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Determination of the Absolute Propagation Rate Constants in Polymerization with Reversible Aggregation of Active Centers[†]

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ABSTRACT: When the propagating active species ($\mathbf{P}_n{}^*$) aggregate reversibly into the nonreactive (dormant) species, $m\mathbf{P}_n{}^* \overset{K_a}{\rightleftharpoons} (\mathbf{P}_n{}^*)_m$, $\mathbf{P}_n{}^* + \mathbf{M} \xrightarrow{k_p} \mathbf{P}_{n+1}{}^*$, both the absolute rate constant of propagation (k_p) and the equilibrium constant of aggregation (K_a) can be determined simultaneously by using an equation derived recently, assuming polymerization to be living: $r_p{}^{1-m} = -mK_a/k_p{}^{m-1} + k_p[\mathbf{I}]_0 r_p{}^{-m}$ (where $r_p = -\mathrm{d}\ln[\mathbf{M}]/\mathrm{d}t$, m is the aggregation degree, $[\mathbf{M}]$ denotes the instantaneous concentration of monomer, and $[\mathbf{I}]_0$ is the starting concentration of initiator ($[\mathbf{I}]_0 = [\mathbf{P}_n{}^*] + m[(\mathbf{P}_n{}^*)_m]$)). This equation has been applied in the present work to analyze several polymerizations studied by other authors who previously used numerical methods in determining the involved rate and equilibrium constants. A few systems have been chosen, namely, the anionic polymerization with the Li^+ counterion of *o*-methoxystyrene, methyl methacrylate, and hexamethylcyclotrisiloxane, as well as the anionic polymerization of oxirane with the Cs^+ counterion. The k_p and K_a found analytically are in good agreement with those determined previously numerically.

Introduction

Aggregation of active centers in the anionic polymerization of vinyl, diene,[1-7] acrylic,[8,9] and heterocyclic monomers[10-16] is a well-documented phenomenon. Recently, we have found that in the polymerization of ϵ-caprolactone initiated with dialkylaluminum alkoxides ($\mathrm{R_2AlOR'}$), the resulting macroalkoxide growing species $\mathrm{R'O[C(O)(CH_2)_5O]_nC(O)(CH_2)_4CH_2O{-}AlR_2}$ also undergo aggregation with the aggregation degree depending on the substituent on the aluminum atom, additional complexing agents, and the solvent used.[17-19]

Usually, the reactivity of the aggregated species differs substantially from that of the nonaggregated ones. Therefore aggregation of the active centers affects the kinetics of polymerization. The nonaggregated species, most often, are the more reactive, as suggested by the fractional orders (externally) of propagation with respect to the active centers.[1-16]

The aggregation of the initiator may also have important consequences. Our recent results on the polymerization of ϵ-caprolactone with $\mathrm{Al[OCH(CH_3)_2]_3}$[19] indicate that the aggregates of a given initiator with various aggregation degrees may substantially differ in reactivity: for example, $\{\mathrm{Al[OCH(CH_3)_2]_3}\}_3$ leads to a much more rapid polymerization of ϵ-caprolactone than that initiated by $\{\mathrm{Al[OCH(CH_3)_2]_3}\}_4$.

In the majority of polymerizations studied till now and involving aggregates of active centers, propagation is first order internally with respect to monomer.[1-14,16-19] Thus, the pertinent kinetic scheme for propagation proceeding exclusively on the nonaggregated species reads

$$(\mathbf{P}_n{}^*)_m \overset{K_{da}}{\rightleftharpoons} m\mathbf{P}_n{}^* \qquad (K_{da} = 1/K_a) \tag{1}$$

$$\mathbf{P}_n{}^* + \mathbf{M} \xrightarrow{k_p} \mathbf{P}_{n+1}{}^* \tag{2}$$

where

$$[\mathbf{I}]_0 = [\mathbf{P}_n{}^*] + m[(\mathbf{P}_n{}^*)_m] \tag{3}$$

$\mathbf{P}_n{}^*$ and $(\mathbf{P}_n{}^*)_m$ denote nonaggregated and aggregated active centers, respectively, m is the aggregation degree, $\mathbf{M}$ is the monomer, K_{da} and K_a are the equilibrium constants of deaggregation and aggregation, respectively, k_p is the propagation rate constant of the nonaggregated species, and $[\mathbf{I}]_0$ is the starting concentration of initiator.

