Chain Length Dependent Propagation Rate Coefficient k_p in Pulsed-Laser Polymerization: Variation with Temperature in the Bulk Polymerization of Styrene and Methyl Methacrylate

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ABSTRACT: The pulsed-laser polymerization (PLP) with subsequent GPC analysis of the resulting polymers was applied to the bulk polymerization of styrene and methyl methacrylate in the temperature range 25−70 °C. The chain length dependence of the rate coefficient of chain propagation k_p previously found in 25 °C experiments was confirmed; its extent increases even slightly with temperature. The effect is interpreted to be caused by a progressive displacement of monomer from the proximity of the radical chain end by the rest of the chain, thus decreasing the local monomer concentration which results in a formal decrease of k_p if the average monomer concentration is inserted into its calculation. Aided by computer simulations based on this concept this decrease could be modeled and parametrized; the difference between the extrapolated values of k_p for zero and infinite chain length $k_p(0)$ and $k_p(\infty)$ amounts to about 40−60% of $k_p(0)$, somewhat depending on temperature, monomer, and modeling function. The variation of the k_p data actually observed is markedly less, of course (about 25−35%). The chain length for which the decrease from $k_p(0)$ to $k_p(\infty)$ is 50% complete was calculated to be on the order of 100, somewhat higher for the (stiffer) poly(MMA) chain.

Introduction

In a recent publication,[1] we have voiced our doubts about the chain length independence of the rate constant of chain-propagation k_p. Our skepticism was based on our results obtained with styrene in bulk and in solution systems and with methyl methacrylate in bulk where we invariably found that the positions of the points of inflection (L)[2] in the chain length distribution (CLD) as evaluated by gel permeation chromatography (GPC) for polymers prepared by pulsed-laser polymerization (PLP) did not increase proportionally to the time t_0 elapsing between two successive pulses according to[3]

$$L = k_p[\mathrm{M}]t_0 \tag{1}$$

This means that the quantity relating L and t_0, i.e., the product k_p times monomer concentration [M], is no constant.[4] It is known, admittedly, that the first propagation steps immediately after the initiation process may proceed somewhat more rapidly than the following ones[5] referring to true polymeric radicals. This phenomenon, however, should be restricted to at most two or three steps so that a radical of chain length three in any case should exhibit the same propagation reactivity as a macroradical of infinite chain length ($k_p(\infty)$), with all extra effects caused by the initiating radical being eliminated. The increased propagation activity of these oligomeric radicals, however, has a limited influence on the average (integral) k_p values $\overline{k_p}(L)$ only. If a number of j propagation steps is assumed to be infinitely fast (which certainly is an exaggeration) then following an argument put forward by Kaminsky et al.,[6] the average rate constant $\overline{k_p}(L)$ observed after L propagation steps would be

$$\overline{k_p}(L) = k_p(\infty)\left(1 + \frac{j}{L}\right) \tag{2}$$

which would result in a 3% error for $L = 100$ and $j = 3$. The effects observed by us were much larger, being approximately 20−25%. Accordingly, such an initial high propagation activity of the radical chains restricted to a few steps is not able to account for our findings.

Of course, we did our best[1] in making a careful analysis of all factors that may lead to falsifications of the k_p data derived from PLP,[7] among them the fact that the point of inflection is a good (but not perfect) measure of L_0,[3,8] the influence exercised by the number of radicals produced per pulse[7] etc. These, however, were shown to be of no importance or to point even into the opposite direction. The trivial argument that our effect would be due to an increase of temperature produced by increasing pulse frequency (decreasing t_0) was refuted by the fact that k_p data originating from higher order points of inflection according to

$$L^{(n)} = nk_p[\mathrm{M}]t_0 \tag{1a}$$

when detectable, fell on the same curve as the data from first-order inflection points within experimental error, as it will become evident also from Figure 1, parts a and b.

It should be noted that at present there is no method available that can determine k_p directly. This holds true also for PLP: Looking at eq 1 or eq 1a makes it clear that k_p is obtained from L and t_0 by dividing k_p[M] by the nominal monomer concentration $[\mathrm{M}]_0$ in the system. This means that not only k_p but also [M] might be guilty of the effect we have observed if [M]—as strictly should be the case—is considered as the *local* monomer concentration. On the basis of simulation data we have in fact interpreted this apparent chain length dependence of k_p as the result of a decrease of this local monomer concentration at the site of propagation: with increasing chain length the trailing rest of the radical chain will

