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Chain Length Dependent Termination in Free Radical Copolymerization. 1. The Copolymerization System Styrene−Methyl Methacrylate in Bulk at 25 °C

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ABSTRACT: The termination behavior in the stationary free radical copolymerization system styrene (ST)−methyl methacrylate (MMA) at 25 °C was reexamined by means of two newly developed methods. In essence, these are adaptations of the now already familiar methods of determining k_t from rates and degrees of polymerization, originally developed for analysis of pulsed laser polymerization (PLP) experiments, for steady-state experiments conducted by photoinitiation using a continuous light source. Like the earlier methods they allow for the determination of the termination coefficient k_t as a function of chain length. The extent of the chain length dependence of k_t, characterized by the parameter b in the power law connecting k_t and radical chain length ν', $k_t = A(\nu')^{-b}$, is found to be on the order of 0.1 over the full composition range (including the two monomers ST and MMA) which is slightly smaller than the data obtained from PLP for the two pure monomers (0.16−0.18). However, there are no large variations as a function of feed composition. The absolute values of k_t either obtained via extrapolation to unity chain lengths ($k_t^{1,1}$) or calculated for a fixed chain length of 500 (k_t^{500}), however, pass through a maximum. In view of the diffusion-controlled character of the termination reaction this result is interpreted by assuming the mobility of the chain ends to be increased when a monomer unit *different* from the terminal unit is incorporated into the penultimate (or penpenultimate) position of the growing chain, especially if MMA is replaced by ST in a MMA terminated chain. Assisted by the alternation tendency of the copolymer system ST−MMA this might finally lead to an overall chain end mobility in excess of that of either homopolymeric radical for intermediate monomer compositions.

Introduction

The binary copolymerization system styrene (ST)−methyl methacrylate (MMA) is the "most popular" and the best investigated of all the multitude of about 10^4 reasonably conceivable binary copolymerization systems. The reason for this is manifold: (a) the constituent monomers ST and MMA themselves are well-behaved and (not unexpectedly) accordingly well-investigated, (b) the copolymer is soluble in the monomer feed at all compositions, thus guaranteeing a homogeneous "bulk" copolymerization, and (c) the copolymerization system ST−MMA features a high degree of symmetry. Although the (homo)propagation rate constants differ by a factor of more than 3 (in favor of MMA) the two (monomer) reactivity ratios are fairly close to each other (both approximately 0.5[1]) leading to an azeotropic point at about 1:1 monomer (and copolymer) composition. This means that the composition drifts when going to higher conversions are moderate even at feed compositions intermediate between pure monomers and the azeotropic point. These characteristics may be responsible for the fact that this system has acquired a kind of "fruit fly" (*Drosophila melanogaster)* status (as Davis et al.[2] have put it) among the copolymerization systems. It comes thus to no surprise that a lot theoretical considerations−quite generally pertinent to other systems, too−had been based on this specific monomer couple: in 1983 Fukuda et al.[3] reported that Mayo's terminal model[4] failed to reproduce the copolymerization *rates* (40 °C) correctly although it was able to describe the copolymer *composition*. Their findings led to the formulation of a so-called *implicit* penultimate effect with four monomer reactivity ratios (see eq 1; the type of monomer unit in the "penultimate" position is indicated by the first number in parentheses assigned to the various rate constants of chain propagation k_p, while the second number refers to the terminal (radical) unit and the third one to the monomer to be added)

$$r_{11} = \frac{k_p(111)}{k_p(112)},\quad r_{21} = \frac{k_p(211)}{k_p(212)},\quad r_{22} = \frac{k_p(222)}{k_p(221)},\quad r_{12} = \frac{k_p(122)}{k_p(121)} \tag{1}$$

These degenerate to the two familiar ones appearing in the terminal model (r_1, r_2) where the nature of the penultimate unit is irrelevant

$$r_1 = r_{11} = r_{21},\quad r_2 = r_{22} = r_{12} \tag{2}$$

This means that the penultimate unit acts in the *same* way on the two propagation rate constants forming the reactivity ratio and its influence cancels out as long as *relative* quantities (compositions, dyad, triad, etc., frequencies) are concerned. The penultimate unit, however, comes into effect when *absolute* quantities (average propagation constants and rates of copolymerization etc.) are considered. This implicit penultimate effect was expressed by *radical* reactivity ratios (s_1, s_2)

$$s_1 = \frac{k_p(211)}{k_p(111)} = \frac{k_p(212)}{k_p(112)},\quad s_2 = \frac{k_p(122)}{k_p(222)} = \frac{k_p(121)}{k_p(221)} \tag{3}$$

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the first number again referring to the penultimate unit, the second to the terminal radical, and the third one to the monomer to be added. In these ratios the propagation rate constant of a radical bearing a penultimate unit *different* from the terminal one is compared to the propagation rate constant of a radical, in which terminal and penultimate units are identical.

