Macromolecules **2001,** *34,* 441−446

Chain Length Dependent Termination in Pulsed-Laser Polymerization. 9. The Influence of Solvent on the Rate Coefficient of Bimolecular Termination in the Polymerization of Styrene

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Received July 20, 2000

ABSTRACT: The chain length dependence of bimolecular termination in the solution polymerization of styrene was examined at 25 °C with the solvents (50% per volume) toluene, cyclohexane, bis(3,5,5-trimethylhexyl)phthalate, and ethyl acetate. Irrespective of which method was applied, the "good" solvent systems with toluene and ethyl acetate exhibited a chain length dependence comparable to or even greater than that observed for the bulk polymerization of styrene, while a markedly weaker chain length dependence was observed with the "bad" solvents cyclohexane and bis(3,5,5-trimethylhexyl)phthalate. This is documented by the exponent *b* in the power law $\bar{k}_t = A\cdot\nu'^{-b}$ connecting the average termination coefficient $\bar{k}_t$ and the chain length ν' of the radical chains at the moment of undergoing bimolecular termination: $b \approx 0.2$ for styrene (in bulk) and in toluene solution, $b \approx 0.3$ in ethyl acetate solution and 0.10 to 0.14 in cyclohexane and bis(3,5,5-trimethylhexyl)phthalate solution, respectively. Only in the case of the bad solvents the bulk viscosity and $\bar{k}_t$ or the prefactor *A* are inversely correlated. In the case of the good solvents, the bulk viscosities were too close to detect such a relationship. The observed values of the parameter *b* (with the exception of the ethyl acetate system) are consistent with the idea of a chain length dependent shielding exercised by the rest of the chains on the two radical chain ends (some sort of "kinetic" excluded volume effect) which is much weaker in bad solvents.

Introduction

The addition of a solvent to a bulk monomer system, i.e., a homogeneous solution, is the simplest variation of the polymerization of pure monomer. Thus, in the early history of polymerization kinetics, the addition of a (hopefully) inert solvent—a so-called dummy solvent merely replacing the monomer without taking part in the polymerization in any respect—helped to establish the order of the overall rate of polymerization, υ_p with respect to monomer, e.g., in the spontaneous polymerization of styrene.[1] According to our present knowledge, however, the solvent can influence any of the various steps in radical polymerization in some way or other. Taking the basic expression for the overall rate of (ideal) radical polymerization

$$\upsilon_p = k_p k_t^{-1/2}\,[M][I]^{1/2}\,(2k_d f)^{1/2} \tag{1}$$

where k_p = rate constant of propagation, k_t = rate constant of (bimolecular) termination between growing chains, defined by $\upsilon_t \equiv k_t[R^\bullet]^2$, υ_t = rate of termination, $[R^\bullet]$ = concentration of polymer radicals, k_d = rate constant of first-order decomposition of the initiator, *f* = initiator efficiency, [M] = monomer concentration, and [I] = initiator concentration, the addition of solvent may influence any of the four quantities appearing on the rhs of eq 1. The extent of the influence on k_d depends strongly on the type of initiator (azo or peroxy), and has long been a subject of textbooks on polymerization kinetics.[2,3] The more subtle effects on *f*, which are subject to changes in viscosity, have been treated in selected examples.[4,5] Much interest has been devoted to the solvent effects acting on the rate constant of propagation k_p. The most prominent theories dealing with this topic are Tüdös' "hot radical" theory[6] and Olivé's EDA-complex theory.[7] So far, neither of these theories has acquired unanimous approval.[8] Most of these theories tried to derive support from experimental data based on measurements of the (overall) rate, which means that solvent effects on the other three quantities (k_d, k_t, *f*) could not be excluded or were not separated, respectively. The situation has changed with the invention of the pulsed-laser polymerization (PLP) technique followed by a careful analysis of the resulting chain length distribution (CLD), which aims directly at determining k_p.[9] In a recently published screening investigation[10] we examined many 1:1 solvent−monomer systems using this technique (acetonitrile, dimethylformamide, benzene, toluene, methyl isobutyrate, bromobenzene, 1,2-dichloroethane, cyclohexane as the solvents and styrene, methyl methacrylate, and a 1:1 mixture of styrene and methyl methacrylate as the monomers). The effects were moderate, and none reached the extent claimed by the theories. The only exception was cyclohexane with styrene as the monomer, which produced a significantly *higher* k_p (compared to bulk polymerization) when k_p was evaluated in the usual manner according to eq 2