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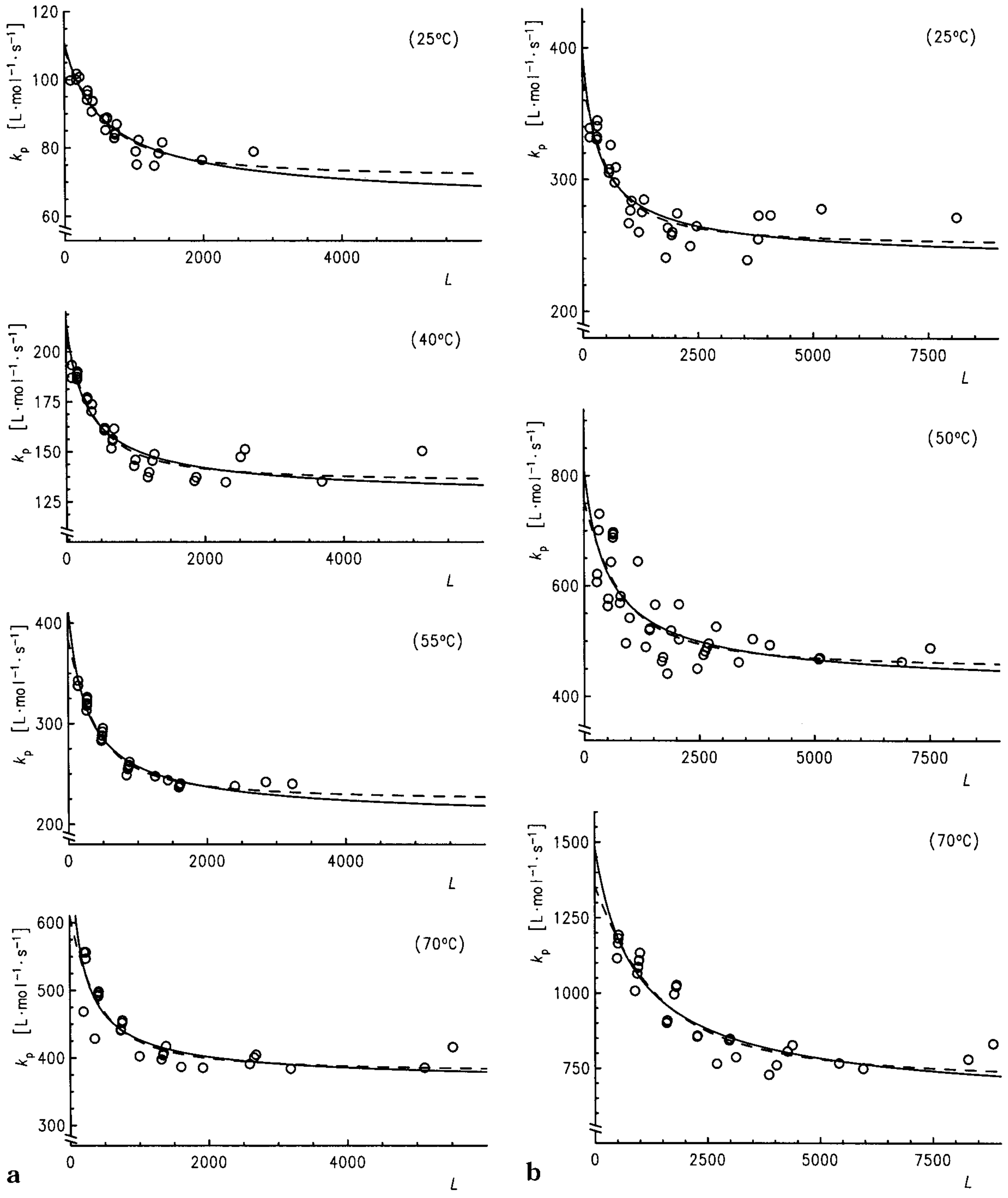

Figure 1. (a) Experimental k_p data vs chain length for styrene (St) in bulk at 25, 40, 55, and 70 °C, derived from the first and second point of inflection. The best nonlinear fits according to the integral function eq 5 (—) and eq 7 (– –) are indicated, the parameters being given in Table 1. (b) Experimental k_p data vs chain length for methyl methacrylate (MMA) in bulk at 25, 50, and 70 °C, derived from the first and second point of inflection. The best nonlinear fits according to the integral function eq 5 (—) and 7 (– –) are indicated, the parameters being given in Table 1.

progressively edge out the monomer of the site of reaction. By computer simulations, this effect was shown to extend to about 30 degrees of polymerization.[1] Because the *experimental* k_p, as derived from PLP, represents a mean over all individual propagation steps (up to L) the decrease in k_p actually extends over a much broader range than that exercised on *individual* degrees of polymerization of the growing chain. Thus, dividing $k_p[M]$ by $[M]_0$, which of course is larger than the local monomer concentration, leads to k_p data decreasing with chain length although the true rate constant k_p might remain untouched. In the absence of a *direct* access to the local monomer concentration and the failure to describe it explicitly, however, these *apparent* k_p data will be the ones polymerization kinetics has to deal with. In the course of our investigation of the temperature dependence of k_t (the rate coefficient of bimolecular chain termination) in the bulk polymerization of styrene and methyl methacrylate where we applied pulsed-laser polymerization, too, we more or less automatically collected k_p data for these systems. It is the aim of this paper to present these data and to provide further evidence of a (formally) chain length dependent k_p in free radical polymerization.

