Cross-Chain Transfer Rate Constants of Styrene-Terminated Radicals to Methyl Acrylate and Methyl Methacrylate

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ABSTRACT: The chain transfer-to-monomer dominated regime of the molar mass distribution of low-conversion emulsion copolymers of styrene and methyl acrylate and of styrene and methyl methacrylate of various compositions, prepared with varying initiator concentrations, was analyzed with size exclusion chromatography. By extrapolation of the values of the slope of the natural logarithm of the number molar mass distribution to zero initiator concentration, it was possible to determine the average chain-transfer coefficient as a function of composition. By calculation of the ratio of the concentrations of styrene-terminated radicals and methyl (meth)acrylate-terminated radicals with an appropriate propagation model, the values of the cross-chain transfer rate constants of styrene-terminated radicals to methyl acrylate and methyl methacrylate could be deduced. These values were interpreted in the light of newly gained insights into radical propagation and transfer reactions.

Introduction

In any free radical (co)polymerization, chain transfer is an important process from the point of view that it affects the molar mass distribution (MMD), which determines many product properties and from the point of view that it affects the rate of polymerization; through the action of chain transfer generally a small radical is formed, which can diffuse much more rapidly than a polymeric radical. In emulsion polymerization systems with a low average number of radicals per particle (<0.5), the escape of radicals from the particles (exit) is rate-determining, and the exit rate is determined by the rate of transfer to monomer[1] or other small molecules capable of diffusing out of the particles.[2] In emulsion polymerization systems with a relatively high average number of radicals per particle and, in general, in homogeneous free-radical polymerizations, the rate of polymerization is determined by termination, the rate of which is enhanced considerably by transfer to monomer or other small molecules. It is therefore important to have reliable values of the rate constants involved in chain transfer for predicting or modeling the MMD and/or rate of polymerization. Note that for modeling the polymerization rate of a certain system, it is important to know the individual rates of transfer to each of the species which can undergo transfer and which can have an effect on the kinetics; for the MMD it is sufficient to know the overall rate of chain transfer, if transfer is the dominating chain-stopping mechanism. In this paper we will present results of the determination of the total rate of chain transfer to monomer as a function of monomer composition in two (emulsion) copolymerization systems (styrene−methyl acrylate and styrene−methyl methacrylate). These data are also interpreted in terms of the rates of transfer to the individual monomers (homo- and cross-chain transfer constants), which are important when studying the kinetics of these systems.[2−5] The chain transfer constants will be discussed using some recently developed theoretical understanding of propagation[6] and transfer[7] reactions in free-radical polymerization.

Methods for Determining the Rate of Chain Transfer

There are two methods for determining chain transfer rate coefficients from the MMD. One uses the Mayo plot,[8,9] where the reciprocal number *average* degree of polymerization is plotted as a function of the rate of polymerization. The value of the intercept gives the ratio between the total rate of chain transfer and the total rate of propagation.[10] If the rates of initiation/termination are known or estimated from experimental data, the rate of transfer can also be calculated directly from the number *average* degree of polymerization using the extended Mayo equation without extrapolation to zero polymerization rate.[11−13] Despite having some disadvantages connected with the use of an average molar mass rather than the distribution,[14] this method has been widely used to obtain data as evidenced by the number of data presented in the Polymer Handbook.[15]

The second method is a technique recognized by an IUPAC working party[16] to obtain reliable chain transfer rate constants from the MMD provided chain transfer is the main chain-stoppage mechanism.[14,17,18] This is the case at very low radical concentrations (low initiator concentrations) and in the high molar mass regime. Note that in emulsion polymerization the radical concentration pertains to the average radical concentration in a latex particle; if the compartmentalization is effective, the total radical concentration in the latex can be much higher than in a homogeneous system. By plotting the natural logarithm of the differential number MMD versus the molar mass and taking the slope (which is equal to the ratio of the rates of chain transfer and propagation multiplied with the molar mass of the monomer unit) the rate coefficient for chain transfer can be obtained easily. Whang et al.[17] used this technique to determine the chain transfer coefficients to monomer of methyl methacrylate at 60 °C using a high-conversion emulsion polymer sample and of styrene at 50 °C using

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a low-conversion emulsion polymer sample. The technique has also been applied to the pulsed laser homopolymerization of styrene in microemulsions,[19] to the pulsed laser bulk polymerization of methyl methacrylate in the presence of two chain transfer agents,[20] and to the pulsed laser polymerization of styrene and methyl, ethyl, and butyl methacrylate with *n*-dodecanethiol.[21]

Although most examples of the determination of chain transfer coefficients using the methods outlined above pertain to transfer to monomer or to a chain transfer agent in homopolymerizations, in a few cases the method has also been applied to transfer in copolymerization; see below.

