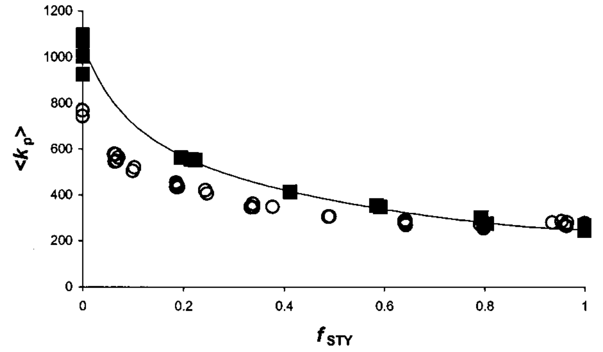


**Figure 10.** Effect of DMF on $k_p$ of MMA−STY copolymerizations (■) in DMF (this work) and (○) in bulk (data from Coote et al.).[20] The solid line is the penultimate unit model with $k_{p(MMA)} = 1065$, $k_{p(STY)} = 250$, $r_{MMA} = r_{STY} = 0.42$, $s_{MMA} = 2$, and $s_{STY} = 0.39$.

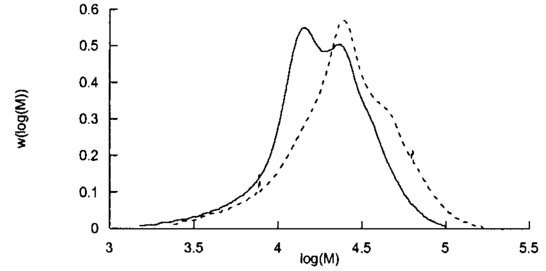


**Figure 11.** Molecular weight distributions for two typical samples from this study: (—) $f_{STY} = 0.215$, [M] = 1.97 M, and $t_f = 0.1$ s (A); (- — -) $f_{STY} = 0.196$, [M] = 1.84 M, and $t_f = 0.2$ s (B). The inflection point molecular weight of (B) (21 281) is approximately twice that of (A) (11 168), which is thus in accordance with the IUPAC consistency criteria.[27]

All of the PLP samples met the IUPAC consistency criteria,[27] as demonstrated for two typical examples in Figure 11.

The $k_p$ of styrene in solution in DMF shows a decrease of approximately 10% from the bulk value,[20] in line with the results reported by Coote and Davis[28] at 40 °C. In MMA, a 40% increase in $k_p$ is observed compared to the bulk value.[20] Intermediate monomer compositions have propagation rate constants that are generally slightly greater than those of the bulk monomer mixture.[20]

It is clear that although there is a solvent effect on the average rate constants of propagation, $\langle k_p \rangle$ of the copolymers, it is not large enough to account for the increase in $\langle C_{CCl_4} \rangle$. Indeed, in some cases (e.g., homo-MMA) the solvent effect on $k_p$ is in the wrong direction to produce the observed increases, which must therefore be due to increases in the rates of transfer. Values of $\langle k_{tr} \rangle$, calculated by multiplying $\langle C_{CCl_4} \rangle$ by $\langle k_p \rangle$, show large increases in the presence of DMF, ranging from 2-fold for homo-STY to 8-fold for homo-MMA.

The effects of DMF on chain transfer constants, $\langle k_p \rangle$ and $\langle k_{tr} \rangle$, of MMA−STY−$CCl_4$ are summarized in Table 8.

**3. Penultimate Unit Effects in DMF.** Figure 12 shows the $\langle C_{CCl_4} \rangle$ values of STY−MMA−$CCl_4$ in DMF, fitted to an explicit penultimate unit model, and using the reactivity ratios reported by Coote.[10] To fit the data, a transfer reactivity ratio of 7.2 is necessary. This is approximately twice that of the chain transfer experiments at 60 °C without DMF ($\tau = 3.3$). Thus, it is apparent that not only are the individual chain transfer constants of both MMA and STY greater in DMF than in bulk, the deviations from the terminal model also increase in the presence of DMF. This is strong evidence for the involvement of polar effects both in the transfer reaction to $CCl_4$ and in the penultimate unit effect.