Experimental Section

Materials. Styrene (St) and methyl methacrylate (MMA) were purified by distillation in an atmosphere of nitrogen under reduced pressure and over an inhibitor remover (Aldrich, *tert*-butylcatechol-remover for styrene, hydroquinone-remover for MMA). The photoinitiator benzoin, applied in concentrations between 0.2 and 1.5×10^{-3} mol·L^{-1} (slightly depending on the system) was twice recrystallized from ethanol. Tetrahydrofuran (THF) for GPC 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 monomer, together with initiator (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 the indicated temperature, and irradiated by a pulsed Nd:YAG, Quanta Ray GCR-130−20 laser with a harmonic generator to generate light of wavelength 355 nm at a pulse energy up to 25 mJ/pulse and a pulse width of 5−6 ns. The beam was expanded by an optical system to a diameter of 3 cm. Laser repetition rates were controlled via an external digital pulse generator (Quantum Composers) between 0.5 and 20 Hz. (The energy reported is the exit energy of the laser; the incident power that reaches the sample is not routinely measured, but is approximately 10% less). Samples were exposed to the laser beam for 2−60 min to allow for about 0.2−2.0% conversion of monomer to polymer.

Analysis. The sample was mixed with a small amount of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), to prevent further polymerization, monomer was carefully evaporated, and the polymer was diluted with THF to a concentration of ∼3 mg/mL. GPC-analyses were performed on a system, consisting of an on-line degasser (ERC-3215, ERC Inc.), an isocratic LC-pump (IsoChrom, Spectra Physics), and four SEC-columns (10^3, 10^4, 10^5, and 10^6 Å SDV, Polymer Standard Service), used at 30 °C with THF as solvent. Detection was made by a differential refractometer (Viscotek, model 200). Molecular weight distributions were evaluated by using both polySt and polyMMA standards (Polymer Standards Service, PSS) of narrow polydispersity. According to the data sheet provided by PSS the molecular weight data of the standards are precise to at least 5%. The computation of the CLD for the estimation of the points of inflection was exactly the same as described previously.[1,9] It is extremely difficult to assess the error inherent in the chain lengths corresponding to L and accordingly to the k_p data calculated via eq 1 because, among other factors, these data are influenced by the *whole* set of standards used. The error in k_p, however, should not exceed 5−10% in an intermediate range of chain lengths, even if a "worst case scenario" is assumed.

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

Results and Discussion

The results obtained for $\overline{k_p}$ of St at 40, 55, and 70 °C are shown in graphical form in Figure 1a, together with the already published results for 25 °C as a reference.[1] In a similar manner the corresponding data for MMA polymerization for 50 and 70 °C are depicted in Figure 1b, again together with data obtained previously[1] for 25 °C. In these figures the values of the propagation coefficient $\overline{k_p}$, calculated by eq 1a, are plotted vs the $L^{(n)}$ data from which they were evaluated.

At the first glance the following qualitative features appear to be worth mentioning:

(a) The decrease of k_p with increasing L_0 persists at higher temperatures for both monomers.

(b) The relative extent of variation of $\overline{k_p}$ seems even to increase with temperature.

(c) The scatter of data seems to be more pronounced with MMA.

To make a quantitative assessment some modeling of $\overline{k_p}$ as a function of chain length is necessary. In this context it is necessary to recall that the k_p data originating from PLP and subsequent analysis of their CLD are averages over the L propagation steps according to

$$\frac{1}{\overline{k_p}(L)} = \frac{1}{L}\int_0^L \frac{1}{k_p(L)}\,\mathrm{d}L \tag{3}$$

with its inversion

$$\frac{1}{k_p(L)} = L\frac{\mathrm{d}(1/\overline{k_p}(L))}{\mathrm{d}L} + \frac{1}{\overline{k_p}(L)} \tag{3a}$$

(Actually, we applied the *normal* direct averaging procedure to $k_p(L)$ in our first communication;[1] this, however, had little influence on the evaluated parameters only in view of the comparatively small variations of $\overline{k_p}(L)$). To find out what this *individual* function $k_p(L)$ looks like, we have carried out simulations on lattices: The number of empty sites in close proximity to a chain end (which may be taken as equivalent to monomer molecules surrounding a chain end) actually decreases with increasing length of the overall chain, indicating a decrease of local monomer concentration during the growth process of a propagating chain. This effect whose extent is somewhat dependent on lattice type and chain stiffness etc. may be interpreted in a way that the pending rest of the chain attached to the radical end competes successfully with the monomer molecules for the sites in the vicinity of the chain end partially edging out the monomer. The variation of the "simulation equivalent" of the local monomer concentration was shown to be rather strong in the short chain range, more or less leveling off for long chains. In this case the function corresponding to $k_p(L)$ *is* accessible, of course, and can be converted into its integral counterpart $\overline{k_p}(L)$ by means of eq 3.