Chain Transfer in Copolymerizations. In a copolymerization system with two monomers *i* and *j*, four different chain transfer reactions to monomer can take place if only the terminal unit of the copolymer radical is taken into consideration (i.e., the penultimate unit of the (polymeric) radical has no effect on the propagation or transfer rate of the terminal radical unit). In such a copolymerization the average chain transfer rate coefficient ($\bar{k}_{\mathrm{tr}}$) is a function of the molar fractions of the monomers and the ratio of polymeric radicals with terminal units *i* and *j*. Four chain transfer rate constants from two radical types to two monomer types need to be taken into account: $k_{\mathrm{tr},ii}$, $k_{\mathrm{tr},jj}$, and the cross-transfer rate constants $k_{\mathrm{tr},ij}$ and $k_{\mathrm{tr},ji}$. C_{ij} is the chain transfer coefficient defined as the ratio of $k_{\mathrm{tr},ij}$ and the corresponding propagation rate constant $k_{\mathrm{p}ij}$.

Assuming the terminal model for propagation and transfer Rudin et al.[11] extended the Mayo equation to chain transfer to monomer in (emulsion) copolymerizations. Assuming that the propagation rate constants are known, the unknown parameters are the two homopolymerization transfer rate constants, the two cross-transfer rate constants, and the rate of initiation. Rudin et al. assumed the rate of initiation to be independent of the monomer composition, so only five experiments were needed to obtain all parameter values. In their method the initiator concentration did not need to be extrapolated to zero. The assumption regarding the rate of initiation is not necessarily correct as the reaction rates of the initiator radicals, which can determine the rate of initiation in homogeneous systems,[22] with different monomers may differ significantly,[23] and likewise the rates of monomer propagation versus termination in the aqueous phase depend on the type of monomer and therefore composition. However, this effect was minimized by ensuring that the experimental rate of initiation is smaller than both the rate of transfer and the ratio of the rate of polymerization and the average degree of polymerization. This method was applied to the emulsion copolymerization of styrene and α-methylstyrene,[11] of styrene and methyl methacrylate,[12] and of styrene and butyl acrylate,[13] but in the latter two cases only the sum of the two cross-transfer constants could be determined, and not the individual cross-transfer constants. Mead et al.[4] applied the same method to the emulsion copolymerization of styrene (S) and methyl acrylate (MA) and determined the sum of the two cross-transfer constants ($C_{\mathrm{SMA}} + C_{\mathrm{MAS}}$), which was used in a kinetic analysis of the emulsion copolymerization of those monomers.

Bamford et al.[24-26] were the first to suggest a penultimate unit effect in chain transfer in copolymerizations, albeit for chain transfer to a chain transfer agent (CTA). First they derived equations based on the terminal model for propagation to describe chain transfer to a very reactive substrate (CTA) in order to calculate C_{A} and C_{B}, the chain transfer constants of both terminal radical types to the CTA. They applied this method to the system S and MA with CBr_4 as the CTA.[24] When this method was applied to the system S−methyl methacrylate (MMA) with CBr_4, it was observed that the chain transfer constant depended on the molar ratio S/MMA, and a penultimate unit effect (PUE) was invoked to explain this.[25] However, this effect was not observed in the systems S−MMA with butane thiol nor in the system S−MA with either CBr_4 or butane thiol.[26]

In this paper the technique recognized by the IUPAC working party[16] is applied to low-conversion emulsion copolymerizations of S and MA and of S and MMA. This technique, which is outlined in the next section, was applied before[2] in the case of the emulsion copolymerization of S and MA. The average chain transfer rate coefficient ($\bar{k}_{\mathrm{tr}}$) was determined at two different monomer compositions, and by using a third literature value for the transfer constant of S, the data were fitted with a straight line. The linear dependence of $\bar{k}_{\mathrm{tr}}$ on the molar fraction of S in the feed (f_{S}) was assumed on the basis of calculations of the ratio of the concentrations of S-terminated radicals and MA-terminated radicals. On the basis of these calculations, it was concluded that the time-averaged concentration of MA-terminated radicals was negligible compared with that of S-terminated radicals. In the present paper we will show more extensive data obtained at several different monomer compositions to check whether there is indeed a linear dependence between $\bar{k}_{\mathrm{tr}}$ and f_{S}. The same is done for the system S−MMA.

Determination of $\bar{k}_{\mathrm{tr}}$ from Molar Mass Distributions. In a regime of molar masses, where chain transfer to monomer is the sole mechanism for chain stoppage (which is the case at very low initiator concentrations and at high molar masses, because in that case the rate of termination is very small compared with the rate of chain transfer[14]), the differential number MMD, *P*(M), can be expressed as:

$$P(M) \sim \exp\left[-\left(\frac{\bar{k}_{\mathrm{tr}}}{\bar{k}_{\mathrm{p}}}\right)\left(\frac{M}{M_{\mathrm{o}}}\right)\right] \qquad (1)$$