$$k_p = L_0/([M]t_0) \tag{2}$$

where L_0 is usually taken as the position of the (first) point of inflection of the CLD, t_0 is the time elapsing between two periodic laser-pulses, and [M] is the overall monomer concentration. In reality, even this exception is an artifact. Since cyclohexane is a nonsolvent for polystyrene at low temperatures while styrene is a solvent, styrene will accumulate in the vicinity of the growing radical for thermodynamic reasons.[11,12] The

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10.1021/ma0012651 CCC: $20.00

quantity actually determined is not k_p itself but the product k_p[M]. This does not cause any problem if the "local" and overall monomer concentrations coincide but is important if one component is preferentially adsorbed. In the cyclohexane−styrene system the local concentration, which should be inserted into eq 2 in a *strict* sense due to the reasons outlined before, is *higher* than the nominal overall concentration, leading to a formal increase in k_p. Although no *pronounced* solvent effects on k_p could be discovered in this screening investigation, this does not deny the existence of occasional specific *strong* solvent effects such as the k_p enhancing effects of benzyl alcohol in styrene or methyl methacrylate polymerization[13] and of *N*-methyl pyrrolidone in styrene polymerization.[14]

Except for the fact that k_t should vary inversely with the viscosity of the system if it is diffusion-controlled, little information is available on the influence of solvents on k_t.[8] This is mostly so because no methods are available for determining k_t directly *and* independently of k_p. The situation is further complicated by the dependence of k_t on the chain lengths of the two radicals involved in the termination process. However, if k_p has been separately determined e.g. by PLP (or a related technique) k_t can be evaluated as an *average* (over chain lengths) by two different methods, developed in our laboratories, from the same sort of experiments which yield k_p. The first one[15] (method A) defines an average $\bar{k}_t^{m}$ by eq 3.

$$\bar{P}_w \upsilon_p = \frac{k_p^{\,2}}{\bar{k}_t^{\,m}}[M]^2(3-\delta) \tag{3}$$

The quantity δ represents the contribution of disproportionation to the overall termination. Actually, $\bar{P}_w\upsilon_p$, is invariant toward initiation conditions[16] (stationary or pseudostationary) in the case of chain length *in*dependent termination. In the case of chain length dependent termination, however, it reflects the (inverse) variation of an average k_t.

The second one (method B) is derived from the expression for the rate of polymerization in pulsed laser polymerization (PLP),[17] υ_p. Originally developed for chain length independent polymerization,[18] too, it yields a *different* average k_t (denoted as $\bar{k}_t^*$) if termination is chain length dependent

$$\upsilon_p = \frac{k_p[M]}{\bar{k}_t^* t_0}\ln\left\{1+\frac{\rho\bar{k}_t^* t_0}{2}\left[1+\left(1+\frac{4}{\rho\bar{k}_t^* t_0}\right)^{1/2}\right]\right\} \tag{4}$$

with ρ being the concentration of radicals produced in each pulse and t_0 being the inverse laser frequency.

According to computer simulations, $\bar{k}_t^*$ is very close to the *true* (event weighted) average $\langle k_t\rangle$, while $\bar{k}_t^{m}$ underestimates $\langle k_t\rangle$ by about 15−20%[17] (a detailed discussion of the nature of the various types of averages is given in ref 19).