The kinetics of the monomer consumption is described by the following equations:

$$r_p = -\frac{\mathrm{d}[\mathbf{M}]}{[\mathbf{M}]\,\mathrm{d}t} = -\frac{\mathrm{d}\ln[\mathbf{M}]}{\mathrm{d}t} = k_p[\mathbf{P}_n{}^*] \tag{4}$$

or, in the integrated form,

$$r_p = \{\ln([\mathbf{M}]_0/[\mathbf{M}])\}/t = k_p[\mathbf{P}_n{}^*] \tag{5}$$

Thus

$$\ln([\mathbf{M}]_0/[\mathbf{M}]) = k_p[\mathbf{P}_n{}^*]t \tag{6}$$

Results of the kinetic measurements are presented in the form of plots of $\ln([\mathbf{M}]_0/[\mathbf{M}])$ vs polymerization time (t), and r_p is given by the slope. The rate constant of propagation cannot, however, be determined directly from the kinetic measurement, because the concentration of the actually growing, nonaggregated species $[\mathbf{P}_n{}^*]$ is not known (cf. eq 5).

It is also usually assumed in the analysis of systems with aggregation of $\mathbf{P}_n{}^*$ that active centers are present predominantly in the aggregated form; i.e., equilibrium 1 is shifted to the left-hand side, $[\mathbf{P}_n{}^*] \approx 0$, and practically $[\mathbf{I}]_0 = m[(\mathbf{P}_n{}^*)_m]$. Finally, the correlation between the relative polymerization rate (r_p) and the total concentration of the active centers ($[\mathbf{I}]_0$) is obtained (with the above given assumption: $m[(\mathbf{P}_n{}^*)_m] \gg [\mathbf{P}_n{}^*]$):

$$\log r_p = \log\{k_p(K_{da}/m)^{1/m}\} + (1/m)\log[\mathbf{I}]_0 \tag{7}$$

Then, plotting $\log r_p$ vs $\log[\mathbf{I}]_0$, one obtains the aggregation degree m directly from the slope of the resulting straight line. The intercept gives the product $k_pK_{da}{}^{1/m}$.

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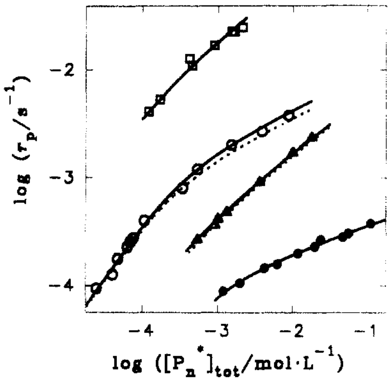

Figure 1. External orders in active centers: dependencies of $\log r_p$ against $\log[\mathbf{P}_n^*]_{tot}$. (△) Polymerization of *o*-methoxystyrene on $\cdots$–$CH_2CH[(o\text{-}CH_3O)C_6H_4]$,$Li^+$ ion pairs, toluene as a solvent, 20 °C (experimental data taken from ref 7). (□) Polymerization of methyl methacrylate on $\cdots$–$CH_2C(CH_3)C(O)OCH_3$,Li^+ ion pairs, THF as a solvent, –65 °C (experimental data taken from ref 9). (○) Polymerization of oxirane on $\cdots$–$CH_2CH_2O^-$, Cs^+ ion pairs, THF as a solvent, 70 °C (experimental data taken from ref 10). (●) Polymerization of D_3 on $\cdots$–$Si(CH_3)_2O^-$, Li^+ ion pairs, THF as a solvent, 22 °C (experimental data taken from ref 14). Points, experimental; lines, calculated by eq 12; solid lines, k_p and K_a determined by the straight-line correlation method (eq 8); dashed lines, k_p and K_a determined by the numerical treatment.

The absolute values of k_p and K_{da} are, however, inaccessible when this approach is used. On the other hand, several kinetic studies were reported giving plots of $\log r_p$ vs $\log[\mathbf{I}]_0$ with a marked curvature;[5-11,13,14,18] some of these are collected in Figure 1. This behavior may stem from the presence of the nonaggregated and aggregated species at comparable concentrations; hence the term $[\mathbf{P}_n^*]$ in eq 3 cannot be neglected, and eq 7 cannot be used to analyze the polymerization kinetics. In fact, plots of $\log r_p$ against $\log[\mathbf{I}]_0$ should "always" be curved. The reasons that the curvature is not observed are related to the accuracy of the kinetic measurements and the range of the $[\mathbf{I}]_0$ applied.

