Chain Transfer to Monomer in the Free-Radical Polymerizations of Methyl Methacrylate, Styrene, and α-Methylstyrene

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ABSTRACT: The monomer chain transfer constant (C_M) has been evaluated for three monomers in bulk polymerization, viz, methyl methacrylate (MMA), styrene (STY) and α-methyl styrene (AMS). The new chain length distribution (CLD) analytical method was utilized to determine values for C_M at the low initiation limit and compared to the traditional Mayo method. The values for C_M obtained at 50 °C using the CLD method were ($C_M \times 10^5$) 5.15, 5.27, and 412 for MMA, STY, and AMS, respectively. The extremely high value for AMS originates in the low propagation rate coefficient for AMS. The values for the chain transfer rate coefficients (k_{tr}) were calculated were ($k_{tr} \times 10^2$ dm^3·mol^{-1}·s^{-1}), 3.34, 1.25, and 0.711 for MMA, STY, and AMS, respectively. The similarity of the values for k_{tr} are discussed in terms of possible mechanisms for the chain transfer to monomer reaction. The strong influence of transfer to monomer as a chain-stopping mechanism in AMS polymerization was confirmed by end group studies using matrix-assisted laser desorption ionization mass spectrometry.

Introduction

Understanding the primary processes in free radical polymerization is important for developing reaction control strategies. As interest in "living" free-radical polymerization reactions has developed, it becomes useful to understand the *limiting* molecular weight that can be achieved for any given monomer system. This limiting molecular weight is primarily governed by chain transfer to monomer in a true free-radical process.[1−3] All other chain stopping events, such as bimolecular termination and chain transfer to additional components in the reaction, only serve to reduce the molecular weight below the chain transfer to monomer limit.

This paper describes the measurement of the monomer chain transfer constant for methyl methacrylate (MMA), styrene (STY), and α-methylstyrene (AMS) in bulk at 50 °C using the recently developed chain length distribution (CLD) method.[1,4−6] The monomer chain transfer constants for MMA and STY have been measured previously by this method, but only in emulsion polymerization systems where the presence of additional components in the reaction, such as surfactant, may act as chain transfer agents. To our knowledge, the monomer chain transfer constant for α-methylstyrene has not previously been measured in a homopolymerization reaction. The results obtained using the CLD method for each monomer are compared to those obtained using the Mayo method.

In addition to those already quoted, the following abbreviations are adopted in the text: SEC, size exclusion chromatography; MALDI−MS, matrix-assisted-laser-desorption−ionization time-of-flight mass spectrometry; AIBN, azobis(isobutyronitrile). The polymeric form is prefixed where appropriate with the letter P.

Determining the Monomer Chain Transfer Constant

The established method for measuring the magnitude of chain transfer to monomer is the Mayo method,[2,7] where the inverse of the number average degree of polymerization is plotted against the rate of polymerization. The value of the monomer chain transfer constant, C_M (equal-to-the ratio of the chain transfer and propagation rate coefficients, k_{tr}/k_p), is determined from the intercept, i.e., by extrapolating to zero rate. This method has seen widespread use, and an extensive collection of C_M values is compiled in the *Polymer Handbook*.[8] There are two primary difficulties often encountered when implementing the Mayo approach. First, the accurate assignment of values for the number average molecular weight, M_n, because this is sensitive to baseline selection in SEC. Second, large errors can be introduced by the extrapolation process.

An alternative method for determining the monomer chain transfer constant based on the chain length distribution has been developed.[1,4−6] This method has some similarities with the Mayo method[9] but has practical advantages which should improve the accuracy of the derived C_M value. The C_M value is obtained from the transfer dominated region of the chain length distribution, i.e., number molecular weight distribution. For high molecular weights (assuming termination is predominantly between short and long chains[1]) the number molecular weight distribution can be written as

$$\lim_{M\to\infty} P(M) = \exp\left(-\frac{(k_{tr}[\mathrm{M}] + \langle k_t\rangle[\mathrm{R}^\bullet])}{k_p[\mathrm{M}]}\frac{M}{m_0}\right) \qquad (1)$$

where $P(M)$ is the number of chains of molecular weight M, m_0 is the molecular weight of the monomer, [M] and [R$^\bullet$] are the monomer and radical concentrations re-

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spectively, k_{tr} and k_p are the rate coefficients for chain transfer and propagation respectively, and $\langle k_t \rangle$ is the average termination rate coefficient.