The two methods were successfully applied to the polymerization of styrene[20] and methyl methacrylate[21] at 25 °C in bulk as benchmark systems, and the styrene investigations were later extended to temperatures up to 70 °C.[22] Apart from the theoretical difference between $\bar{k}_t^{m}$ and $\bar{k}_t^*$, a moderate dependence of the average k_t was found in all cases when $\bar{k}_t^{m}$ or $\bar{k}_t^*$, respectively, were plotted vs the (average) length ν' of the radical chains at the moment of termination; ν' is related to the number-average degree of polymerization $\bar{P}_n$ of the polymer by a constant factor according to eq 5.

$$\nu' = \bar{P}_n(1+\delta)/2 \tag{5}$$

Writing the chain length dependence of $\bar{k}_t$ as a power law of the form

$$\overline{k_t} = A\nu'^{-b} \tag{6}$$

we found the exponent b to be in the range of 0.16−0.18 for styrene[20] and methyl methacrylate[21] at 25 °C with the chain length dependence becoming still weaker at higher temperatures for styrene.[22]

In addition, a third method[23] (method C) was developed, mainly with the aim of controlling the results concerning the chain length dependence of k_t obtained by the two other methods. This is based essentially on the analysis of the CLD of a polymer prepared by PLP at very low frequencies (low-frequency PLP, LF−PLP). Under these conditions, nearly all radicals have died out when the next pulse arrives so that practically all radicals in the system have the same chain length at any given time (within the very narrow Poisson distribution). Assuming a power law

$$k_t^{(x,x)} = k_t^{(1,1)}x^{-b} \tag{7}$$

into which the general expression

$$k_t^{(x,y)} = k_t^{(1,1)}(\bar{x},\bar{y})^{-b} \tag{8}$$

($\bar{x}$, $\bar{y}$ being some average of the two chain lengths x and y and $k_t^{(x,y)}$ being the rate constant of bimolecular termination between two radical chains of length x and y) degenerates because of the approximation $x \approx y$ due to the conditions chosen, the (number) CLD can be calculated for termination by disproportionation ($x_P^{\,D}$) to be

$$x_P^{\,D} = \frac{k_t^{\,0}\rho}{\Theta}P^{-b}\left(1+\frac{k_t^{\,0}\rho}{(1-b)\Theta}P^{1-b}\right)^{-2} \tag{9}$$

and for termination by combination ($x_P^{\,C}$) to be

$$x_P^{\,C} = \frac{k_t^{\,0}\rho}{4\Theta}\cdot\left(\frac{P}{2}\right)^{-b}\left(1+\frac{k_t^{\,0}\rho}{(1-b)\Theta}\left(\frac{P}{2}\right)^{1-b}\right)^{-2} \tag{10}$$

the latter being normalized to $^1/_2$. (Θ is an abbreviation for the frequency of propagation steps k_p[M]). The overall (number) distribution for an arbitrary contribution of disproportionation δ is constructed from eqs 9 and 10 according to eq 11.

$$x_P = \frac{2}{1+\delta}(\delta x_P^{\,D} + (1-\delta)x_P^{\,C}) \tag{11}$$

The experimental CLD can be finally fitted to the theoretical one. Contrary to methods A and B, no preknowledge of k_p is necessary. However, no absolute value of k_t can be evaluated. The results obtained by methods A and B concerning the exponent b (bulk polymerization of styrene in the temperature range of 25−70 °C[20,22] and bulk polymerization of methyl methacrylate at 25 °C[21]) were satisfactorily confirmed by method C. *This* paper applies the three methods to the solution polymerization of styrene in order (a) to look for a correlation between the *extent* of chain length dependence of $\bar{k}_t$ and the thermodynamic quality of the solvent, and (b) to check whether the *extent* of chain length dependence of $\bar{k}_t$ is influenced by the viscosity of the solvent−monomer mixture.