This simulation favors a Langmuir-type of behavior for the corresponding individual function $k_p(L)$

$$k_p(L) = k_p(0) - \frac{A}{B+L}L \tag{4}$$

which according to eq 3 would translate into an integral function $\overline{k_p}(L)$

$$\overline{k_p}(L) = (k_p(0) - A)\left[1 - \frac{AB}{(k_p(0)-A)L}\ln\left(\frac{(k_p(0)-A)L}{Bk_p(0)} + 1\right)\right]^{-1} \tag{5}$$

An exponential decay of the individual function from $k_p(0)$ to $k_p(\infty)$ according to

$$k_p(L) = (k_p(0) - k_p(\infty))\exp\{-kL\} + k_p(\infty) \tag{6}$$

or, in its integral form

$$\overline{k_p}(L) = kLk_p(\infty)\left[\ln\left(\frac{(k_p(0) - k_p(\infty))}{k_p(0)} + \frac{k_p(\infty)}{k_p(0)}\mathrm{e}^{kL}\right)\right]^{-1} \tag{7}$$

Table 1. Values of Parameters of Nonlinear Fits According to Eq 5 (Langmuir-Type Function) and Eq 7 (Exponential Function) for Styrene (St) and Methyl Methacrylate (MMA) at Different Temperatures[a]

		Langmuir-type function				exponential function		
monomer	T/°C	$k_{\rm p}(0)$	$k_{\rm p}(\infty)$	A	B	$k_{\rm p}(0)$	$k_{\rm p}(\infty)$	$k/10^{-3}$
styrene	25	111.05 ± 8.96	62.59 ± 10.01	48.46	275.72	109.08 ± 5.61	70.86 ± 5.00	3.092
	40	216.14 ± 22.49	126.35 ± 9.97	89.79	137.32	206.50 ± 10.58	134.29 ± 5.62	4.221
	55	420.03 ± 45.60	202.85 ± 13.10	217.18	125.08	385.23 ± 13.66	222.34 ± 5.86	4.224
	70	754.74 ± 424.61	361.96 ± 35.28	392.78	66.48	610.46 ± 75.96	376.86 ± 23.04	4.251
methyl methacrylate	25	399.77 ± 85.83	237.40 ± 22.15	162.37	161.92	375.18 ± 34.06	249.00 ± 12.81	3.065
	50	797.23 ± 242.08	400.34 ± 86.37	396.89	296.87	751.62 ± 113.62	443.43 ± 46.16	2.063
	70	1487.00 ± 357.65	608.53 ± 124.91	878.47	453.77	1356.80 ± 139.94	696.21 ± 68.38	1.232

[a] The variations indicated refer to 95% confidence intervals.

also gave absolutely satisfactory but somewhat inferior results compared to eq 5.

The simulation data, of course, could be easily converted into their integral form and their parameters corresponding to $k_{\rm p}(0)$, A and B, or $k_{\rm p}(0)$, $k_{\rm p}(\infty)$, and k, respectively, determined from either fit with very small deviations. $k_{\rm p}(0)$ certainly is subject to considerable error because of the steep ascent of $k_{\rm p}$ on approach to zero chain length. Furthermore, it should be noted in this context that the (extrapolated) quantity $k_{\rm p}(0)$ has no real physical meaning and is by no means comparable to the rate constants found for the addition of monomer to “monomeric” radicals for two reasons. As a first point, there is no radical of zero chain length in reality which undergoes true propagation (due to the kinetic scheme propagation starts when the radical is a “monomeric” one, i.e., has unity chain length ($L = 1$)). In practice, however, extrapolation to zero is much easier than extrapolation to $L = 1$. Furthermore, the difference between $k_{\rm p}(0)$ and $k_{\rm p}(1)$ will be rather small and can be easily calculated from the fit parameters using eqs 4 or 6, if desired. The second argument originates from the fact that the model proposed for describing the observed phenomenon as already mentioned in the preceding section (Introduction) is based on the “shielding” that is exercised by the rest of the chain and that leads to a progressive impoverishment of monomer at the radical site, finally reaching a markedly lower local monomer concentration (in comparison with the bulk monomer concentration) for long chains. The variation of $k_{\rm p}$ with chain length that was observed for oligomeric radicals certainly is caused by other factors that have nothing in common with this shielding effect. Thus it is no surprise at all that experimental $k_{\rm p}$ data given for monomeric model radicals[5,10] *disagree* with the $k_{\rm p}(0)$ data given in *this* work.