It should be noted that the implicit penultimate model was later on proved to be physically unrealistic and incompatible with a lot of experimental findings, and ab initio calculations[5] and an *explicit* penultimate model should be applied instead. Nevertheless, Fukuda's work is highly remarkable from the *experimental* point of view for two reasons: (a) The experimental k_p data, best characterized by $s_{ST} = 0.30$ and $s_{MMA} = 0.52$, were originally obtained by means of (classical) rotating sector (RS) experiments (yielding k_p/k_t) combined with stationary rate measurements (yielding $k_p{}^2/k_t$). Despite the moderate general reliability of this procedure,[6] these data could later on be fully confirmed by more precise methods aiming at the direct determination of k_p, i.e., either using the pulsed laser polymerization (PLP) method[7] or the analogously applied RS method.[8] (b) As a byproduct of Fukuda's research,[3] the (average) rate constants of termination, k_t, were determined for this system with a remarkable result: The large increase of k_t formerly calculated for intermediate ST−MMA compositions and attributed to polar effects operative in the (cross) termination reaction between radicals of different type could largely be ascribed to the fact that the $k_p{}^2/k_t$ data from stationary copolymerizations were incorrectly analyzed by wrongly applying the terminal model to the propagation rate constants. In more detail, Fukuda et al. were able to show that the unrealistically high values of the so-called φ parameter—long ago introduced by Walling[9] to explain the comparatively low rates of copolymerization at intermediate feed compositions in order to express the preference ($\varphi > 1$) of a "cross-termination" between different radicals (type 1 and type 2) over the geometric mean of the termination between like radicals—defined by

$$\varphi = \sqrt{k_{t,12}{}^2/(k_{t,11}k_{t,22})} \tag{4}$$

would be fully unreasonable for a diffusion-controlled reaction like chain termination. Although Fukuda et al. convincingly demonstrated that k_t exhibited a continuous increase (accompanied by a convex upward curvature) with increasing styrene content in the monomer feed (contrary to the maximum evolving according to the Walling procedure), they could not definitely distinguish between the various models put forward for the composition dependence of the average k_t in copolymerization. In particular, no discrimination was possible between the "trivial" model (with $\varphi = 1$) and the Atherton−North "diffusion" model,[10] which averages k_t according to the copolymer composition

$$k_t = X_1 k_{t,1} + X_2 k_{t,2} \tag{5}$$

with X_1 and X_2 being the fractions of monomers 1 and 2 incorporated into the copolymer and $k_{t,1}$ and $k_{t,2}$ the termination rate constants in the homopolymerization of monomers 1 and 2 (corresponding to $k_{t,11}$ and $k_{t,22}$ in eq 4).

In the meantime, it was unambiguously established that k_t is subject to a (negative) chain length dependence. This chain length dependence—albeit moderate for ST and MMA—might further complicate the situation because of the "variation" of the conditions of polymerization when passing from a monomer like ST ($k_p \approx 80$ L mol^{-1} s^{-1} at 25 °C) to MMA ($k_p \approx 300$ L mol^{-1} s^{-1} at 25 °C). The range of chain lengths in which termination occurs may hence considerably shift to higher chain lengths and accordingly to lower values of effective (mean) k_t values if the experiments—as is usual—are carried out at constant rate of initiation. As a consequence, it was clear that revisiting the situation had to include the assessment of the chain length dependence of k_t in the copolymerization system ST−MMA. Actually, the two pure monomer systems, ST as well as MMA, had been investigated by ourselves applying various methods: The first one[11] (in the following denoted as method A) gives an average (denoted $\overline{k_t^m}$) defined by

$$\overline{k_t^m} = \frac{k_p{}^2}{\overline{P_w} v_p}[M]^2(3 - \delta) \tag{6}$$

(To be consistent with our earlier papers we adhere to the definition where k_t counts the disappearance of a *pair* of radicals. Numerical values of k_t in this paper therefore are twice those based on the IUPAC recommended definition of k_t that counts the disappearance of *single* radicals.) This method makes use of the invariance of the second moment of the CLD (represented by the product of the weight-average degree of polymerization $\overline{P_w}$ and the rate of polymerization v_p, strictly speaking a second moment per time) toward initiation conditions[12] (stationary or pseudostationary) in the case of chain length independent termination and negligible chain transfer, with the quantity δ representing the contribution of disproportionation to overall termination. The second one (method B) is derived from the expression for the rate of polymerization v_p in pulsed laser polymerization (PLP),[13] equally developed originally for chain length independent polymerization,[14] yielding a *different* average k_t (denoted as $\overline{k_t^*}$)

$$\overline{k_t^*} = \frac{k_p[M]}{v_p t_0}\ln\left\{1 + \frac{\rho \overline{k_t^*} t_0}{2}\left[1 + \left(1 + \frac{4}{\rho \overline{k_t^*} t_0}\right)^{1/2}\right]\right\} \tag{7}$$

with ρ being the concentration of radicals produced in each pulse and t_0 again being the inverse laser frequency. The experimental average k_t values for ST and MMA obtained from different chain length regimes could well be represented by a power law of the type

$$\overline{k_t} = A(\nu')^{-b} \tag{8}$$

ν' being the mean chain length of the radicals in the moment of undergoing termination related to the number-average degree of polymerization by