where M is the molar mass, M_{o} is the average molar mass of the monomer units in the copolymer, and $\bar{k}_{\mathrm{p}}$ is the average propagation rate coefficient. If the ratio $\bar{k}_{\mathrm{tr}}/\bar{k}_{\mathrm{p}}$ can be obtained in this way from the MMD of a copolymer (see below) and a proper value for $\bar{k}_{\mathrm{p}}$ is available, $\bar{k}_{\mathrm{tr}}$ can be calculated using eq 1 and expressions for the average molar mass of the monomers and the copolymer composition, which can be calculated from eqs 2 and 3:

$$M_{\mathrm{o}} = F_i M_0{}^i + (1 - F_i) M_0{}^j \qquad (2)$$

where F_i is the molar fraction of monomer *i* in the copolymer and the $M_0{}^i$ the molar mass of monomer *i*. In this paper the terminal model is applied to calculate the copolymer composition from the molar fraction f_i of monomer *i* in the monomer feed and the reactivity ratios r_i and r_j:

$$F_i = \frac{r_i f_i^{\,2} + f_i(1 - f_i)}{r_i f_i^{\,2} + 2 f_i (1 - f_i) + r_j (1 - f_i)^2} \qquad (3)$$

A proper value for $\bar{k}_{\mathrm{p}}$ has become available for some systems with the advent of techniques such as pulsed

Table 1. Mark−Houwink Constants Used for Universal Calibration

	K (10^{-2} dm^3/kg)	a
S[27]	1.62	0.71
MA[27]	0.788	0.885
MMA[31]	1.78	0.69

laser polymerization. Fortunately this also applies to the monomer systems used in this work[27−30] (see Results and Discussion).

There are three points that ought to be taken into account concerning the sample conditions: (1) In copolymerizations the ratio $\bar{k}_{tr}/\bar{k}_p$ can be obtained from the MMD if the pertaining copolymer sample was obtained at low conversion, because due to the generally occurring composition drift the values of $\bar{k}_{tr}$ and $\bar{k}_p$ will change, but very probably not proportionally, so that their ratio becomes dependent on conversion. (2) It has been shown that the nucleation stage in emulsion polymerization can affect the kinetics determining the MMD,[17] so it is preferred that the nucleation stage be avoided. This can be achieved by using a seed latex with an MMD which does not interfere with that part of the MMD of the (co)polymer that will be analyzed. (3) As stated, eq 1 is valid only if the only chain stopping event is chain transfer to monomer. Therefore, it is advisable to keep the initiator concentrations as low as possible, as this will favor low radical concentrations and therefore lower the chance of bimolecular termination.

Experimental Section

The monomers styrene (S, Merck, p.a.), methyl acrylate (MA, Merck, p.a.), and methyl methacrylate (MMA, Merck, p.a.) were distilled before use and stored at 4 °C. Sodium persulfate (Merck) was used as initiator, anhydrous sodium carbonate (Merck) as buffer, and hydroquinone (Fluka) as inhibitor. These were used without further purification. The seed latex used was a monodisperse poly(S) latex with a particle diameter of 87 nm, as determined by transmission electron microscopy.

The low-conversion seeded emulsion copolymerizations were performed in a dilatometer. Both monomers were added to the seed latex in the dilatometer, and the mixture was stirred for several hours or left standing overnight. After water had been added to the mixture, it was heated to a temperature of 50 ± 0.5 °C. The reactions were chemically initiated with sodium persulfate, which was added as an aqueous solution with a volume such that the addition to the seed latex, extra monomers and water already present filled the dilatometer up to the maximum volume. Typically 8−10 g of S + MA were added to ca. 0.6 g of poly(S) (from the seed latex), with a total of ca. 55 g of water. The molar fraction of styrene in the polymer particles was varied from 0 to 1. Monomer partitioning equations were used to calculate what amounts of seed latex, S, MA, and water were needed in each experiment to (1) obtain a certain fraction of S in the polymer particles and (2) to attain interval 2 conditions, so that the total monomer concentration in the particles did not change; see also ref 2. The exact total amounts therefore varied a bit depending on the fraction of S in the particles that was required. At every fraction three different amounts of initiator were used varying between 1.0×10^{-21} and 2.1×10^{-20} mol of initiator/particle. The particle concentration was about 3×10^{16}/dm^3 of water. To prevent composition drift, the reactions were stopped at 5% conversion with hydroquinone. The meniscus level in the capillary of the dilatometer was used to determine the conversion. The change in meniscus level from 0 to 5% conversion was calculated beforehand with the difference in the densities of both monomers and the obtained copolymers. The samples were analyzed with size exclusion chromatography (SEC) on a chromatographic system (Waters Division of Millipore) equipped with two Shodex linear columns (KF80M, 30 cm) and a Waters Model 410 refractive index detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 1 cm^3 min^{-1}. Poly(S) standards were used for calibration.