Once the concept of the decrease of local monomer concentration at the chain end caused by displacement effects exercised by the rest of the chain of length L is assumed to be correct any experimental data (which are of the $\overline{k_{\rm p}}(L)$ type, of course) can be fitted according to eq 5 or eq 7, the behavior of $\overline{k_{\rm p}}(L)$ parametrized and the parameters used to obtain the individual $k_{\rm p}(L)$ function from eqs 4 or 6. The quality of the experimental $\overline{k_{\rm p}}(L)$ data themselves, of course, is much too bad to prove or disprove the correctness of this concept or even to make a decision between eqs 5 and 7.

The parameters obtained by fitting the experimental data displayed in Figure 1, parts a and b, according to eqs 5 and 7 are shown in Table 1. The solid lines in Figure 1, parts a and b, correspond to the Langmuir fit, eq 5, while the broken curve is based on the exponential fit, eq 7.

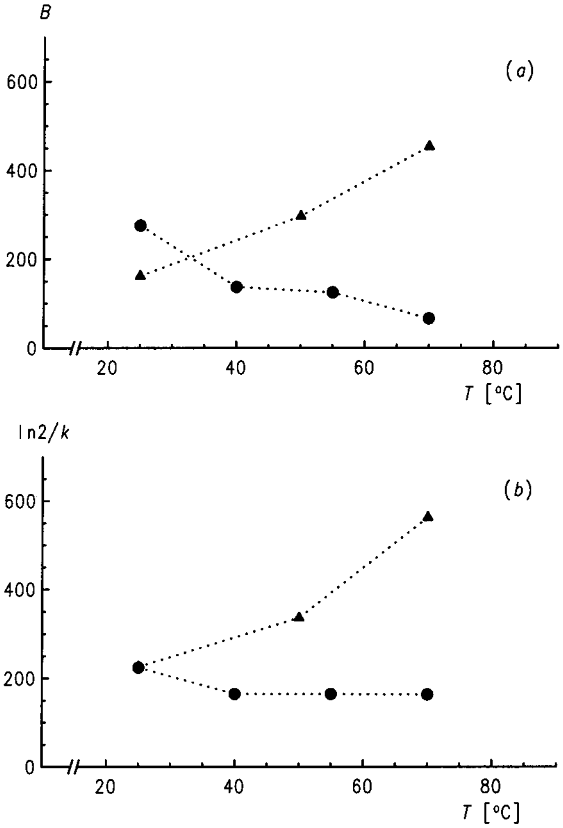

Figure 2. Values of parameters of nonlinear fits according to (a) eq 5 and (b) eq 7 for (●) styrene (St) and (▲) methyl methacrylate (MMA) at different temperatures. Values of B and (ln 2)/k directly correspond to the chain length $k_{\rm p}({}^1\!/_2)$ at which $k_{\rm p}$ equals the mean value of $k_{\rm p}(0)$ and $k_{\rm p}(\infty)$.

It is helpful to recall the meaning of the parameters: The overall range covered by the $k_{\rm p}$ data is given by A or $k_{\rm p}(0) - k_{\rm p}(\infty)$ while the (initial) steepness of the descent of the calculated individual $k_{\rm p}(L)$ data is represented by A/B or $k(k_{\rm p}(0) - k_{\rm p}(\infty))$, respectively. To give an impression on their temperature dependence they are presented in graphical, albeit somewhat modified form in Figures 2 and 3. In Figure 2, B (from the Langmuir fit) and (ln 2)/k (from the exponential fit) are compared with each other: both quantities refer to the chain length at which $k_{\rm p}$ equals the mean of $k_{\rm p}(0)$ and $k_{\rm p}(\infty)$, to be defined as $k_{\rm p}({}^1\!/_2)$ in the following. On the whole, the data are of the same order of magnitude for the two models implying that there is not much difference between them. It is noticeable, however, that the MMA data exhibit a different trend of little significance compared to the styrene data: while there is a slight decrease of these characteristic quantities for St the corresponding MMA data show a marked increase,