$$\nu' = \overline{P_n}(1 + \delta)/2 \tag{9}$$

For ST[15] as well as for MMA[16] at 25 °C b values of 0.16−0.18 were obtained for both averages, $\overline{k_t^m}$ and $\overline{k_t^*}$. Computer simulations[13] demonstrated that the latter quantity $\overline{k_t^*}$ is very close to the *true* (event weighted) average $\langle k_t \rangle$ while $\overline{k_t^m}$, in agreement with experiments, underestimates $\langle k_t \rangle$ by about 15−20% for this extent of chain length dependence. A third method (C) is based on a procedure in extenso described recently.[17] Essentially, it consists of carrying out a three-parameter nonlinear regression, fitting the experimental CLD (determined by SEC) to the theoretical expression of an ideal single-pulse polymerization derived using a power law (all radicals are supposed to have the same length i)

$$k_t^{i,i} = k_t^{1,1} i^{-b} \tag{10}$$

where $k_t^{1,1}$ (approximately equal to the quantity A in eq 8[18]) is the hypothetical rate constant of termination between two radicals of unity chain length, however, with otherwise all the properties of a macroradical. This method is completely independent of all the quantities entering the two other methods, such as k_p, ρ, υ_p, $\overline{P_n}$, and $\overline{P_w}$, and is nearly insensitive toward the choice of δ. Two of the three parameters evaluated in this way are of only minor interest and are moreover interrelated through a normalization constant that unfortunately cannot be determined independently. The third parameter, on which all the concern is concentrated, corresponds to the exponent b characterizing the chain length dependence of the termination reaction. Method C returned slightly larger b values for the two monomers ($\approx$ 0.20), but in general, the agreement is quite satisfactory.

Of course, it would be quite tempting to apply one of these methods also to the copolymerization system ST–MMA. Rather surprisingly, however, it has been overlooked so far that once the k_p data are established it is not necessary to resort to pseudostationary polymerization and accordingly to apply PLP methods in the investigation of k_t and its chain length dependence: Method A and method B can be easily modified to be applicable to stationary polymerizations, too.[19] As a matter of fact, eq 6 can be used as it stands, because of its indifference toward initiation conditions, stationary or pseudostationary. Within the context of using data from steady-state polymerizations, it will be named method A′. With respect to method B the appropriate rate equation for stationary polymerization has to be used instead of eq 7

$$\overline{k_t^*} = \frac{{k_p}^2}{\overline{P_n}\upsilon_p}[\mathrm{M}]^2 \frac{2}{1+\delta} \tag{11}$$

In essence this equation represents the relationship between rate of polymerization and rate of initiation with the latter expressed by the number-average degree of polymerization in absence of chain transfer reactions, in the same way as this has been the case with eq 7. In effect the quantity ρ that is not readily accessible otherwise was expressed by

$$\rho = 2\upsilon_p t_0/(\overline{P_n}(1+\delta)) \tag{12}$$

The method of calculating k_t data from eq 11 accordingly will be named method B′. Thus, the task of this paper is a 2-fold one:

(a) The first is to establish a method of determining k_t and its chain length dependence from *stationary* polymerizations.

(b) The second is to apply this method to a reanalysis of termination in the copolymerization system ST–MMA.

Experimental Part

Materials. ST and MMA were purified by distillation in an atmosphere of nitrogen under reduced pressure and in the presence of an inhibitor remover (Aldrich, *tert*-butylcatechol-remover for styrene, hydroquinone-remover for MMA). The photoinitiator benzoin, applied in concentrations between 0.4 and 9.4 × 10^{-3} mol L^{-1} was twice recrystallized from ethanol. Tetrahydrofuran (THF) for SEC measurements was refluxed over potassium, distilled in an atmosphere of nitrogen, and stabilized with 2,6-di-*tert*-butyl-*p*-cresol.

Polymerizations. The freshly distilled monomers were mixed accordingly to the desired monomer feed concentrations and initiator was added. The reaction mixture (total volume 2.5 mL) was charged to Pyrex ampules (3 cm × 1 cm × 1 cm) and subsequently degassed by a number of freeze–pump–thaw cycles on a high vacuum line. Each cell was placed in a thermostat, adjusted to 25 °C, and irradiated by UV-light from a high-pressure Hg lamp SH 2/LAX 1530, essentially eliminating all wavelengths other than 365 nm by use of appropriate filters. Samples were exposed to UV light for 2–60 min to allow for about 0.2–1.0% conversion of monomer to polymer.