If the concentration of initiator is reduced, the radical concentration, and hence the rate of termination, will drop. This eventually leads to the termination rate being insignificant compared to the chain transfer rate and so $\langle k_t \rangle[\mathrm{R}^\bullet] \ll k_{tr}[\mathrm{M}]$, allowing eq 1 to be simplified as

$$\lim_{M\to\infty[\mathrm{I}]\to 0} P(M) = \exp\left(-\frac{k_{tr}M}{k_p m_0}\right) \qquad (2)$$

Thus in the limit of low initiator concentration, the ratio k_{tr}/k_p ($= C_M$) can be determined from the slope, Λ, of the molecular weight distribution, plotted as $\ln P(M)$ vs M, i.e., $C_M = -\Lambda m_0$. An advantage of this method, over the Mayo method, is that the transfer-dominated region of the molecular weight distribution can be identified and used to calculate the monomer chain transfer constant, negating the need for an extrapolation procedure.

The number molecular weight distribution, $P(M)$, is obtained from the calibrated SEC distribution, $W(\log M)$, as follows:

$$P(M) = W(\log M)\frac{\log e}{M^2} \qquad (3)$$

The procedure for obtaining the transformed SEC distribution, $W(\log M)$, from the raw SEC chromatogram is described elsewhere.[6,10]

Experimental Section

Materials. The monomers MMA, styrene and AMS (Aldrich, 99%) were purified by drying over calcium hydride, followed by vacuum distillation. Complete removal of inhibitor was ensured by passing the monomers through a column of activated basic alumina. AIBN was purified by recrystallization from methanol.

Polymerizations. The polymerizations were performed in 20 mL sealable flasks. A stock solution of AIBN ($\sim 10^{-2}$ mol·L^{-1}) in monomer was prepared. Successive dilutions of the stock solution yielded a series of solutions with different initiator concentrations. The solutions were deoxygenated by purging with argon for 10 min prior to polymerization. Polymerizations were performed at 50 °C in a constant temperature water bath and the reactions stopped by cooling in an ice bath followed by the addition of hydroquinone. The reaction conditions for MMA, STY, and AMS are given in Tables 1−3, respectively. In all cases the reactions were stopped before the conversion reached 5%.

Analyses. The polymer was isolated by evaporating off the residual monomer: initially in a fume cupboard to remove the bulk of the liquid and then in a vacuum oven. Conversion was determined by gravimetry. PMMA and PSTY molecular weight distributions were measured by SEC on a modular system, comprising an autoinjector, guard column, Waters Ultrastyrogel Linear 7 m column, and a differential refractive index detector. The eluent was tetrahydrofuran at 1 mL·min^{-1} and the system was calibrated with PSTY standards (8×10^6 to 3.25×10^3 g·mol^{-1}) from Polymer Laboratories. The molecular weight of PMMA was determined from the PSTY standards via the universal calibration procedure and the following Mark−Houwink constants: PSTY,[11] $K = 14.1 \times 10^{-3}$ mL·g^{-1} and $\alpha = 0.700$; PMMA,[12] $K = 12.8 \times 10^{-3}$ mL·g^{-1} and $\alpha = 0.697$.

PAMS molecular weight distributions were measured by SEC on a modular system, comprising an autoinjector, guard column, two mixed-bed columns (60 cm mixed C, and 30 cm mixed E, Polymer Laboratories), and a differential refractive index detector. The eluent was tetrahydrofuran at 1 mL·min^{-1} and the system calibrated with PAMS standards (1.25×10^6 to 3.5×10^3 g·mol^{-1}) from Polymer Laboratories.

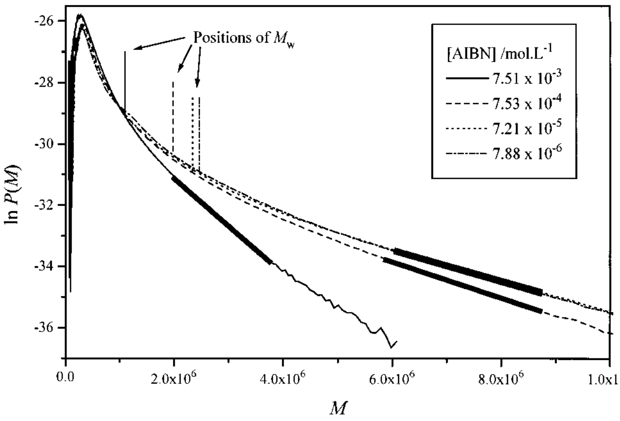

Figure 1. CLD method: Molecular weight distributions for MMA with different initiator concentrations plotted as $\ln P(M)$ vs M. The two experiments with the lowest initiator concentration give the same slope, Λ, indicating that the limit $[\mathrm{I}] \to 0$ has been reached. The slopes were measured up to a maximum molecular weight of 8.7×10^6 g·mol^{-1} (the limiting high molecular weight calibrant taking universal calibration into account).