Apparently, there were attempts to solve the kinetic scheme given by eqs 1 and 2 without any simplifying assumption like $[\mathbf{P}_n^*] \approx 0$. However, it seems that the proper analytical solution has not been applied, because a number of authors analyzed kinetics described by eqs 1 and 2 numerically, determining k_p and K_a this way.

We have recently found a way of solving analytically the discussed kinetic scheme (propagation on the nonaggregated species, reversibly aggregating into the inactive species), giving direct access to both k_p and K_a. The success is based on operating with two experimentally measurable variables (r_p and $[\mathbf{I}]_0$) and two parameters (k_p and K_a) in such a way that a straight-line relation is obtained. This relatively simple equation reads[17]

$$r_p^{\,1-m} = -m/K_{da}k_p^{\,m-1} + k_p[\mathbf{I}]_0\, r_p^{\,-m} \qquad (8)$$

where $r_p = \{\ln([\mathbf{M}]_0/[\mathbf{M}])\}/t = k_p[\mathbf{P}_n^*]$. Thus when $r_p^{\,m-1}$ is plotted against $[\mathbf{I}]_0 r_p^{\,-m}$, the rate constant k_p is obtained directly from the slope, and K_{da} is calculated after determining the intercept. The r_p are measured from the slopes of the dependencies of $\ln([\mathbf{M}]_0/[\mathbf{M}])$ vs time. The value of m is either assumed (m is usually equal to 2, 3, or 4) or predetermined experimentally by using eq 7. The method described above has successfully been applied in our recent analysis of the polymerization of ε-caprolactone initiated with dialkylaluminum alkoxides (R_2AlOR').[17,18]

We should add that Szwarc correctly pointed out that there should be an analytical solution for the kinetic equations describing the set of reactions (1) and (2)[3] and then gave the solution for $m = 2$ but did not analyze any kinetic data.[5]

In the present paper the analytical approach described above and called the "linear analytical method" is applied to a few cases treated previously numerically.

Determination of k_p and K_{da} by a Linear Analytical Method

Anionic Polymerization of *o*-Methoxystyrene. van Beylen and Smets[7] studied the kinetics of the anionic polymerization of *o*-methoxystyrene with Li^+ counterion in toluene as a solvent at 20 °C. The order of propagation increased from $1/m = 0.51$ to 0.67 when the total concentration of the active centers ($[\mathbf{P}_n^*]_{tot} = [\mathbf{P}_n^*] + m[(\mathbf{P}_n^*)_m]$ decreased from 1.82×10^{-2} to 5.32×10^{-4} mol·L^{-1} (Figure 1, experimental points represented by triangles). $[\mathbf{P}_n^*]_{tot}$ were determined from molecular weights of the resulting poly(*o*-methoxystyrene). A slight curvature of the $\log r_p \div \log[\mathbf{P}_n^*]_{tot}$ plot is clearly seen. The authors assumed that the actually growing species, lithium alkyl ion pairs, were in dynamic equilibrium with their dimers. The latter species were considered to be unreactive toward monomer. In this system, the concentration of the reactive, monomeric active centers was described by the following expression:[7]

$$[\mathbf{P}_n^*] = -K_{da}/4 + (K_{da}^{\,2}/4 + 2K_{da}[\mathbf{P}_n^*]_{tot})^{1/2}/2 \qquad (9)$$

where K_{da} denotes the equilibrium constant of deaggregation, $K_{da} = 1/K_a$. In further treatment van Beylen and Smets assumed the values of K_{da} and calculated $[\mathbf{P}_n^*]$ for various $[\mathbf{P}_n^*]_{tot}$ from eq 9. Then the measured r_p were correlated graphically with the calculated $[\mathbf{P}_n^*]$. The whole procedure was repeated several times until the best fit to the data was obtained for a certain K_{da}. Finally, from the relationship $r_p = k_p[\mathbf{P}_n^*]$, the propagation rate constant k_p was computed for various r_p and $[\mathbf{P}_n^*]$. The best fit to the experimental data was obtained for k_p = 0.83 mol^{-1}·L·s^{-1} and K_{da} = 10^{-3} mol·L^{-1} (i.e., K_a = 10^3 mol^{-1}·L).