Analysis. Immediately after irradiation, 100 μL of the sample was injected directly without dilution into the size exclusion chromatography system, consisting of an on-line degasser (ERC-3215, ERC Inc.), an isocratic LC pump (Iso-Chrom, Spectra Physics), and four SEC columns (10^3, 10^4, 10^5, 10^6 Å SDV, Polymer Standards Service), used at 30 °C with THF as solvent. Detection was by a dual-detector (Viscotek, model 200), which consisted of a differential refractometer (DRI) and a differential viscometer (DV). In the case of conventional or weighted calibration, a differential refractometer (Waters, model 2410) was used. Conversions were determined by the calibrated area under the differential refractometer signal, the d*n*/d*c* values for different copolymer compositions in relation to that of PMMA and PST were quantified using different concentrations of copolymers of different compositions. The remaining sample was mixed with a small amount of 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO), to prevent further polymerization, the monomer was carefully evaporated off, and the polymer was diluted with THF to a concentration of ≈3 mg mL^{-1}. SEC analyses were performed again in order to obtain *accurate* molecular weight distributions. Molecular weight distributions were calculated by using both PST and PMMA standards (Polymer Standards Service) of narrow polydispersities. The copolymers were measured either by universal calibration (combination of DRI and DV detector) or using combined PMMA/PST calibration curves, calculated according to the composition of the copolymer samples via linear combination. Number-average degrees of polymerization and weight-average degrees of polymerization were evaluated from the molecular weight distributions. The composition was calculated using the reactivity ratios published by Madruga et al.,[20] $r_{\mathrm{ST}} = 0.48$ and $r_{\mathrm{MMA}} = 0.41$. The k_p data for analysis were taken from our study using the rotating sector method[8] at 25 °C (with subsequent analysis of the CLD) and the elaborate investigations of Coote et al.[2] interpolated for this temperature. The remarkable agreement between these two sets of data is demonstrated in Figure 1. Although the choice of the fraction of disproportionation has no dramatic effect on $\overline{k_t^{\mathrm{m}}}$, there is some problem with respect to the calculations, eqs 6 and 11, respectively. For $x_{\mathrm{ST}} = 1$ and $x_{\mathrm{ST}} = 0$ the situation is quite clear: one might resort to the literature data $\delta = 0.1$[21] (ST) and $\delta = 0.7$[22] (MMA). More delicate is the situation for the ST/MMA copolymerization system. The scarce information[23,24] available suggests that δ should be the same as for pure ST over most of the composition range and will approach the value for pure MMA ($\delta = 0.7$) only for compositions very rich in MMA. This is consistent with the observation that the ST-terminated radicals dominate the

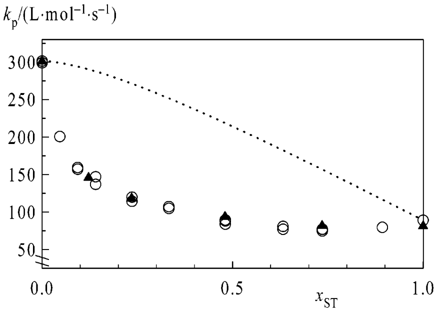

Figure 1. Experimentally determined k_p data: rotating sector[6] (full triangle up) and pulsed laser polymerization[2] (open circle), in both cases with subsequent analysis of the chain length distribution by size exclusion chromatography. The dotted line shows the function resulting from Mayo's terminal model.

radical population up to high MMA contents.[8] The copolymerization data were consequently analyzed using $\delta = 0.1$, the same value as for $x_{ST} = 1$ for all comonomer compositions. It should be noted that any error in δ will influence the absolute values of k_t only, but not their chain length dependence.

Curve-Fitting Procedures. All the necessary multiparameter nonlinear regressions were carried out with Prism 3.00, by GraphPad Software.

Error Estimation. Because of the complex structure of the procedure used for estimating k_t it is profitable to have some idea about the errors to be expected. The total error originates from two different sources. The first type comprises the error connected with the scatter of individual data points (and their mean, respectively, if—as usual—more than one data point is available) while the second refers to those errors which come into play *additionally* with the way *how* the individual experimental data are converted into k_t values, especially in copolymerization systems. This more important type of errors is caused by the uncertainty of the quantities entering into the equations used for calculating $\overline{k_t^*}$ and $\overline{k_t^m}$ (eqs 2 and 7). Because the method itself so far was the same for all compositions, the error caused by the factors from the first group is of similar magnitude as that in homopolymerization systems and will be fairly of the same order as for the related methods of determining k_t, e.g. by PLP-associated methods. In accordance with the data given in refs 2 and 8, we have assumed a SD (standard deviation of the mean values) of 5% for k_p; the SDs for $\overline{P_n}$ and $\overline{P_w}$ were estimated to be 12 and 6%, respectively, and that of v_p to be 1%. With respect to δ in the copolymerization system ST−MMA, SD = 0.3 ($\delta = 0.1$) was chosen for all copolymerization systems. For homopolymerization of ST, SD = 0.1 ($\delta = 0.1$), and for homopolymerization of MMA, SD = 0.3 ($\delta = 0.7$). The error bars shown in the diagrams (Figures 6−9) and the SD in Table 1 demonstrating the composition dependence of k_t refer to the *combined* (total) SD, calculated based on error propagation and summation.