Four solvents have been chosen: toluene, cyclohexane, bis(3,5,5-trimethylhexyl)phthalate, and ethyl acetate. Toluene was selected because of its structural and thermodynamic proximity to the monomer styrene, cyclohexane was selected because of its nonsolvent properties at 25 °C, and the phthalate and ethyl acetate were selected for reasons of their high (phthalate) and low (ethyl acetate) viscosities.

Experimental and Calculation Details

The PLP experiments for methods A and B were carried out at 25 °C, as described in our recent communications,[20,21] except for the use of a solvent in the proportion of 1:1 by volume. The overall procedure (sample preparation, polymerization, analysis of the CLD by size exclusion chromatography (SEC), and calculational procedure) was exactly the same as outlined previously. Conversions were kept below 0.5% in all cases. With methods A and B, a variation of the degree of polymerization of the resulting polymer is essential. Accordingly the pulse frequency was varied in the range 0.2−10 s^{-1} and the sensitizer concentration (benzoin) between 0.2 and 1.5 mM, the total number of laser shots amounting to 2000−27000 (depending on sensitizer concentration and pulse frequency). Method C (LF−PLP) was performed according to the prescription given in ref 23. Here the pulse frequency was much lower, of course (0.01−0.02 s^{-1}). The same refers to the total number of pulses (180−320).

The absence of thermal initiation during the time necessary for performing the PLP experiments was carefully checked by dummy experiments in the dark together with occasional dilatometric experiments which exhibited the absence of an inhibition period. All of the necessary data with the exception of δ and t_0 (rate of polymerization v_p, number- and weight-average degree of polymerization, and rate constant of propagation k_p) were extracted from the CLD. The quantity ρ required for method B was calculated from eq 12.

$$\rho = 2v_p t_0[\bar{P}_n/(1+\delta)] \qquad (12)$$

To obtain reliable results for the parameter b, care was taken to cover a sufficiently broad range of ν' values by proper variation of experimental conditions, mainly t_0 and ρ (the latter by variation of sensitizer concentration). Our experimentally determined data of the rate constant of propagation k_p depended slightly on chain length,[24] strictly speaking on the quantity L_0 which in itself provides the access to k_p by means of the basic relationship in eq 2, L_0 being taken as the position of the point of inflection preceding the maximum in the CLD. This variation consisted in a slight decrease of k_p with increasing L_0 up to a borderline value of L_0', $750 < L_0' < 1000$, depending on the polymerization system. If L_0 or (if higher order points of inflection were considered) its multiples exceeded L_0' this decrease came to an end, the k_p values plateaued or even increased very slightly for $L_0 > L_0'$. The data analysis was therefore carried out using k_p values which were observed for half the estimated L_0' values. The k_p data (together with other essential basic data) entering the calculations are compiled in Table 1 in the beginning of the next section. Variations of the parameter δ—if not too excessive—do not seriously influence the results (in our previous studies on styrene polymerization at 25 °C a value of $\delta = 0.1$ was used). For sake of better consistency and comparability, this value of δ (corresponding to predominant termination by combination) was chosen also in this paper.

Table 1. Basic Data Used to Evaluate Termination Coefficients and Their Chain Length Dependence and Initial System Viscosity η

solvent (1:1 solvent:styrene)	[M], mol·L^{-1}	k_p, L·mol^{-1}·s^{-1}	δ	η, mPa·s
none	8.651	80	0.1	0.696
ethyl acetate	4.325	70	0.1	0.563
toluene	4.325	80	0.1	0.624
cyclohexane	4.325	90	0.1	0.669
bis(3,5,5-trimethylhexyl)-phthalate	4.325	90	0.1	2.585