The MALDI−MS spectrum of PAMS was obtained on a Voyager-DE RP from PerSeptive Biosystems. The machine was operated in reflector mode, with a delayed extraction of 100 ns, and low mass gate set at 600 Da. The mass scale was calibrated using bovine insulin. The matrix solution (0.5 μL mixture of 9-nitroanthracene and silver trifluoroacetate in tetrahydrofuran) was deposited on the sample slide and allowed to dry. Subsequently the polymer was deposited on the surface of the matrix (0.5 μL of polymer solution 4 mg·mL^{-1} in tetrahydrofuran), and allowed to dry.

Results and Discussion

Chain Transfer to Monomer in Methyl Methacrylate. Figure 1 shows the molecular weight distributions for the MMA experiments plotted as $\ln P(M)$ vs M (as indicated in eqs 2 and 3), highlighting the linear region at high molecular weight where the slope, Λ, was measured. The portion of the distribution beyond the molecular weight of the highest calibrant was not considered. The values of Λ from Figure 1 as well as those from a second set of reactions are listed in Table 1. As the initiator concentration is reduced, termination plays a diminishing role in the reaction, and the form of the $\ln P(M)$ vs M plots in the high molecular weight region can be approximated by eq 2. The distributions from the two experiments with the lowest initiator concentrations give the same Λ in the linear region indicating that the limit $[\mathrm{I}] \to 0$ has been reached. The mean of these was used to calculate the values for C_M and k_{tr}, shown in Table 4. The value for C_M, determined by the CLD method, 5.15×10^{-5}, compares well with literature values using this method in emulsion polymerization,[5,13] 5.7×10^{-5}, and is well within the range reported in the *Polymer Handbook*,[8] $(1.0−8.5) \times 10^{-5}$. It should be noted, however, that Stickler and Meyerhoff[14] reported a value for C_M of 1.08×10^{-5}. The lower value obtained by Stickler and Meyerhoff may reflect their rigorous purification procedure, which may suggest some influence of chain transfer to “adventitious impurities” in the reactions reported here.

The value for C_M determined using the Mayo method (Figure 2) 7.67×10^{-5}, compares well to that of the CLD

Table 1. Reaction Conditions and Results for MMA Experiments

experiment	[AIBN]/mol·L^{-1}	reaction time/min	conversion/%	Λ	M_w
MT1	7.51×10^{-3}	60	3.84	-1.55×10^{-6}	1.09×10^{6}
MT2	7.53×10^{-4}	125	2.12	-5.90×10^{-7}	1.98×10^{6}
MT3	7.21×10^{-5}	120	0.66	-5.04×10^{-7}	2.34×10^{6}
MT4	7.88×10^{-6}	1205	1.24	-5.13×10^{-7}	2.46×10^{6}
MT5	1.04×10^{-2}	95	4.00	-1.64×10^{-6}	8.79×10^{5}
MT6	1.04×10^{-3}	265	0.95	-7.15×10^{-7}	1.89×10^{6}
MT7	1.16×10^{-4}	690	1.86	-5.26×10^{-7}	2.40×10^{6}

Table 2. Reaction Conditions and Results for Styrene Experiments

experiment	[AIBN]/mol·L^{-1}	reaction time/min	conversion/%	Λ	M_w
ST1	9.20×10^{-3}	115	2.10	-5.70×10^{-6}	3.05×10^{5}
ST2	8.31×10^{-4}	285	1.64	-1.59×10^{-6}	9.30×10^{5}
ST3	9.62×10^{-5}	710	2.82	-7.00×10^{-7}	1.55×10^{6}
ST4	9.00×10^{-6}	710	1.20	-5.13×10^{-7}	2.20×10^{6}
ST5		730	0.92	-5.00×10^{-7}	2.14×10^{6}