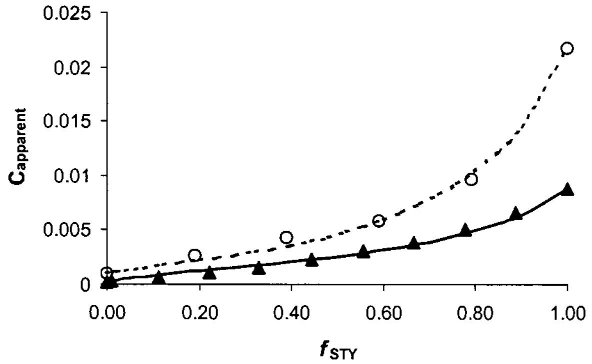


**Figure 12.** $CCl_4$ polymerization experimental data fitted to the PUE model (▲) in bulk and (○) in DMF solution.

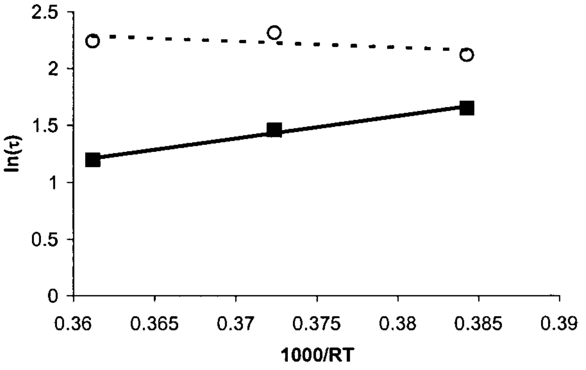


**Figure 13.** Arrhenius plots for the transfer reactivity ratios ($\tau$) of $CCl_4$ (■) and $CBr_4$ (○).

**Table 9. Transfer Reactivity Ratios ($\tau$) for $CCl_4$ and $CBr_4$ in MMA−STY Copolymerizations**

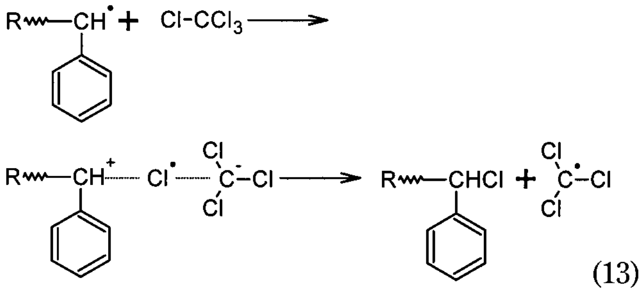
| temp (°C) | $\tau(CCl_4)$ | $\tau(CBr_4)$ |
|---|---|---|
| 40 | 5.2 ± 0.5 | 8.3 ± 0.2 |
| 50 | 4.3 ± 0.4 | 10.1 ± 0.7 |
| 60 | 3.3 ± 0.3 | 9.4 ± 0.3 |
| 60 (in DMF) | 7.2 ± 1 | |

**4. The Magnitude and Origin of the PUE.** Table 9 shows the values of the transfer reactivity ratio, $\tau$ (equal to the ratio of the rates of transfer from STY−STY-terminated radicals and MMA−STY-terminated radicals to $CX_4$), for both $CCl_4$ and $CBr_4$. These values show that $\tau$ decreases with temperature in the $CCl_4$ system, but no such trend is seen in the $CBr_4$ system. However, $\tau$ is greater in the $CBr_4$ system than in the $CCl_4$ system at each temperature studied.

The transfer reactivity ratios for $CCl_4$ and $CBr_4$ are plotted in an Arrhenius plot (Figure 13), which confirms that the trend with temperature is seen only in the $CCl_4$ system. $\tau$ decreases with temperature because $C^{MS}_{CCl_4}$ increases with temperature faster than $C^{SS}_{CCl_4}$ (where $C^{SS}_{CCl_4}$ is the chain transfer constant to $CCl_4$ of a radical with both the terminal and penultimate units of the chain being STY, and $C^{MS}_{CCl_4}$ is the chain transfer constant to $CCl_4$ of a radical with STY as the terminal unit and MMA as the penultimate unit).