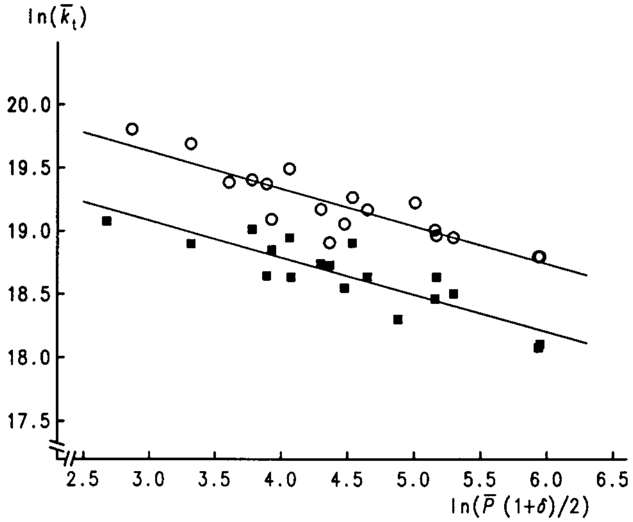

Figure 1. Plots of ln($\bar{k}_t$) vs ln(ν'). $\nu' = \bar{P}_n(1+\delta)/2$ is the chain length of the radicals at the moment of their termination, according to eq 6, for method A ($\bar{k}_t^m$, ■) and method B ($\bar{k}_t^*$, ○) for the system styrene−ethyl acetate (1:1 by volume) at 25 °C for 10% disproportionation ($\delta = 0.1$). The slope of the best linear fit (—) represents the negative value of parameter b of eq 6.

Method C is based on a procedure *in extenso* described quite recently.[23] It is completely independent of all the quantities entering into the two other methods such as k_p, ρ, v_p, $\bar{P}_n$, and $\bar{P}_w$, and is nearly insensitive toward the choice of δ. Essentially, it consists of carrying out a three-parameter nonlinear regression, fitting the experimental CLD (determined by SEC) to that derived for an ideal single-pulse polymerization ignoring the Poissonian character of chain growth,[23] eqs 9−12, by means of Prism 3.00 by Graphpad Software after being transformed into eq 13.

$$w_{\log P} = aP^2\left\{\delta\frac{P^{-b}}{\left(1+c\left(\frac{1}{1-b}\right)P^{1-b}\right)^2} + \frac{1-\delta}{4}\,\frac{\left(\frac{P}{2}\right)^{-b}}{\left(1+c\left(\frac{1}{1-b}\right)\left(\frac{P}{2}\right)^{1-b}\right)^2}\right\}\frac{2}{1+\delta} \qquad (13)$$

Two out of the three parameters evaluated in this way are of only minor interest (a and c) and moreover are interrelated through a normalization constant which unfortunately cannot be determined independently. The third parameter, on which all the concern is concentrated, corresponds to the exponent b in eqs 6−8, characterizing the chain length dependence of termination.

Bulk viscosities of the pristine polymerization systems were determined by means of an Ubbelohde viscometer at 25 °C.

Results and Discussion

The main results using methods A and B, based on the input data collected in Table 1, are presented in graphical form in Figures 1−4. An example for the fit according to method C is given in Figure 5. For easy comparison, Table 2 offers a compilation of the results