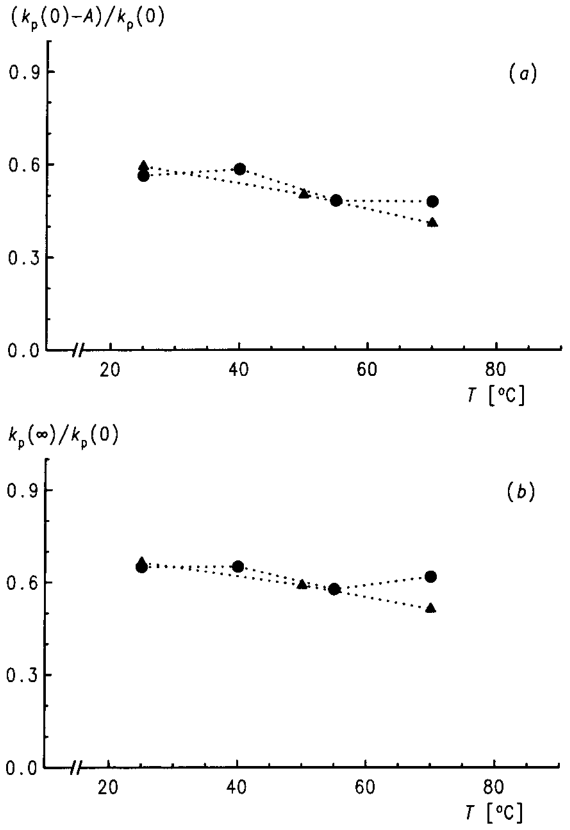

Figure 3. Values of parameters of nonlinear fits according to (a) eq 5 and (b) eq 7 for (●) styrene (St) and (▲) methyl methacrylate (MMA) at different temperatures. Values of $(k_p(0) - A)/k_p(0)$ and $k_p(\infty)/k_p(0)$ correspond to the extent of the chain length dependence of k_p and equal the fraction to which it is lowered at infinite chain length.

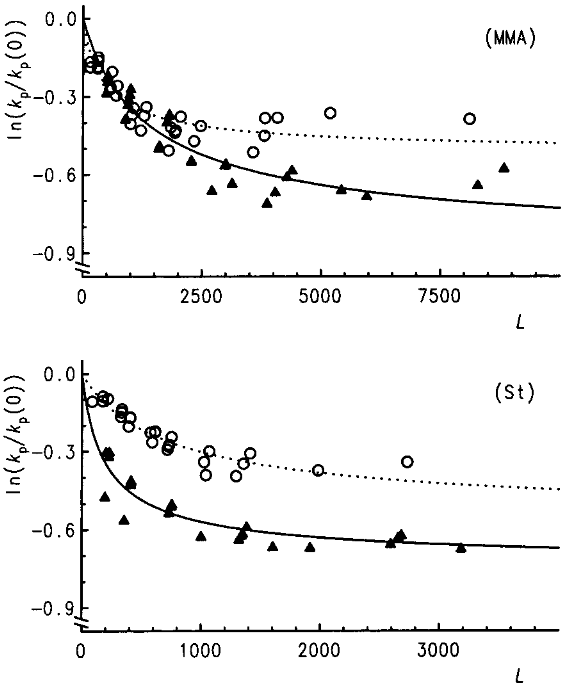

Figure 4. Semilogarithmic plot of experimental k_p data, reduced by $k_p(0)$, vs chain length for methyl methacrylate (MMA) and styrene (St) in bulk, 25 °C (○, ···) and 70 °C (▲, −). Curves and $k_p(0)$ values were calculated according to eq 5.

implying that it takes longer and longer chains in MMA polymerization to reach $k_p(\infty)$ with increasing temperature. If significant, this different temperature dependence of the "rate" at which k_p decreases with chain length might be associated with the greater stiffness of the pMMA chains in comparison with the pSt chains that is also reflected in lower k_t data of the former ones at comparable chain lengths.[11,12] This interesting behavior will be subject of future investigations. Figure 3 informs on how much $k_p(L)$ drops on a relative scale, more precisely on the ratio. Roughly speaking, this ratio is in the range of 40−60%, with some decrease to be registered with increasing temperature, however, with no significant differences in the behavior of MMA and St to be observed. The $k_p(\infty)/k_p(0)$ data from the exponential fit, however, are somewhat higher than their counterparts from the Langmuir fit. This is to some extent connected with the fact that the function corresponding to eq 5 (full lines in Figure 1, parts a and b) still exhibits a noticeable decrease for the longest chains investigated while the alternative function corresponding to eq 7 (dashed lines in Figure 1, parts a and b) mostly appears to have leveled off already. The most impressive overall picture of the temperature effect is conveyed by plotting the reduced 25 and the 70°C data for St and MMA on a logarithmic ordinate (Figure 4). This makes impressively clear that the decrease of k_p with chain length becomes much stronger at higher temperature, even on this relative scale. It is a little surprising to note that the exponential function apparently is statistically somewhat better suited to describe the experimental data intervals than the Langmuir type function: while the 95% confidence of $k_p(0)$ and $k_p(\infty)$ are well separated for all systems in the former case, there is a small overlap for the 70 °C styrene data in the latter.