The $E_a$ value for $\tau_{CCl_4}$ is −20.6 kJ/mol, and ln $A$ is −6.23. The very low value of the preexponential factor and the decrease of $\tau$ with temperature indicates that both $A$ and $E_a$ are greater for $k_{MS,CCl_4}$ than $k_{SS,CCl_4}$ (using the same terminology to represent STY and MMA units). This indicates that both enthalpic and entropic effects are likely to be important in the PUE.

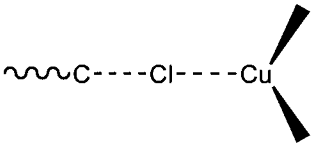
The transfer reactivity ratio for the polymerizations in DMF at 60 °C is much greater than that of the bulk $CCl_4$ system at 60 °C. The increase of $\tau$ with a change to a polar solvent system is strong evidence for a polar and therefore explicit origin of the PUE in chain transfer. The most likely explanation for this is that the polar solvent, DMF, helps to stabilize a polar transition state in the chain transfer process, such as the following (eq 13):[29]



The evidence obtained from this study would suggest also that radical stabilization cannot be the sole cause of the PUE in this polymerization system.

This is because of the assumptions made in eqs 7 and 8 in the derivation of the PUE model. If radical stabilization was wholly responsible for the PUE, then the magnitude of the PUE should be the same for both propagation and chain transfer, because the same radical is involved in each case. In that case, $\tau_A s_A$ would equal 1, the chain transfer constants $C_S^A$ and $C_S^{A'}$ would be equal, and the experimental data would fit the terminal model. Since this is clearly not the case, radical stabilization cannot be solely responsible for the PUE in chain transfer.

**5. Implications for ATRP.** In ATRP, an equilibrium between the halogen-capped chain end and the free radical is assumed to exist. The exact nature of the transition state is unknown, but the following simplistic representation may be valid:



Partial charge transfer in this transition state could play a significant role lowering the reaction barrier, similar to the polar effects postulated in $CCl_4$ and $CBr_4$ transfer reactions. In ATRP strong solvent effects have been observed, and they seem to be strongest in polar solvents.[30]

However, it is clear that in an equilibrium process the polar stabilization should affect both the forward and backward reactions with no net effect, and thus neither the copolymer composition (in the case of ATRP copolymerizations) nor the rate should be affected.[31] The strong solvent effect that is observed in ATRP experiments may be attributed to a number of other possibilities, viz.: (1) nonideal solvent effects (e.g., bootstrap, etc.); (2) differential stabilization of the Cu(I) and Cu(II) species; (3) a different ATRP mechanism (e.g., complexation and/or concerted steps).

## Conclusions

In this study, MMA/STY copolymerizations were carried out in the presence of the chain transfer agents $CCl_4$ and $CBr_4$. The importance of polar effects was investigated by repeating the $CCl_4$ experiments in solution in DMF. The values of the chain transfer constants for each system were calculated, and attempts were made to fit the data to a number of models. In addition, composition and propagation rate data were obtained for the MMA−STY−DMF system. The chain transfer data were shown to fit a model in which a PUE in chain transfer was assumed to be present and not equal to the PUE in propagation. This PUE is of a large magnitude, causing changes in the rate of transfer ranging from 3-fold ($CCl_4$, 60 °C) to as much as 10-fold ($CBr_4$, 50 °C). In the case of $CCl_4$, the PUE is dependent on temperature, while any temperature dependence in $CBr_4$ transfer is obscured by experimental error.

The polar nature of the chain transfer agent radicals and the change in the magnitude of the PUE with the addition of a polar solvent to the system suggest that the PUE in chain transfer in these systems is at least partly due to polar effects. It was shown that the magnitude of the PUE on chain transfer in these systems is not equal to that on propagation; therefore, radical stabilization cannot be solely responsible for the PUE. Thus, an explicit rather than implicit PUE must be operating in these systems, and this PUE has a significant enthalpic component.

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**Supporting Information Available:** Tables containing primary data for all chain transfer experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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