Table 3. Reaction Conditions and Results for AMS Experiments

experiment	[AIBN]/mol·L^{-1}	reaction time/h	conversion/%	Λ	M_w
AT1	8.63×10^{-3}	27.3	0.27	-1.25×10^{-4}	2.21×10^{3}
AT2	8.18×10^{-4}	215	0.21	-1.23×10^{-4}	3.49×10^{3}
AT3	7.80×10^{-5}	215	0.12	-1.25×10^{-4}	4.46×10^{3}
AT4	7.20×10^{-6}	215	0.12	-1.24×10^{-4}	4.10×10^{3}
AT5		215	0.10	-1.23×10^{-4}	4.40×10^{3}

Table 4. Monomer Chain Transfer Constants and Rate Coefficients for the Polymerizations of MMA, STY, and AMS at 50 °C

monomer	C_M (CLD)	C_M[a] (Mayo)	k_{tr}[b]/dm^3·mol^{-1}·s^{-1}
MMA	5.15×10^{-5}[c]	7.67×10^{-5}[d]	3.34×10^{-2}
STY	5.27×10^{-5}[e]	5.09×10^{-5}[f]	1.25×10^{-2}
AMS	4.12×10^{-3}[g]	1.13×10^{-2}[h]	7.11×10^{-3}

[a] Determined using DP_n defined as $M_w/(2m_0)$.[14] [b] Determined from C_M measured by CLD method, where k_p in dm^3·mol^{-1}·s^{-1} at 50 °C for MMA = 649,[15] for STY = 238,[16] and for AMS = 1.73.[17] [c] Determined from the average of Λ from samples MT3, MT4, and MT7 in Table 1. [d] Determined from the intercept in Figure 2. [e] Determined from the average of Λ from samples ST4, and ST5 in Table 2. [f] Determined from the intercept in Figure 4. [g] Determined from the average of all Λs in Table 3; $C_M = -\Lambda m_0[M]/([M] - [M]_c)$. [h] Determined from the intercept in Figure 6; method C_M = intercept × $[M]/([M] - [M]_c)$.

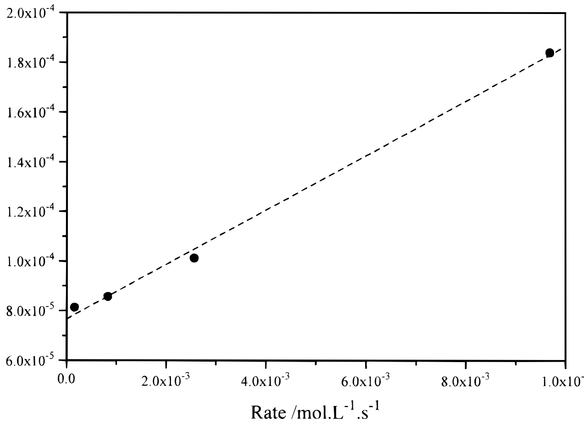

Figure 2. Mayo method: Dependence of $1/DP_n$ on rate of polymerization for MMA reactions. The intercept of the fitted line gives C_M.

method. The number average degree of polymerization, DP_n, used in the Mayo method was determined by the method of Stickler and Meyerhoff,[14] where the weight average molecular weight, M_w, is used with an assumed polydispersity of two, i.e., $DP_n = M_w/(2m_0)$. M_w is used instead of M_n as it is less sensitive to SEC baseline selection.

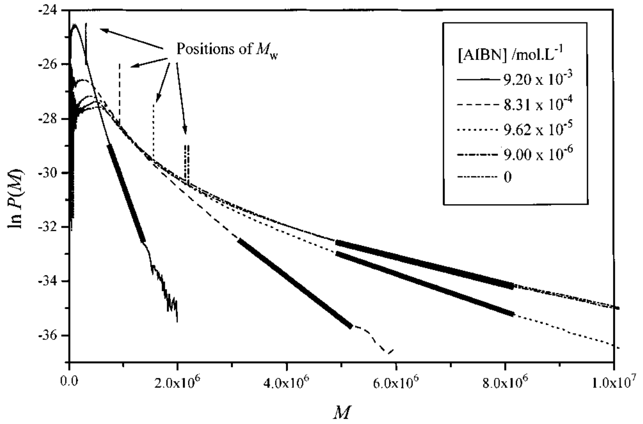

Figure 3. CLD method: Molecular weight distributions for styrene with different initiator concentrations plotted as ln $P(M)$ vs M. The two experiments with the lowest initiator concentration and no initiator give the same slope, Λ, indicating that the limit [I] → 0 has been reached. The slopes were measured up to a maximum molecular weight of 8×10^6 g·mol^{-1} (the limiting high molecular weight calibrant).