An important point is to compare the results of this analysis to the IUPAC benchmark data published for St[13] and MMA.[14] These data collected from a variety of different research groups are mostly averages of investigations spread over quite a range of pulse frequencies (pulse separations t_0). Accordingly, we have carried out Arrhenius plots for $k_p(0)$, $k_p({}^1/_2)$, and $k_p(\infty)$ from both modeling functions and for the two monomers, St and MMA and compared the evaluated Arrhenius parameters to the IUPAC benchmark values (Table 2 and Figures 5 and 6). It is immediately evident from Table

Table 2. Frequency Factor A and Activation Energy E_a for Styrene (St) and Methyl Methacrylate (MMA) Calculated by Using Selected Values of k_p Derived from Eq 5 (Langmuir-Type Function) and Eq 7 (Exponential Function): Extrapolation to Zero Chain Length, $k_p(0)$; Extrapolation to Infinite Chain Length, $k_p(\infty)$; and the Mean Value of Those Two Values, $k_p({}^1/_2)$

		Langmuir-type function			exponential function			IUPAC benchmark values
monomer		$k_p(0)$	$k_p({}^1/_2)$	$k_p(\infty)$	$k_p(0)$	$k_p({}^1/_2)$	$k_p(\infty)$	
styrene	$A/10^7$	25.74	12.03	3.24	6.35	4.11	2.19	4.27
	E_a/kJ·mol^{-1}	36.36	35.06	32.56	32.88	32.28	31.31	32.51
methyl methacrylate	$A/10^5$	81.09	25.68	2.99	62.95	25.72	6.11	26.73
	E_a/kJ·mol^{-1}	24.64	22.34	17.72	24.16	22.39	19.37	22.36

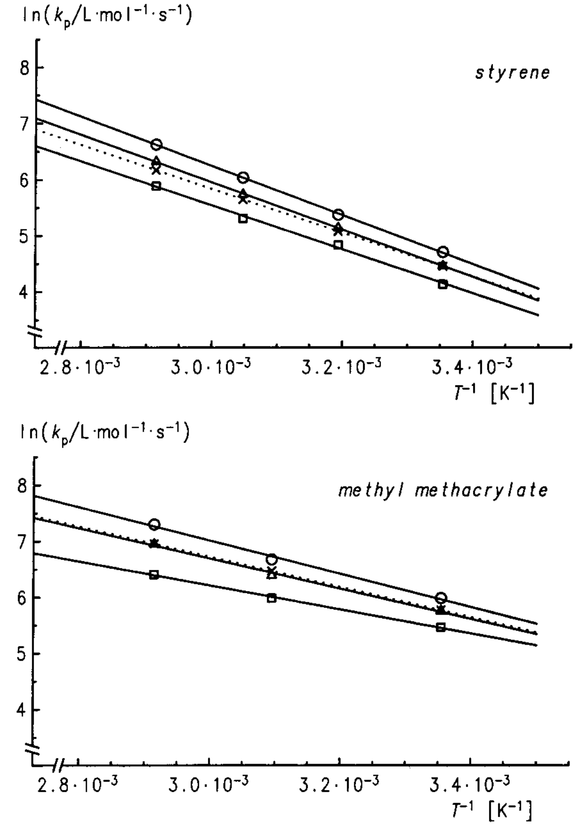

Figure 5. Arrhenius plots for selected k_p values derived from fitted Langmuir-type function eq 5 for styrene (St) and methyl methacrylate (MMA), respectively: (○) $k_\mathrm{p}(0)$; (△) $k_\mathrm{p}(^1/_2)$ and (□) $k_\mathrm{p}(\infty)$; best linear fits (—). IUPAC benchmark values (×) are given as reference; best linear fit (···).