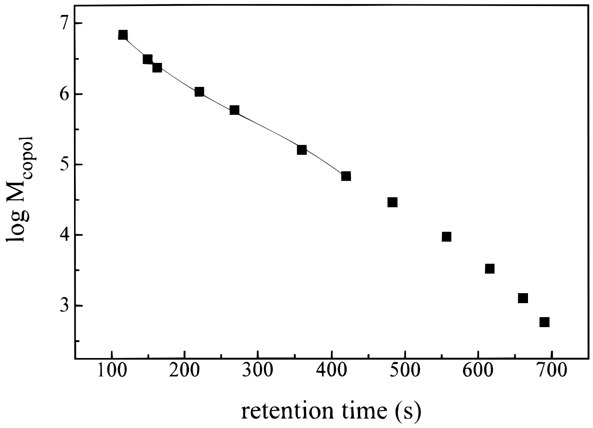

Figure 1. Example of the fit of the calibration curve for the obtained copolymer. The system shown here is S−MMA with a molar fraction of MMA in the particles of 0.2. Only molar masses above about 10^5 g mol^{-1} are taken into account.

Results and Discussion

A. Determination of the Average Chain Transfer Rate Coefficient $\bar{k}_{tr}$ as a Function of Composition.

For the system S−MA, the fraction of MA in the particles (f_{MAp}) was varied between 0 and 1, and in the system S−MMA, f_{MMAp} was varied between 0 and 0.6. The obtained copolymers consequently varied in composition as well, and to correct for the difference in hydrodynamic volume between the poly(S) standards used and the copolymers, universal calibration was applied in a way depending on the copolymer composition. The Mark−Houwink constants for the calibration are shown in Table 1.[27,31] In principle these constants can be used only for the calibration of the two homopolymers poly(M(M)A), and there are no constants available for the whole range of copolymers. Davis et al.[27] were faced with the same problem when determining the MMD of copolymers in their pulsed laser experiments. To overcome this, they used the following equation:

$$M_{copol} = M_o^{copol}\left(\frac{M_S}{M_0{}^S}F_S + \frac{M_{M(M)A}}{M_0{}^{M(M)A}}(1 - F_S)\right) \qquad (4)$$

where M_{copol} is the molar mass of the copolymer and M_S is the molar mass according to the direct calibration with the poly(S) standards. $M_{M(M)A}$ is the molar mass the sample would have if it were a homopolymer of M(M)A and if calculated by using universal calibration. M_0^S is the molar mass of S and $M_0^{M(M)A}$ is the molar mass of M(M)A. So M_{copol} is the weighted average (on a molar basis) of M_S and $M_{M(M)A}$. This equation was applied to convert the poly(S) calibration curve to obtain calibration curves for each copolymer composition. For the fits of these calibration curves with polynomials only the molar masses above approximately 10^5 g mol^{-1} are used; see Figure 1.

From the SEC data and the calibration curve of the copolymers a differential log MMD was calculated by multiplying the SEC traces, dW(log M_{copol})/dV_{el}, with the reciprocal slope of the calibration curve dV_{el}/d(log M_{copol}). This weight distribution is then converted into the

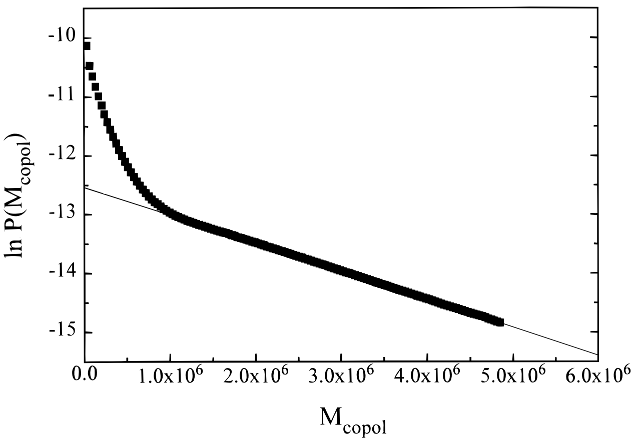

Figure 2. Example of a plot of the natural logarithm of $P(M_{copol})$ against M_{copol}. The plot shown here pertains to the system S−MA at $f_{MAp} = 0.40$ and 2.1×10^{-20} mol of initiator/particle. The maximum molar mass shown in this plot corresponds to the highest SEC standard used.

differential number fraction distribution $P(M_{copol})$ by using eq 5:[32]

$$P(M_{copol}) = \frac{dW(\log M_{copol})}{dV_{el}} \frac{dV_{el}}{d \log M_{copol}} \frac{1}{{M_{copol}}^2} \quad (5)$$

where V_{el} is the elution volume. An example of a plot of the natural logarithm of $P(M_{copol})$ against M is shown in Figure 2. The maximum molar mass taken into account in this plot corresponds to the highest SEC standard used. For high molar masses the curve is linearly dependent on the molar mass so the main chain-stoppage mechanism is indeed transfer to monomer.