Chain Transfer to Monomer in Styrene. A similar analysis was performed for the polymerization of styrene. The ln $P(M)$ vs M distributions, with highlighted linear regions, are shown in Figure 3. As the initiator concentration is lowered, the slope, Λ, of the linear region at high molecular weight decreases, until a limiting value of 5.27×10^{-5} is reached at the two lowest initiator concentrations (0 and 9.00×10^{-6} mol·L^{-1}). A value for C_M of 5.09×10^{-5} was determined by the Mayo method (Figure 4) and compares well to that of the CLD method. The values of C_M and the corresponding values for k_{tr} are shown in Table 4. The C_M values both compare well with the published values obtained using the CLD method in emulsion polymerization,[18] $(4.3-5.0) \times 10^{-5}$ (calculated from, their reported k_{tr} values), is reasonably close to the value reported by Tobolsky and Offenbach,[19] 3.6×10^{-5}, and falls well within the range of values reported in the *Polymer Handbook*,[8] $(3.5-7.8) \times 10^{-5}$.

Chain Transfer to Monomer in α-Methylstyrene. The monomer α-methylstyrene has a ceiling tempera-

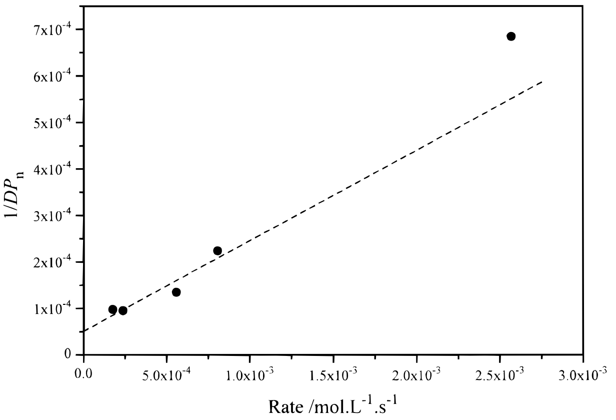

Figure 4. Mayo method: Dependence of 1/DP$_n$ on the rate of polymerization for styrene reactions. The intercept of the fitted line gives C_M. The point with the highest rate was omitted in fitting.

ture, i.e., the temperature above which it cannot be polymerized, of 61 °C.[2,21] Thus, depropagation needs to be taken into account when calculating the chain transfer constant. Under conditions that depolymerization is important, the propagation reaction should be written as an equilibrium reaction[2]

$$R^{\bullet}_{n} + M \underset{k_{dp}}{\overset{k_p}{\rightleftharpoons}} R^{\bullet}_{n+1} \tag{4}$$

where k_{dp} is rate coefficient for depropagation. From eq 4, the overall rate of polymerization can be written as

$$R_p = k_p[M][R^{\bullet}] - k_{dp}[R^{\bullet}]$$
$$= (k_p[M] - k_{dp})[R^{\bullet}] \tag{5}$$

At any given temperature there is monomer concentration, $[M]_c$, for which the rates of the forward and the backward reactions in eq 4 are equal, and hence the overall rate of polymerization, R_p, is zero. Therefore

$$k_{dp} = k_p[M]_c \tag{6}$$

Substituting eq 6 into eq 5 gives

$$R_p = k_p([M] - [M]_c)[R^{\bullet}] \tag{7}$$

As a result, the term k_{tr}/k_p in eq 2 for the CLD method and in the use of the Mayo method is replaced by $k_{tr}[M]/(k_p([M] - [M]_c))$. Thus, for the CLD method $C_M = -\Lambda m_0[M]/([M] - [M]_c)$ and for the Mayo method C_M = intercept × $[M]/([M] - [M]_c)$. At 50 °C, the bulk concentration of α-methylstyrene monomer is $[M] = 7.5$ mol·L^{-1} and the equilibrium monomer concentration is calculated to be $[M]_c = 5.4$ mol·L^{-1}.[21]