Table 1. Compilation of the Results Obtained by Method A′ and B′ for Photoinitiated Steady State Polymerization for the Copolymerization System ST−MMA in Bulk at 25 °C

x_{ST}	X_{ST}	b	$k_t^{1,1}$ (10^8 L mol^{-1} s^{-1})	k_t^{500} (10^8 L mol^{-1} s^{-1})	k_p (L mol^{-1} s^{-1})	δ
			Method A′ ($\overline{k_t^m}$)			
0.000	0.000	0.105	0.839 ± 0.158	0.438 ± 0.077	300	0.7
0.122	0.212	0.098	1.796 ± 0.293	0.977 ± 0.153	146	0.1
0.235	0.330	0.067	1.769 ± 0.310	1.164 ± 0.182	118	0.1
0.480	0.500	0.041	1.684 ± 0.304	1.306 ± 0.205	94	0.1
0.735	0.670	0.038	1.556 ± 0.262	1.229 ± 0.192	82	0.1
1.000	1.000	0.089	1.470 ± 0.186	0.845 ± 0.103	80	0.1
			Method B′ ($\overline{k_t^*}$)			
0.000	0.000	0.144	1.114 ± 0.215	0.457 ± 0.082	300	0.7
0.122	0.212	0.108	2.116 ± 0.451	1.081 ± 0.225	146	0.1
0.235	0.330	0.097	2.303 ± 0.518	1.261 ± 0.263	118	0.1
0.480	0.500	0.067	2.163 ± 0.492	1.431 ± 0.299	94	0.1
0.735	0.670	0.066	1.947 ± 0.458	1.295 ± 0.270	82	0.1
1.000	1.000	0.090	1.496 ± 0.266	0.858 ± 0.140	80	0.1

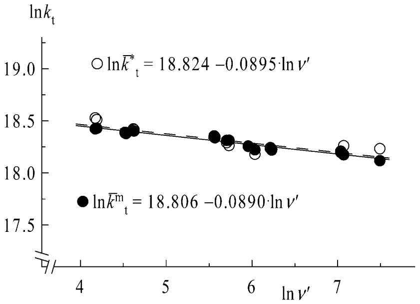

Figure 2. k_t data for the polymerization of ST in bulk at 25 °C obtained by method A′ ($\overline{k_t^m}$; full circle; —) and method B′ ($\overline{k_t^*}$; open circle; - - -).

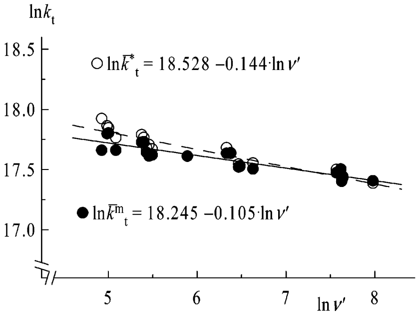

Figure 3. k_t data for the polymerization of MMA in bulk at 25°C obtained by method A′ ($\overline{k_t^m}$; full circle; —) and method B′ ($\overline{k_t^*}$; open circle; - - -).

Results and Discussion

Pure Monomers Styrene (ST) and Methyl Methacrylate (MMA). The first task of this study was to subject the two monomers to the procedures outlined above. The data obtained for ST at 25 °C, $k_p = 80$ L mol^{-1} s^{-1} and $\delta = 0.1$, using method A′, eq 5, and method B′, eq 11, are presented in Figure 2 while the results from the same procedure for MMA, 25 °C, using $k_p = 300$ L mol^{-1} s^{-1} and $\delta = 0.7$ are given in Figure 3. The most obvious result in both cases is that the exponents b are markedly smaller than those obtained from the analogous PLP experiments, especially in the case of ST. Common with these results, however, is the fact that there is still a significant chain length dependence of k_t left that is fairly of the same order for the two monomers. It is difficult to give a reasonable explanation for this difference. One should, however, have in mind that the chain length distribution (CLD) is sensibly different for polymer samples prepared by PLP on one hand and by steady-state polymerization on the other. This might have some consequences, if—as it has been published recently[25]—there exists some chain length dependence of k_p. Slight errors in the choice of the inserted absolute values of k_p and δ alone, however, cannot be held responsible for the difference observed, as we have tested.

The Comonomer Composition 1:1. This specific comonomer composition has long played an important role not only because it is close to the azeotropic point of the system but also because it may additionally serve as a first discriminator concerning the polymerization mechanism involved: a cationic initiation mechanism leads to PST, an anionic one to PMMA while in the case

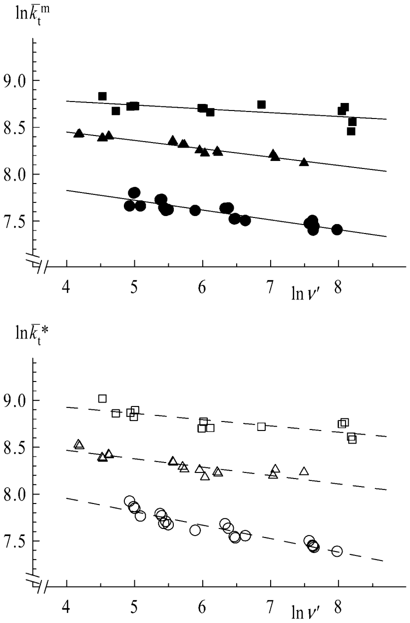

Figure 4. k_t determined according to method A′ ($\overline{k_t^m}$; full symbols) and according to method B′ ($\overline{k_t^*}$; open symbols) for the homopolymerization of MMA (triangle up) and ST (circle) in bulk and for the copolymerization system ST−MMA. $x_{ST} = 0.5$ (square).