Application of our eq 8 to the same set of experimental data is illustrated in Figure 2a. k_p = 0.75 mol^{-1}·L·s^{-1} and K_a = 0.86×10^3 mol^{-1}·L were determined, close enough to the values obtained by Van Beylen and Smets. The respective plot of r_p^{-1} vs $[\mathbf{P}_n^*]_{tot} r_p^{-2}$, shown in Figure 2a, gives a good straight line with a linear regression coefficient (r) equal to 0.991.

Anionic Polymerization of Methyl Methacrylate. Müller et al.[8,9] studied the anionic polymerization of methacrylates with Li^+ as counterion in THF solvent at –65 °C. For methyl methacrylate (MMA) the slope of the tangents of the plot $\log r_p$ vs $\log[\mathbf{P}_n^*]_{tot}$ increased from $1/m = 0.58$ to 0.78 when $[\mathbf{P}_n^*]_{tot}$ decreased from 2.1×10^{-3} to 1.2×10^{-4} mol·L^{-1} (Figure 1, experimental points represented by squares). Under these polymerization conditions the presence of "free" ions was excluded and dimerization of the active centers was assumed. The molar fractions of the monomeric (nonaggregated) ion pairs (α) were calculated from eq 10:

$$\alpha = \frac{[\mathbf{P}_n^*]}{[\mathbf{P}_n^*]_{tot}} = \frac{(1 + 8K_a[\mathbf{P}_n^*]_{tot})^{1/2} - 1}{4K_a[\mathbf{P}_n^*]_{tot}} \qquad (10)$$

The monomeric ion pairs were assumed to be the only propagating active species. Finally, k_p = 46 mol^{-1}·L·s^{-1} and K_a = 2×10^{-3} mol^{-1}·L were found numerically by using a nonlinear least squares method.

Application of the linear analytical method, based again on eq 8, gives a plot with k_p = 43.6 mol^{-1}·L·s^{-1} and K_a =

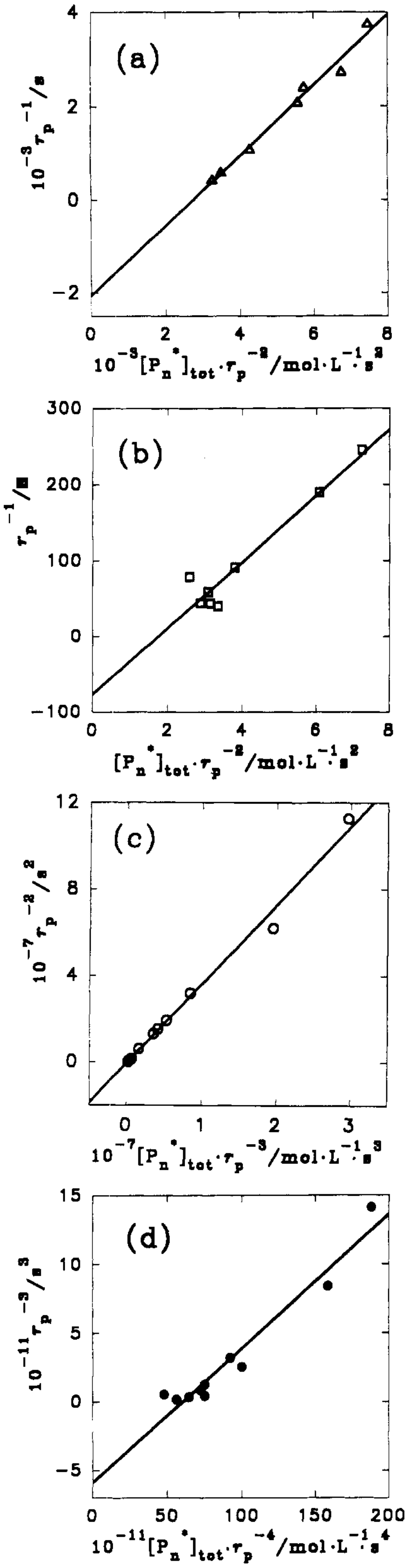

Figure 2. Plots of r_p^{1-m} vs $[\mathbf{P}_n{}^*]_{tot}r_p^{-m}$ according to eq 8: determination of the propagation rate constants (k_p) and the constants of aggregation equilibria (K_a). Anionic polymerization of (a) *o*-methoxystyrene, (b) methyl methacrylate, (c) oxirane, and (d) hexamethylcyclotrisiloxane. Other conditions are as in the caption to Figure 1.