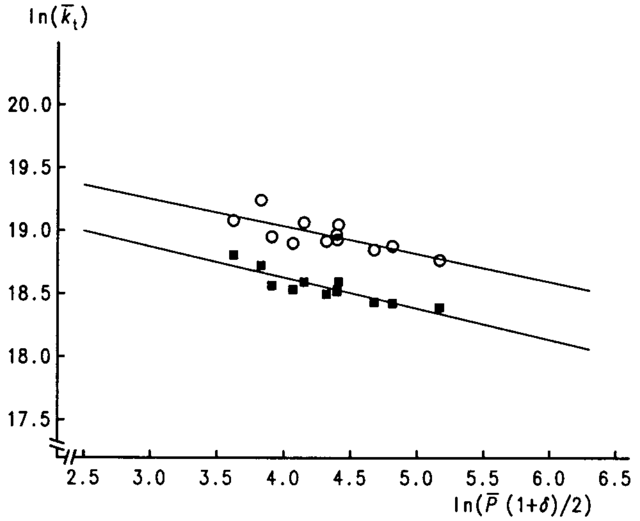

Figure 2. Plots of $\ln(\bar{k}_t)$ vs $\ln(\nu')$. $\nu' = \bar{P}_n(1 + \delta)/2$ is the chain length of the radicals in the moment of their termination, according to eq 6, for method A ($\bar{k}_t^m$, ■) and method B ($\bar{k}_t^*$, ○) for the system styrene-toluene (1:1 by volume) at 25 °C for 10% disproportionation ($\delta = 0.1$). The slope of the best linear fit (—) represents the negative value of parameter b of eq 6.

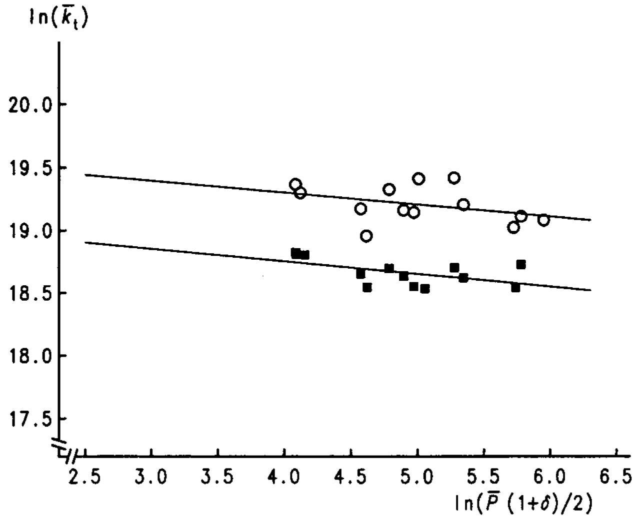

Figure 3. Plots of $\ln(\bar{k}_t)$ vs $\ln(\nu')$; $\nu' = \bar{P}_n(1 + \delta)/2$ is the chain length of the radicals in the moment of their termination, according to eq 6, for method A ($\bar{k}_t^m$, ■) and method B ($\bar{k}_t^*$, ○) for the system styrene-cyclohexane (1:1 by volume) at 25 °C for 10% disproportionation ($\delta = 0.1$). The slope of the best linear fit (—) represents the negative value of parameter b of eq 6.

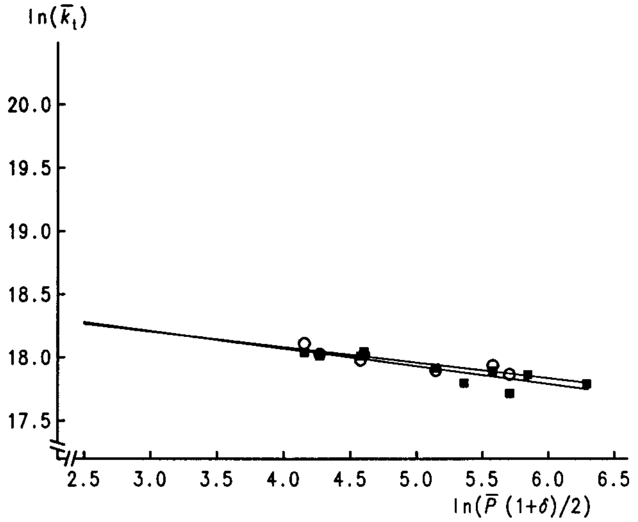

Figure 4. Plots of $\ln(\bar{k}_t)$ vs $\ln(\nu')$; $\nu' = \bar{P}_n(1 + \delta)/2$ is the chain length of the radicals in the moment of their termination, according to eq 6, for method A ($\bar{k}_t^m$, ■) and method B ($\bar{k}_t^*$, ○) for the system styrene-bis(3,5,5-trimethylhexyl)phthalate (1:1 by volume) at 25 °C for 10% disproportionation ($\delta = 0.1$). The slope of the best linear fit (—) represents the negative value of parameter b of eq 6.