The average chain transfer rate coefficient $\bar{k}_{tr}$ can be calculated by multiplying the slope of the linear part with the average molar mass of the monomer units in the copolymer M_o and the average propagation rate coefficient of the copolymerization $\bar{k}_p$; see eq 1. M_o was calculated with eqs 2 and 3 using the parameter values of Table 2.[33−37] As for $\bar{k}_p$, it appears that in these S−(meth)acrylic systems the propagation rate is affected by the penultimate unit of the polymeric radical as well as by the terminal unit. $\bar{k}_p$ can be expressed as follows:[28]

$$\bar{k}_p = \frac{r_i f_i^2 + 2 f_i f_j + r_j f_j^2}{\left(\dfrac{r_i f_i}{\bar{k}_{pii}}\right) + \left(\dfrac{r_j f_j}{\bar{k}_{pjj}}\right)} \quad (6)$$

where $\bar{k}_{pii}$ can be calculated according to a particular model. In the case of the implicit penultimate model for propagation ($\bar{r}_i = r_i$):[38]

$$\bar{k}_{pii} = \frac{k_{piii}(f_i r_i + f_j)}{f_i r_i + f_j/s_i} \quad (7)$$

where k_{piii} is the homopropagation rate constant of monomer i, s_i is a radical reactivity ratio in the penultimate model (in the case of the terminal model ($s_i = 1$) and $\bar{k}_{pii}$ is simply the homopropagation rate constant $k_{piii} = k_{pii}$). Equations 6 and 7 were used with the parameters of Table 2 to calculate the values of $\bar{k}_p$ in both monomer systems. From the transfer constants obtained with the three different initiator concentrations at each composition, it is now possible to determine the value of $\bar{k}_{tr}$ at each composition. These are plotted against the ratio of initiator concentration [I] and the seed particle concentration N_c. An example is shown in Figure 3.

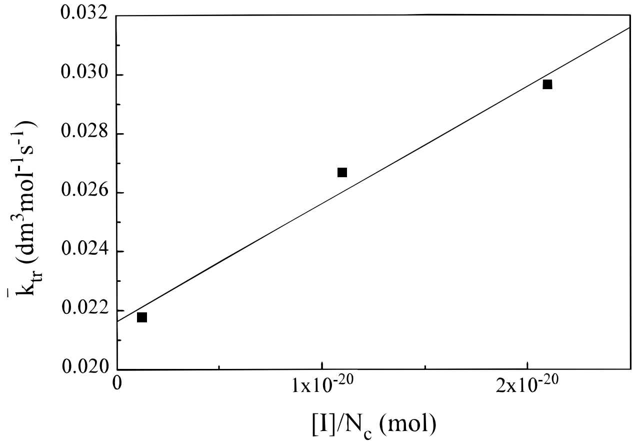

Figure 3. Example of a plot of $\bar{k}_{tr}$ against the ratio of initiator concentration and the seed particle concentration. The results shown pertain to the system S−MA at $f_{MAp} = 0.30$.

Table 2. Homopropagation Rate Constants (k_{piii}) and Reactivity Ratios (r_i/s_i) for the Systems S−MA and S−MMA Used for the Calculation of F_i, $\bar{k}_p$, and A_{ij}

S−i	k_{piii} (dm^3/mol s)	r_S/s_S	r_i/s_i
S−MA	258^{33}−10700^{34}	$0.73^{36}/0.59^{2,a}$	$0.19^{36}/0.02^{2,a}$
S−MMA	258^{33}−616^{35}	$0.523^{30,b}/0.30^{30}$	$0.46^{30,b}/0.53^{30}$

[a] For the system S−MA the values $s_S = s_{MA} = 0.41$ were used for calculation of A_{SMA}.[2] [b] For the system S−MMA the values $r_S = 0.48$ and $r_{MMA} = 0.42$ were used for calculating the copolymer composition with eq 3.[37]

Theoretically, transfer is the only chain-stopping mechanism when no initiator is present. In practice this means that the initiator concentration should be as low as possible and, to have a better estimate for $\bar{k}_{tr}$, the values obtained at the different initiator concentrations should be extrapolated to a value of zero of the initiator concentration. There is no theoretical basis for a linear extrapolation as applied here but is very likely to be correct as will be outlined below. The slope of ln $P(M_{copol})$ versus M_{copol} is also determined partly by termination, but as can be seen in Figure 3, this does not contribute much at the initiator concentrations used (i.e., the slope in Figure 3 is not large). Note that these systems display zero−one kinetics.[2,3,5] It has been argued that the only intraparticle termination event operating in zero−one systems is instantaneous termination between a long radical and a monomeric radical (formed by chain transfer).[1] This monomeric radical can only have entered the particle already containing the long radical, after having escaped from another particle first (exit). In that case the rate of chain stopping by termination is equal to the rate of reentry of monomeric radicals (ρ_{re}) and not to the total rate of entry (ρ) as suggested by Clay et al.[18] This also means that the contribution of termination is very small and that the error introduced by not extrapolating to a zero initiator concentration is negligible, because for a system to be zero−one, the rate of chain transfer to a small molecule should be much higher than the rate of entry ρ_I[1,2] (ignoring the effect of thermal entry). The linear extrapolation to zero initiator concentrations as applied here is therefore probably as good as any. Note that if persulate-derived oligomers can also cause instantaneous termination upon entry (so that termination is