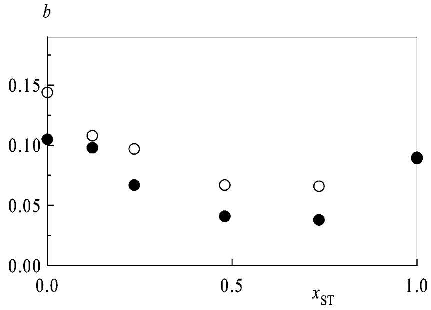

Figure 5. Parameter b vs x_{ST} for $\overline{k_t^m}$ (full circle, method A′) and $\overline{k_t^*}$ (open circle, method B′), respectively.

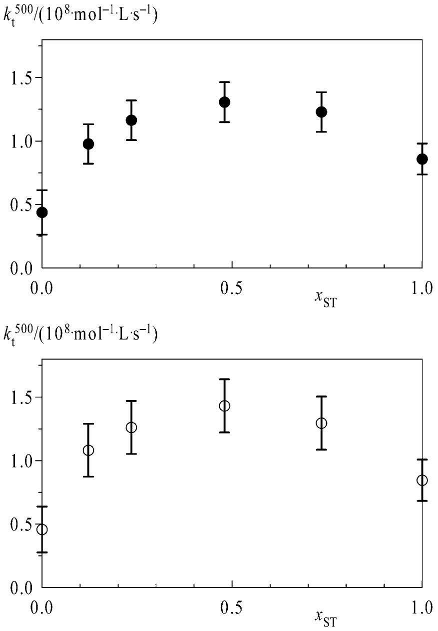

Figure 6. k_t^{500} determined according to method A′ ($\overline{k_t^m}$; full circle) and method B′ ($\overline{k_t^*}$; open circle), respectively.

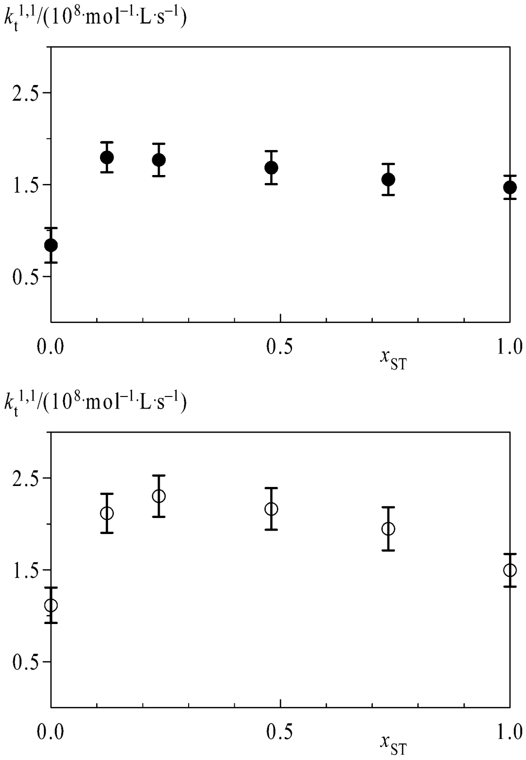

Figure 7. $k_t^{1,1}$ determined according to method A′ ($\overline{k_t^m}$, full circle) and method B′ ($\overline{k_t^*}$, open circle), respectively.

of free radical initiation a 1:1 statistic copolymer results. In this work, its behavior casts a first light on the composition dependence of k_t: the most remarkable result—as is shown in Figure 4—is that k_t is markedly larger than for any of the two pure monomers. This definitely rules out any theory that fails to allow for a maximum as a function of copolymer composition. The chain length dependence of k_t is still somewhat weaker ($b = 0.07$ and $b = 0.04$, respectively) than what was observed for the two pure monomers.