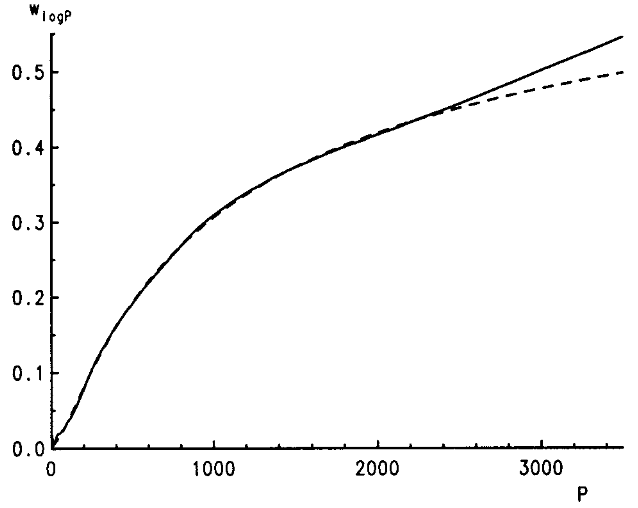

Figure 5. Experimental weight fraction $w_{\log P}$ on a logarithmic scale of chain lengths P vs chain length P for LF−PLP of styrene in cyclohexane (1:1 per volume) at 25 °C (—) and fitted theoretical curve (- - -) according to eq 13 (method C) for 10% disproportionation ($\delta = 0.1$) with $P_{\min} = 14$ as the lower limit of fitting range and $P_{\max} = 2500$ as the upper one.

Table 2. Compilation of the Results Obtained for the Various Systems by Means of the Different Methods (*A* and *b* Being the Parameters Contained in Eq 6)

solvent (1:1 solvent:styrene)	$\bar{k}_t^m$ (method A) b	$\bar{k}_t^m$ (method A) A, $10^8 \times$ L·mol^{-1}·s^{-1}	$\bar{k}_t^*$ (method B) b	$\bar{k}_t^*$ (method B) A, $10^8 \times$ L·mol^{-1}·s^{-1}	method C b
none	0.19	2.25	0.16	2.43	0.20−0.24
ethyl acetate	0.29	4.67	0.30	8.16	0.28−0.32
toluene	0.25	3.28	0.22	4.43	0.23−0.26
cyclohexane	0.10	2.09	0.10	3.52	0.08−0.12
bis(3,5,5-trimethylhexyl)phthalate	0.14	1.23	0.12	1.17	