Figure 5 shows the ln $P(M)$ vs M distributions for the AMS experiments. The results for AMS differ from those obtained for MMA and styrene as chain transfer to monomer appears to dominate as the chain stopping mechanism in all experiments, regardless of the initiator concentration. The values of Λ are listed in Table 3, and the values for C_M and k_{tr} are listed in Table 4. The value of C_M determined by the Mayo method is about three times higher than that determined by the CLD method. In this case, there is considerable error in the extrapolation used in the Mayo method, as is evident from Figure 6, which may account for the discrepancy. Although C_M for AMS is over 2 orders of magnitude higher than MMA and STY, k_{tr} is similar because the propagation rate coefficient, k_p, of AMS is very low (~1.7 dm^3·mol^{-1}·s^{-1} at 50 °C[17]). It is the high C_M that causes the molecular weight distribution to be transfer controlled even at relatively high initiator concentrations. A consequence of the high value of C_M is that the maximum achievable molecular weight in an AMS homopolymerization is quite low ($M_n \approx 8 \times 10^3$ g·mol^{-1}).

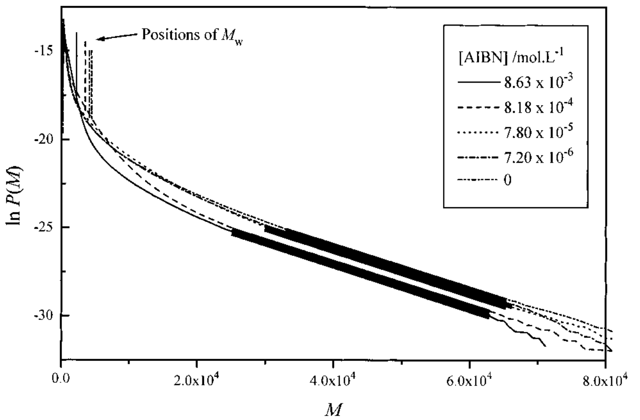

Figure 5. CLD method: Molecular weight distributions for AMS with different initiator concentrations plotted as ln $P(M)$ vs M. All the experiments have the same value of Λ, indicating that the transfer to monomer is the dominant chain stopping mechanism.

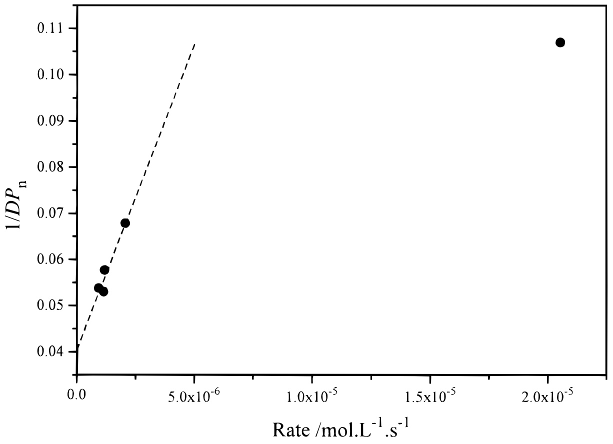

Figure 6. Mayo method: Dependence of 1/DP$_n$ on the rate of polymerization for AMS reactions. The intercept of the fitted line gives C_M. The point with the highest rate was omitted in fitting.

Direct confirmation of the dominance of chain transfer to monomer in AMS polymerization can be obtained from MALDI–MS. The spectrum is shown in Figure 7. Each peak in the spectrum corresponds to a polymer chain of specific molecular weight. Chains with the same end groups but different degrees of polymerization form a series of peaks separated by the molecular weight of the repeat unit (118.2 for AMS). Two series of peaks can be identified in Figure 7, marked by solid squares and open circles. The dominant series (solid squares) have a molecular weight that is described by $m = 118.2\mathrm{DP}_n + 107.9$, where DP$_n$ is the degree of polymerization, 118.2 is the molecular weight of the AMS repeat unit, and 107.9 is the molecular weight of the silver counterion. This corresponds to polymer chains without initiator (AIBN) end groups. These chains are