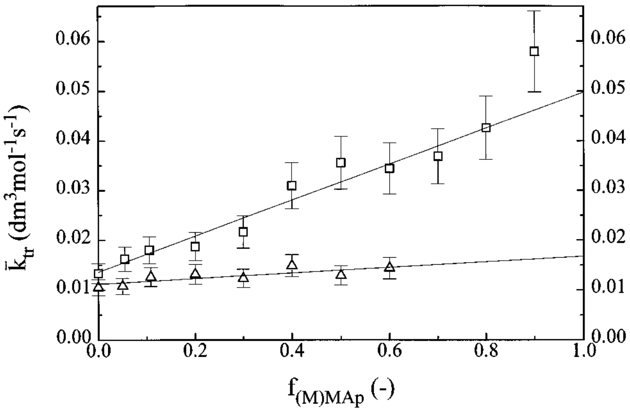

Figure 4. Plot of $\bar{k}_{tr}$ against $f_{M(M)Ap}$ for both the S−MA (□) and the S−MMA (△) system, fitted with eq 10; see below. The point at $f_{MAp} = 0.9$ for S−MA was neglected in the fit.

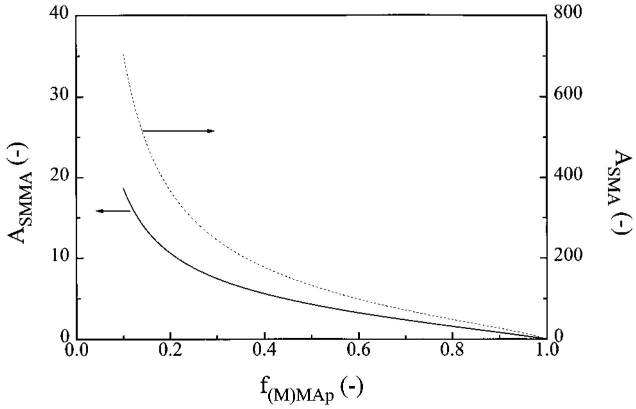

Figure 5. Plot of A_{SMA} (left y axis) and A_{SMMA} (right y axis) at 50 °C as a function of the molar fraction of methyl (meth)-acrylate $f_{M(M)A}$ calculated with eqs 7 and 9 and using the data from Table 2, with the exception of the s values in the system S−MA: $s_S = s_{MA} = 0.41$.[2]

given by the total rate of entry[18,39])—which is suggested by the fact that the initiator concentration does have an effect on the total molecular weight distribution—the method of extrapolation to zero initiator concentration is still valid.

The values for $\bar{k}_{tr}$ thus obtained are shown in Figure 4, a plot of $\bar{k}_{tr}$ against the molar fraction of S in the particles. Two types of errors were taken into account. One error arises from errors in the values of the Mark−Houwink constants. This is estimated to result in an error of 10% in $\bar{k}_{tr}$ when $f_{M(M)Ap} = 1$ and 0% when $f_{M(M)Ap} = 0$. The second source of errors are the SEC analyses, which is assumed to be 5% error for SEC.[34] For the system S−MMA it should be noted that no values for the radical reactivity ratios s_S and s_{MMA} were available at 50 °C, so the values valid at 40 °C were used. The error caused by using these lower temperature reactivity ratios was not taken into account, but is probably neglible as radical reactivity ratios are likely to be temperature-independent.[40,41]

A first conclusion based on these results is that as the fraction of M(M)A increases, so does $\bar{k}_{tr}$. k_{tr} of pure MA could not be determined unequivocally, but it appears to be at least as large as 1 dm^3/mol s, which is in agreement with the value 0.9 dm^3/mol s, calculated by using C_m given Fehervari et al.[42] and the k_p given in Table 2. The dependence of $\bar{k}_{tr}$ on composition in the system S−MA resembles that of $\bar{k}_p$,[2,27] i.e., a slow increase with f_{MA} and a sharp increase when $f_{MA} > 0.8$−0.9. The k_{tr} of S as determined here ((1.1−1.3) × 10^{-2} dm^3/mol s) is in good agreement with the range of values of C_m given in the Polymer Handbook[15] (k_{tr} = (0.9−2) × 10^{-2} dm^3/mol s using the C_m values and the k_p of S in Table 2) and the value found by using the same technique as we used without extrapolation to zero initiator concentration (1.5 × 10^{-2} dm^3/mol s).[43]