obtained by all three methods. The following facts may be deduced: (a) The overall agreement with respect to the exponent b is surprisingly good. This might indicate that each of the three methods is correct and reliable. Because any disturbing factors which may affect the results will do this to a different extent in the three methods (e.g., the presence of nonnegligible chain transfer will influence method A more strongly than method B) this agreement indicates that these adverse factors (especially chain transfer) are not important in the systems investigated. (b) With the exception of the phthalate system, the (theoretically justified and expected) gradation between $\bar{k}_t^*$ and $\bar{k}_t^m$, which is due to the different averaging inherent in the two methods (method A, which yields $\bar{k}_t^m$, favors the smaller contributions originating from longer chains), is observed. There is no reasonable explanation for the absence of this effect in the phthalate system; this system, however, presented by far the most problems with respect to its experimental handling, mostly because of the low volatility of the solvent which prevented its quantitative removal. This interfered unfavorably with the reliable evaluation of the low molecular weight part of the CLD and was the reason method C, for which this part of the CLD is of particular importance, could not be applied in this case. (c) With respect to the parameter *b* the solvents can be divided into two groups. The first one, comprising toluene and ethyl acetate, which represent good solvents for polystyrene, exhibit *b* parameters equal to or even exceeding that found in the bulk polymerization of styrene. In these systems k_p is comparable to (or even a little lower than) the bulk polymerization value. The other two solvents, cyclohexane and bis(3,5,5-trimethylhexyl)phthalate, are poor solvents (due to the presence of 50% of styrene in the polymerization system the solutions remain homogeneous during reaction, of course). As a consequence the growing chains are preferentially surrounded by the "solvent" styrene thus increasing the monomer concentration beyond the nominal bulk value.[10] If this nominal [M] value is inserted into eq 2 formally, a higher k_p is obtained (actually, the PLP method yields the *product* k_p[M]). This appears to be equally the case with these two solvents. With respect to termination, the reduced solvent quality of the overall system severely changes the thermodynamics. As a consequence, the chain length dependent shielding effect which we believe to be primarily responsible for the chain length dependence of k_t in the bulk polymerization of styrene and methyl methacrylate (and of course also in the solution polymerization in solvents like toluene) becomes weaker. This is expressed by a much lower value of the *b* parameter. In theory this shielding effect should nearly vanish in a Θ system ($b \approx 0.05$). Because of the presence of styrene, however, the systems are still far away from being a Θ system. Parameters *b* in the range 0.10−0.14 therefore can be taken as indicative of reduced but not completely removed solvent quality. (d) Accordingly, considering the influence of the bulk viscosity, only systems of comparable solvent quality should be compared. In accordance with expectations, the prefactor *A* is larger for the low viscosity ethyl acetate system than for the toluene system. A similar tendency is observed if the low viscosity cyclohexane system is compared to the highly viscous phthalate system. We varied the system viscosity, however, to see if there is a change in the rate-determining step in the complicated overall termination reaction (hopefully accompanied by a marked change in chain length dependence) under these conditions. Unfortunately, there are two factors that make it rather difficult to check this point. First, as already described before, viscosity effects may be superimposed on thermodynamic effects, and second, the viscosity range that was reasonably accessible experimentally in our investigation was not overwhelmingly large and amounts to a factor of only ca. 5. Thus, the only indication to be derived from our investigations is the comparatively high value of *b* for the low viscosity ethyl acetate system which is in *moderate* agreement only with the predictions of the shielding effect (some sort of "kinetic" excluded volume effect preventing the radical chain ends to meet each other) for athermal systems[25] for which *b* should equal 0.17 within the limits of experimental error as it was found for the bulk polymerization of styrene and methyl methacrylate at 25 °C.[20,21] It should not be overlooked that the difference in the system viscosity in the ethyl acetate system and the toluene system is rather small. Thus, it would be difficult to attribute a rather substantial increase of the parameter *b* to such a small (negative) viscosity increment. A different explanation could be based on the fact that the change of thermodynamic conditions into the direction of an *exothermal* solution, of course, is expected to increase the parameter *b*. According to our general experience, however, this kind of variation always is accompanied by much less dramatic changes than the change into the direction of endothermal conditions, irrespective of the fact that at present we have no proof of the exothermicity of the ethyl acetate system. The only consequence to be derived, therefore, is to admit that under certain conditions there may well be systems for which the chain length dependence of k_t exceeds the extent due to the mere entropic effect caused by the mutual shielding of radical chains from each other by the "rest" of the chains in an athermal system as postulated by other groups.[26,27]

Conclusions

The relationship between the extent of chain length dependence of the rate coefficient of bimolecular termination and the thermodynamic conditions to which the growing chains are exposed is in fair accordance with the idea of a shielding of the radicals by the rest of the chains.[25] In comparison to the influence exercised by thermodynamic conditions the influence of the bulk viscosity on the extent of chain length dependence appears to be negligible, at least for the range of bulk viscosities examined.

Acknowledgment. We want to express our gratitude to the Austrian Science-Fund (Project No. 13114CHE) for generous financial support.

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MA0012651