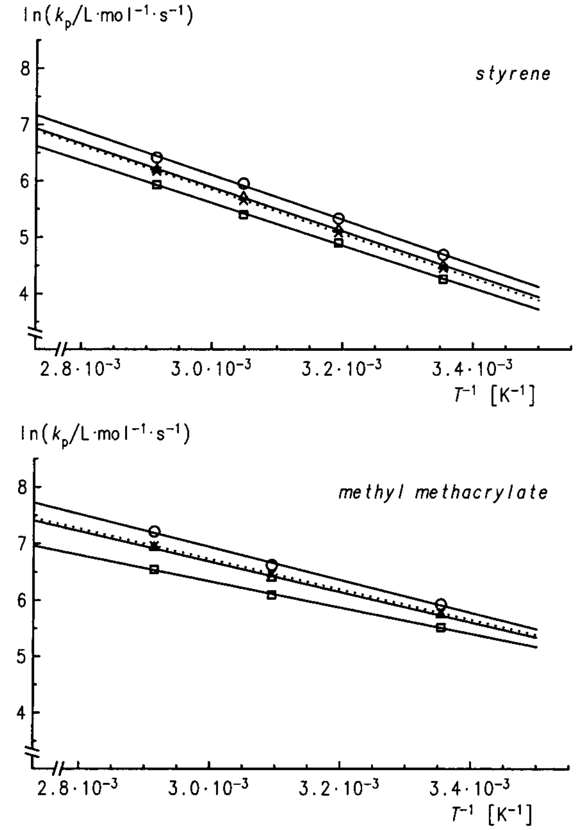

Figure 6. Arrhenius plots for selected k_p values derived from fitted exponential function eq 7 for styrene (St) and methyl methacrylate (MMA), respectively: (○) $k_\mathrm{p}(0)$; (△) $k_\mathrm{p}(^1/_2)$ and (□) $k_\mathrm{p}(\infty)$; best linear fits (—). IUPAC benchmark values (×) are given as reference; best linear fit (···).

2 that the benchmark values (not quite unexpectedly) are rather close to those obtained for $k_\mathrm{p}(^1/_2)$, especially for MMA. The only (slight) deviation exists for the Langmuir fit based on data for styrene. The same conclusion can also be drawn for the various $k_\mathrm{p}(T)$ data in Figures 5 and 6, where we have included the benchmark values for comparison, displayed by a dotted line: in all three cases (except the Langmuir fit for St) the Arrhenius straight lines referring to the benchmark data can be scarcely distinguished from the Arrhenius lines for $k_\mathrm{p}(^1/_2)$.

This very good agreement of the benchmark data (that rather reasonably originate from a practicable *intermediate* range of chain lengths) with the $k_\mathrm{p}(^1/_2)$ data demonstrates (a) that the quality of the results obtained in our laboratory is comparable to that achieved by other groups (the data presented here are rather new and did *not* enter the compilations given in the benchmark papers) and (b) that the benchmark data mostly correspond to the situation where k_p has dropped halfway from $k_\mathrm{p}(0)$ to $k_\mathrm{p}(\infty)$.

Critically analyzing those benchmark data reveals the decreasing tendency of k_p with increasing t_0 (decreasing pulse frequency) already in this context (see the critical discussion of these data given in ref 1): application of higher pulse frequencies always resulted in higher k_p values than those obtained with smaller frequencies or those averaged over a whole range of pulse frequencies. It is evident, therefore, that the same effect of chain length dependent k_p was present there, too, but apparently was given no further consideration at that time.

This study of the temperature dependence of this effect also had another important aim: by varying the temperature, the characteristic chain lengths on which all our conclusions are based are transferred into a range of higher chain lengths. The existence of this effect also at higher temperatures, for St as well as for MMA, together with the fact that the determination of the characteristic chain length from a PLP-prepared and GPC-analyzed sample has only to rely on the correctness of the calibration function at this very point also rules out a failure of this calibration function: it would be extremely improbable that the calibration function would cause errors always pointing into the same direction, irrespective of the monomer investigated (St or MMA). An error in the calibration function would always produce the same artificial shape of the k_p vs L_0 curve, irrespective of the conditions under which the polymer was produced. The existence of a temperature effect on the formal chain length dependence of the propagation rate coefficient finally proves the independency of the GPC errors.

Conclusions

After having developed such a powerful and convenient method for the determination of a crucial quantity like an *individual* rate constant in free radical polymerization,[3] it is to some extent disappointing to see now its limitations which, however, have less to do with the method itself but predominantly are due to the complexity of the systems investigated. Most probably, it was the appeal of this PLP–GPC technique, which has been promoted into a benchmark method within very short time and has attracted research groups all over the world, and the enthusiasm associated with it that pushed all the (necessary) critical judgment and skepticism into the background, not noticing and not accepting inconvenient results in the form of a chain length dependent k_p. The implications of a chain length independent k_p on polymerization kinetics are numerous. They will be subject of future investigations and may cause rewriting of those chapters in the relevant textbooks that are based on the constancy of k_p. First of all, however, a lot of further work will have to be invested into this subject in order to deepen our knowledge. It is very probable that the method applied in these investigations will be PLP−GPC again.

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References and Notes

(1) Olaj, O. F.; Vana, P.; Zoder, M.; Kornherr, A.; Zifferer, G. *Macromol. Rapid Commun.* **2000**, *19*, 913.

(2) Normally referred to as L_0 in our publications; we have decided to omit this subscript in the context of this communication because this quantity is later on used as an argument of (modeling) functions where a subscript 0 would be misleading.

(3) Olaj, O. F.; Bitai, I.; Hinkelmann, F. *Makromol. Chem.* **1987**, *188*, 1689.

(4) Note added in revision: A similar effect was also reported (orally, not contained in the preprint) quite recently by S. Beuermann on occasion of the IUPAC-sponsored Conference on Free Radical Polymerization held at Il Ciocco, Lucca, Italy, June 3−8, 2001.

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