B. Interpretation of $\bar{k}_{tr}$ in Terms of Cross-Chain Transfer. The data in Figure 4 represent the overall rate of chain transfer to monomer. However, as stated in the Introduction, for describing the polymerization kinetics in a certain system, the rates of chain transfer to the individual monomers are important as well. These rates cannot be obtained directly from the above-presented data. A model describing the process of chain transfer is needed, and because the rates of propagation are much higher than those of transfer, also a model for propagation is needed to describe the relative concentrations of the different radical types; see below. Although Bamford and co-workers[26] found indications for a penultimate effect in the system S−MMA with CBr$_4$ as the chain transfer agent we used the terminal model for the description of the chain transfer kinetics. A justification for this simplification will be given in section C, where we discuss some mechanistic aspects of the chain transfer processes of this system (see below).

Table 3. Relevant Transfer Reactions and Their Respective Rate Constants (10^{-2} dm^3 mol^{-1} s^{-1}) at 50 °C

reaction	k_{tr}
∼∼MA$^•$ + MA → ∼∼MA + MA$^•$	∼100
∼∼MMA$^•$ + MMA → ∼∼MMA + MMA$^•$	0.7,[47] 3.5[48]
∼∼S$^•$ + MA → ∼∼S + MA$^•$	5
∼∼S$^•$ + MMA → ∼∼S + MMA$^•$	1.6
∼∼S$^•$ + S → ∼∼S + S$^•$	1.1−1.3

As we have chosen a terminal model for chain transfer, we need to take into account only two different types of radicals with different terminal monomer units. The expression for the average chain transfer rate coefficient to monomers i and j is then as follows:[2]

$$\bar{k}_{tr} = \bar{k}_{tr,i}f_i + \bar{k}_{tr,j}f_j = \left(k_{tr,ii}\frac{A_{ij}}{1 + A_{ij}} + k_{tr,ji}\frac{1}{1 + A_{ij}}\right)f_i + \left(k_{tr,ij}\frac{A_{ij}}{1 + A_{ij}} + k_{tr,jj}\frac{1}{1 + A_{ij}}\right)f_j \quad (8)$$

where $\bar{k}_{tr,i}$ is the average chain transfer rate coefficient to monomer i, f_i the molar fraction of monomer i, $k_{tr,ij}$ the cross-chain transfer rate constant of transfer from a polymeric radical with terminal unit i to monomer j and A_{ij} the ratio of polymeric radicals with a terminal unit of type i and polymeric radicals with a terminal unit of type j. A_{ij} can be expressed as follows for the ultimate and penultimate models:[2]

$$A_{ij} = \bar{k}_{pjj}\bar{r}_i f_i/\bar{k}_{pii}\bar{r}_j f_j \quad (9)$$

where $\bar{k}_{pii}$ is a composed propagation rate coefficient (eq 7) and $\bar{r}_i$ is a reactivity ratio equal to r_i in the systems used here. Calculation of A_{ij} for both systems, using the restriction $s_S = s_{MA}$ for the system S−MA,[2] gives high values for A_{SMA}, especially at high molar fractions of S, and moderately high values for A_{SMMA}; see Figure 5. In the case of S−MA (i = S; j = MA) $k_{tr,MAMA}$ is much larger than $k_{tr,SS}$ (see above), but A_{SMA} is so large that the product of $k_{tr,MAMA}$ and 1/(1 + A_{SMA}) is negligible in comparison with the other terms in eq 8, except possibly, at high f_{MA}. In the case of S−MMA (i = S; j = MMA) the value of A_{SMMA} is smaller than the corresponding value of A_{SMA} at the same composition, but the difference between $k_{tr,SS}$ and $k_{tr,MMAMMA}$ (=(0.6−5) × 10^{-2} dm^3/mol s, calculated using the range of values for C_m in the Polymer Handbook[15] and the k_p of MMA in Table 2 (see also Table 3)) is also smaller and therefore the contribution of the product of $1/(1 + A_{SMMA})$ and $k_{tr,MMAMMA}$ in eq 8 is also negligible in the case of S−MMA. This means that there is no significant contribution from the polymeric radicals with a terminal MA or MMA unit to chain transfer, if $k_{tr,M(M)AS}$ is not larger than $k_{tr,M(M)AM(M)A}$. For both systems eq 8 then reduces to