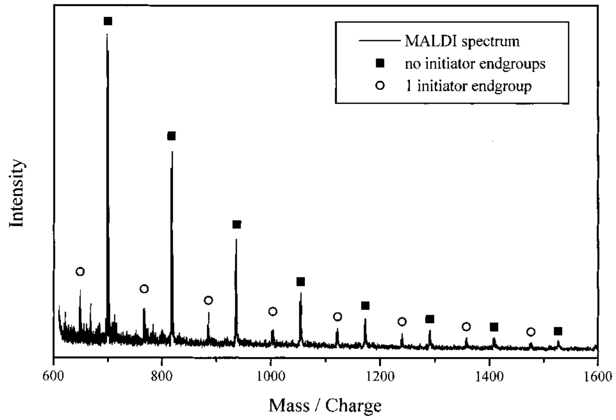

Figure 7. MALDI−MS spectrum of PAMS prepared with AIBN initiator. The dominant peaks (marked with solid squares) correspond to polymer chains without initiator end groups, and the second series of peaks (marked with open circles) correspond to polymer chains with only one initiator (AIBN) end group. See text for an explanation of how these end groups can be formed.

initiated by monomeric radicals (created by chain transfer to monomer) and most likely stopped by chain transfer to monomer (or possibly by termination by disproportionation or combination with another chain arising from transfer). The second series of peaks (open circles) have molecular weight that is described by $m = 118.2\mathrm{DP}_n + 68.1 + 107.9$; where 68.1 is the molecular weight of the AIBN-initiating species. This corresponds to polymer chains with one initiator (AIBN) end group per chain. These chains may have been formed by several different processes. First, these chains may have been initiated by AIBN and terminated by one of the following three reactions: (i) chain transfer to monomer, (ii) termination by disproportionation, or (iii) termination by combination with a chain initiated by chain transfer to monomer. Another possibility is that the chain is initiated by chain transfer to monomer and terminated by combination with a chain initiated by AIBN (i.e., the reverse of case iii in the previous sentence).

The MALDI−MS mass spectrum provides evidence that chain transfer to monomer dominates as a chain stopping and initiating mechanism in the polymerization of AMS. Although the MALDI−MS spectrum yields a number molecular weight distribution, $P(M)$, of the polymer, the distribution is not quantitative[20] and so cannot be used to measure the monomer chain transfer constant. It is also noted that the MALDI−MS spectrum only shows chains of low molecular weight, which may not be representative of the entire molecular weight distribution.

General Observations. The k_{tr} values obtained for each monomer, given in Table 4, are very similar. It is difficult to comment specifically on this observation, as it is not known which part of the monomer or growing polymer chain (or possible impurity, as noted earlier) is responsible for chain transfer. The most meaningful comparison would be to compare the activation energies and frequency factors of k_{tr}, as similarities or differences in these values would strongly suggest either similar or different reaction pathways for each of the monomers. However, some general comments may be made.

The closeness of the STY−AMS pair is surprising when it is considered that monomer chain transfer constant for methyl acrylate (MA) (in the analogous MA−MMA pair) is up to 100 times higher than for MMA.[18] A chain transfer reaction involving the phenyl ring in STY and AMS seems unlikely, as the chain transfer constant of STY with benzene[8] is about an order of magnitude lower than those observed in this work. In the copolymerizations of STY with MMA and MA, similar values of the cross chain transfer rate coefficients of the PSTY radical with styrene, MMA, and MA monomers, have been explained by suggesting that the β-hydrogen on the backbone PSTY radical is abstracted.[18] Chain transfer to monomer in AMS polymerization may occur via a similar mechanism, with hydrogen abstraction taking place from either the backbone or (more likely) the α-methylgroup of the PAMS radical. In this regard the closeness of the values obtained for MMA and AMS support a mechanism involving hydrogen abstraction from the α-methyl group. It has also been suggested that chain transfer to monomer in styrene polymerization may actually be to a Diels−Alder intermediate formed from the reaction of two styrene monomer units.[22,23]

Conclusions

The values for the monomer chain transfer constant and rate coefficient, C_{M} and k_{tr}, were measured at 50 °C for the monomers MMA, STY, and AMS in bulk. The values for k_{tr} show little dependence on the monomer type. The chain transfer constant, C_{M}, for AMS is over 2 orders of magnitude higher than MMA or STY, and so chain-stopping reactions in the bulk polymerization of AMS are dominated by chain transfer to monomer. This behavior is primarily caused by the low chain propagation rate coefficient of AMS rather than an abnormally high k_{tr} value. It is felt that the CLD method for determining C_{M} gives better results than the Mayo method since the transfer-dominated region of the molecular weight distribution can be identified and used to measure the monomer chain transfer constant, avoiding the need for an extrapolation (which can introduce large errors).

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