Other Comonomer Compositions. In the same way the comonomer compositions $x_{ST} = 0.122$, $x_{ST} = 0.235$, and $x_{ST} = 0.735$ were analyzed, too. They very consistently fit into the picture already obtained. The exponent b is always about 0.1 (or slightly below, especially if it is evaluated according to method A′) and passes through a slight minimum. This is demonstrated in Figure 5. As an important result, accordingly, there are no great differences with respect to the chain length dependence of k_t over the whole range of monomer feed composition which means that—as an excellent approximation—the whole copolymerization system ST−MMA can be treated in the same fashion with respect to the chain length dependence of k_t. The k_t data *definitely* form a curve convex upward with a distinct maximum, independently *which* method (A′ or B′) is used and whether data referring to the same chain length $\nu' = 500$ (for better comparison in view of the slight differences observed concerning the parameter b) or the quantity $k_t^{1,1}$ from eq 10 are analyzed (Figures 6 and 7, respectively). Because the standard deviation (SD) of the mean values as well as the SD of the values for each composition is rather small (about 2% for k_t^{500} and a little larger for $k_t^{1,1}$) and even the error arising from the uncertainty in the input values necessary for calculating k_t (the total error indicated by the error bars), albeit larger, is still small enough to separate the error bars (referring to the combined *total* error) for the 1:1 mixture from the error bars for the two pure monomers with respect to the k_t^{500} data, this observation has to be taken as *significant*. Apart from the fact that there is a teeny overlap between the error bars referring to the 1:1 mixture and pure ST for the more sensitive $k_t^{1,1}$ data when analyzed according to method A′ (not according to method B′) the only remarkable difference between the behavior of k_t^{500} and $k_t^{1,1}$ is that the maximum for k_t^{500} is close to $x_{ST} = 0.5$ while the position of the maximum of $k_t^{1,1}$ is shifted toward more MMA-rich compositions. The complete set of data is compiled (together with the data for pure monomers and the 1:1 composition) in Table 1. It should be noted that these findings are in good qualitative agreement with the earlier results which had been obtained by RS−SEC techniques according to Method A without taking into account the difference in chain lengths formed with different comonomer ratios.[8] In that communication the behavior of k_t as a function of feed composition was explained by a Walling-type φ factor of about 3, which was much smaller than necessary ($\varphi \approx 10-20$) if the k_p data calculated from Mayo's terminal model (upper curve in Figure 1) and not those from the direct experimental determination of k_p were inserted into eq 6. A preference of cross termination caused by differences in polarity, however, is out of question due to the generally accepted diffusion-controlled character of the termination reaction. Nevertheless, the particular type of dependence of k_t on x_{ST} implies the existence of an additional factor that favors the termination reaction between polymer radicals originating from intermediate comonomer compositions. In the Atherton−North model, eq 5, k_t is connected with the copolymer composition allowing for the fact that the diffusion behavior of the radical chains is somehow influenced by their composition. According to the current view, it is the diffusion behavior of the *terminal* segment(s) that is the rate-determining step in termination. Assuming the composition of the terminal segments resembling the overall copolymer composition it is reasonable to plot the k_t data vs the *copolymer composition* and not vs the monomer feed composition. This is done in Figures 8 and 9 for k_t^{500} and $k_t^{1,1}$ respectively. Of course, the maxima are retained in these plots in a significant manner so that the Atherton−North model that makes a mere weighted averaging of the two homopolymer k_t data is unable to account for the observed curve form. Obviously, there must be some nonlinear "extra" effects acting on k_t: when some comonomer is added to the homopolymerization of ST or MMA, a partial replacement of the ST or MMA units in the chain (end) necessarily takes place. This might be favored by the specific properties of the ST−MMA system already mentioned in the Introduction section: both monomer reactivity ratios being close to 0.5 not only implies a preference for the incorporation of the minority monomer into the chain but also is responsible for an alternation tendency of the two monomer units. This will certainly also hold for the chain ends. It is evident that at least one of the cross termination coefficients has to exceed the higher one of the two homopolymerization termination coefficients (certainly that between −ST−ST* radicals) in order to make k_t higher in some intermediate comonomer composition than in either homopolymerization system. The most probable candidates responsible for such an effect could be the reactions involving the −ST−MMA* radical which will significantly contribute to the overall radical populations in intermediate and especially MMA rich monomer feeds. The arguments are the following ones:

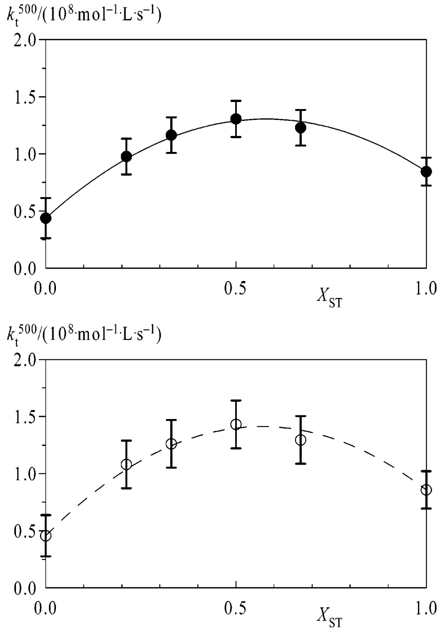

Figure 8. k_t^{500} determined according to method A′ ($\overline{k_t^{m}}$, full circle) and method B′ ($\overline{k_t^{*}}$, open circle), respectively, vs copolymer composition X_{ST}. The curves correspond to eq 13 with $\psi = 3.4$ for method B′ (- - -) and $\psi = 3.2$ for method A′ (—).