$$\bar{k}_{tr} = k_{tr,SS} + (k_{tr,SM(M)A} - k_{tr,SS})f_{M(M)A} \qquad (10)$$

and this equation can be used with the data in Figure 4 to calculate values for the cross-chain transfer constants $k_{tr,SM(M)A}$. As can be seen in Figure 4, there is a linear dependence of $\bar{k}_{tr}$ on $f_{M(M)Ap}$ for both systems. For the S−MA system $\bar{k}_{tr}$ at $f_{MAp} = 0.9$ seems to be too high to lie on this line. It is possible that at high fractions of MA the relative concentration of MA-terminated radicals is not neglible anymore. For the S−MMA system reactions were carried out with f_{MMAp} between 0 and 0.6, and all resulting points can be fitted with a straight line. So it seems that eq 10 can be used to describe chain transfer to monomer for both systems, at least for molar fractions of MMA in the particles below 0.6 for the S−MMA system and for molar fractions of MA below 0.8 for the S−MA system, and that the contribution of transfer from M(M)A-terminated radicals can be ignored. For both systems the cross-chain transfer rate constants can be calculated, which results in $k_{tr,SMA} = 5 \times 10^{-2}$ dm^3/mol s and $k_{tr,SMMA} = 1.6 \times 10^{-2}$ dm^3/mol s. Several other authors have published data for $k_{tr,SMMA}$ (12 × 10^{-2},[44] 8 × 10^{-2},[45] and 4 × 10^{-2} dm^3/mol s[46]), but invariably the terminal model was used for propagation, which may account for the higher values found, because the use of the terminal model for propagation results in higher $\bar{k}_p$ values if the same reactivity ratios r_i and homopropagation constants are used.

C. Mechanistic Interpretation. In the preceding sections, the terminal model was used for the description of the overall transfer rate coefficient, a choice based upon the observation by Bamford and coworkers[24−26] that the systems S−MA and S−MMA did not show a PUE in the transfer constant of the chain transfer reaction with butane thiol. Considering the fact that the transfer to monomer reactions involve hydrogen transfer, it is likely that the present systems will resemble the transfer with butane thiol more than the transfer with CBr_4. Hence, the terminal model is likely to be a reasonable approximation, and the errors resulting from this assumption will be small.

The results obtained in this study for the cross-chain transfer reactions to MA and MMA are rather interesting when compared to their respective transfer to monomer reactions in homopolymerizations. In Table 3, we have summarized these results. As can be seen from this table, $k_{tr,M}$ in the homopolymerization of MA is at least a factor of 30 larger than the $k_{tr,M}$ in the homopolymerization of MMA,[47,48] whereas this is reduced to a factor of 3 when the terminal unit of the radical is S. This factor of 3 can easily be attributed to a steric effect in the frequency factor of the reaction, but a factor of 30 solely due to steric effects is highly unlikely.[49] These results strongly suggest that the transfer mechanisms in the cross-transfer reactions to MA and MMA are different to the ones in their respective homopolymerizations. It may also suggest that the H transfer takes place from the S-terminated radical to the monomer and not from the monomer to the radical: $\sim CH_2{-}C^{\bullet}HPh + CH_2{=}CR(COOCH_3) \rightarrow \sim CH{=}CHPh + CH_3{-}C^{\bullet}R(COOCH_3)$, where Ph denotes the phenyl substituent in S, and R denotes a H or CH_3 in MA and MMA, respectively. This is in line with the explanation that the difference of a factor of 3 between MA and MMA may be caused by a steric effect. If the H is transferred from the radical to the monomer, it is likely that the activation energies for both processes are similar, as the H will add to double bonds of a similar nature. Furthermore, abstraction of a H atom from the radical will occur at the second carbon atom, which means that steric effects will play a more significant role than when the reaction would take place at the terminal carbon, i.e., a hydrogen transfer reaction from the monomer to the radical.

This hypothesis may be readily checked by performing studies on the temperature dependence of the obtained rate parameters. If the factor of 3 is indeed caused by steric effects, then this factor should remain constant with temperature.

In summary, the result that the transfer reaction of S-terminated radicals with S, MA, and MMA (or their respective impurities) have similar rate constants, strongly suggests that the mechanisms for those three reactions are similar. Although no conclusive evidence exists, the findings are consistent with the idea that the mechanisms of these transfer reactions involve the transfer of a hydrogen atom from the S-terminated radical to the monomer.

Conclusions

For high molar masses the main chain-stoppage mechanism appeared to be transfer to monomer for both investigated monomer systems at the initiator concentrations used. The average chain transfer rate coefficient is linearly dependent on the molar fraction of S, so the simplified equation for the average chain transfer rate coefficient, derived by assuming relatively high values of the ratio of S-terminated radicals and M(M)A-terminated radicals, can be used to describe chain transfer to monomer for both monomer systems. The values of the cross-chain transfer rate constants of S-terminated radicals in both systems have been calculated. The chain transfer rate constant of S-terminated radicals to S has been calculated from the results of both systems and is in good agreement with the literature values. Furthermore, the cross-transfer rate constant to MMA obtained in this study is in accord with literature data, taken into account that these were obtained using the terminal model for propagation. The value for the cross-transfer reaction to MA was found to be only a factor of 3 higher than that for MMA, which is in sharp contrast to the situation of the homopolymerizations. The factor of 3 difference is likely to be caused by steric effects.

Studies on the temperature dependence of these rate constants will shed more light on the exact nature of these transfer reactions and perhaps in the near future computational resources will be large enough to tackle this problem theoretically.

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