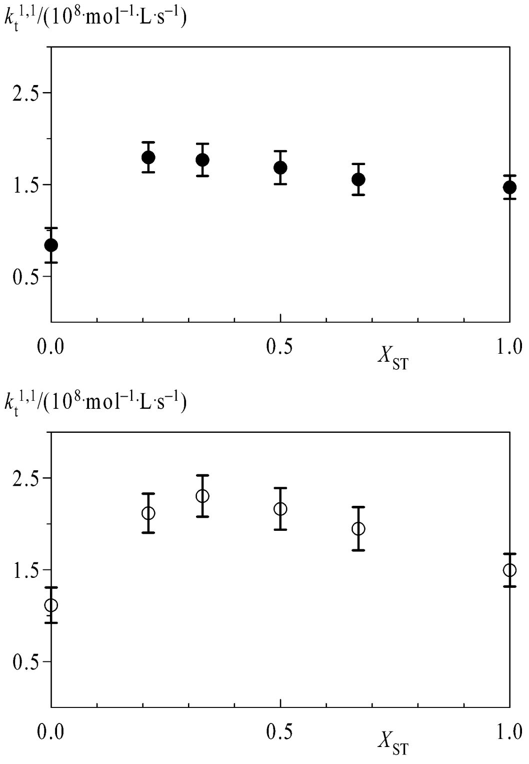

Figure 9. $k_t^{1,1}$ determined according to method A′ ($\overline{k_t^{m}}$, full circle) and method B′ ($\overline{k_t^{*}}$, open circle), respectively, vs copolymer composition X_{ST}.

(a) We assume the bimolecular termination to be controlled by the mutual diffusion of the chain ends bearing the radical site.

(b) According to Smoluchowski the rate constant of a bimolecular diffusion-controlled process is given by the product $(D_1 + D_2)(r_1 + r_2)$ where D_i is the diffusion coefficient of the "chain end" i and r_i its contribution to the collision distance $r_1 + r_2$.

(c) In the radical −ST−MMA*, the effective "flexible joint" is shifted away from the chain end, thus increasing r_i in comparison with the −ST−ST* radical and, as a consequence, enabling the −ST−MMA* radical to "explore" a larger area. Certainly, this will be accompanied by some decrease of D but there might be well a net overall gain.

This interpretation is also consistent with the rather steep increase with increasing styrene content in MMA-rich compositions (compared with the less pronounced increase when adding MMA to ST) where the replacement of −MMA−MMA* radicals by −ST−MMA* plays the major role. To some extent a similar argument might also apply to the replacement of ST in the penultimate position of a −ST−ST* radical by an isolated MMA unit: the flexibility of the bond connecting MMA and ST in a −MMA−ST* radical is possibly higher than that connecting the two ST units in −ST−ST* radicals because of the replacement of one bulky substituent at the penpenultimate carbon atom by two smaller ones. Unfortunately, no independent proof is yet available for this hypothesis.

Formally, the k_t behavior can be well reproduced by an equation of the form

$$(k_t^{1,1})_{\mathrm{Cop}} = X_{\mathrm{ST}}^{\ 2}(k_t^{1,1})_{\mathrm{ST}} + X_{\mathrm{MMA}}^{\ 2}(k_t^{1,1})_{\mathrm{MMA}} + 2\psi\overline{(k_t^{1,1})}X_{\mathrm{ST}}X_{\mathrm{MMA}} \quad (13)$$

Here $(k_t^{1,1})_{\mathrm{Cop}}$ is the quantity derived from the experiments, $\overline{(k_t^{1,1})}$ is a mean value of $(k_t^{1,1})_{\mathrm{ST}}$ and $(k_t^{1,1})_{\mathrm{MMA}}$ (in the present case it makes no difference whether arithmetic or geometric), and ψ is the quantity accounting for the extra effect associated with the mobility increase by exchange of a majority unit by a minority one. As is demonstrated in Figure 8, ψ values between 3 and 4 will give a good description of the data points.

Conclusions

This investigation has demonstrated two important things:

(i) Once k_p data are available, steady-state experiments can be used to determine k_t and its chain length dependence with the same effort but much less sophisticated instrumentation. In addition, kinetic data originating from stationary experiments may be advantageous over pseudostationary data and may be better suited when being used in modeling steady-state processes, which constitute the majority of the industrial important applications.

(ii) These methods can also be used to analyze copolymerization systems. In the reinvestigation of the system ST−MMA, it was found that although the extent of the chain length dependence of k_t does not vary extensively over the whole composition range (including the two pure monomers), k_t passes through a maximum as a function of comonomer composition. This is difficult to explain in the context of the *current* theories of chain termination in free radical polymerization based on the diffusion-controlled nature of termination because they do not allow for any nonlinear extra effects. Without abandoning the idea of diffusion-control, therefore, we suggest the increase of the termination rate coefficient for intermediate comonomer and copolymer compositions, respectively, to be due to an increase of chain-end mobility that is induced by the exchange of one of the (nonterminal) units in the end region of the growing MMA terminated chain by the more flexible ST unit. Of course, this interpretation would need support from investigations of other copolymerization systems. It appears, however, that an equation formally similar to the one put forward by Walling[9] many decades ago—the justification of which is incompatible with diffusion control—is able to give a qualitatively correct description of the results.

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Note Added after ASAP Posting

This article was released ASAP on 1/20/2004. In reference 5, the year was changed from 2000 to 1999. The correct version was posted on 01/28/2004.

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