1.67×10^3 mol·L^{-1} (Figure 2b), again close enough to the values determined previously by the numerical treatment.

Anionic Polymerization of Oxirane. Kazanskii et al.[10,11] studied the anionic polymerization of oxirane with Na^+, K^+, and Cs^+ as counterions in ethereal solvents. For all of these counterions fractional external orders in active centers at high concentrations were observed. For example, for Cs^+ counterion in THF at 70 °C the order decreased from $1/m = 1$ to $^1/_3$ when the total concentration of active centers increased from 2.5×10^{-5} to 9×10^{-3} mol·L^{-1}. The curvature of the plot $\log r_p$ against $\log[\mathbf{P}_n{}^*]_{tot}$ is illustrated in Figure 1 (experimental points represented by hollow circles). Conductometric studies excluded the presence of unpaired ions. Thus, apparently, cesium alkoxide chain ends aggregate into trimers. Kazanskii determined the absolute propagation rate constant directly from the kinetic data at low $[\mathbf{P}_n{}^*]_{tot}$ when $m = 1$. At these conditions $k_p{}^{app} = k_p$ (where $k_p{}^{app} = r_p/[\mathbf{P}_n{}^*]_{tot}$). At higher $[\mathbf{P}_n{}^*]_{tot}$ the molar fraction of the monomeric ion pairs $\alpha = k_p{}^{app}/k_p$. Thus, the aggregation equilibrium constant K_a could be calculated from eq 11 as

$$K_a = \frac{1-\alpha}{3\alpha^3[\mathbf{P}_n{}^*]_{tot}{}^2} \qquad (11)$$

This approach gave finally $k_p = 3.5$ mol^{-1}·L·s^{-1} and $K_a = 3 \times 10^6$ mol^{-1}·L.

Our treatment gave $k_p = 3.56$ mol^{-1}·L·s^{-1} and $K_a = 1.99 \times 10^6$ mol^{-1}·L, as a result of plotting the kinetic data in the coordinates $r_p{}^{-2}$ vs $[\mathbf{P}_n{}^*]_{tot}r_p{}^{-3}$ (Figure 2c).

Anionic Polymerization of Hexamethylcyclotrisiloxane (D_3). Wilczek and Kennedy[14] studied the kinetics of the anionic polymerization of D_3 with Li^+ counterion in THF as a solvent at temperatures from 0 to 60 °C. External orders in the active centers were fractional and depended on their total concentration. For example, at 22 °C the slope of the plot of $\log r_p$ vs $\log[\mathbf{P}_n{}^*]_{tot}$ increased from 0.25 to ~0.33 when $[\mathbf{P}_n{}^*]_{tot}$ decreased from 0.11 to 1.2×10^{-3} mol·L^{-1} (Figure 1, experimental points represented by filled circles). Under these conditions polymerization of D_3 proceeds exclusively with lithium silanolate ion pairs as the active centers. Consequently, it was assumed that the active centers aggregate into nonreactive tetramers and, possibly, trimers, being in a dynamic equilibrium with the actually propagating, nonaggregated species. Finally, the kinetic data were tentatively analyzed by means of eq 7, and therefore only an apparent rate constant of propagation was determined.

We have analyzed these kinetic data with eq 8 assuming first $m = 4$. The result of this analysis is given in Figure 2d: the plot of $r_p{}^{-3}$ vs $[\mathbf{P}_n{}^*]_{tot}r_p{}^{-4}$ gives a satisfactory straight-line correlation ($r = 0.972$). $k_p = 0.098$ mol^{-1}·L·s^{-1} and $K_a = 1.37 \times 10^8$ mol^{-3}·L^3 were determined. It should be stressed that an attempt to use eq 8, but with the assumption that $m = 3$, for the analysis of these data was unsuccessful: the linear regression coefficient was as low as $r = 0.22$ and the slope of the resulting line was negative, leading to $k_p < 0$. This result suggests that the ···$-Si(CH_3)_2O^-,Li^+$ ion pairs aggregate in the discussed system predominantly into tetramers.

Calculation of the log r_p vs log$[\mathbf{P}_n{}^*]_{tot}$ Dependencies

Equation 7, relating the rate of propagation with the total concentration of the active centers, was derived after assuming $[\mathbf{P}_n{}^*] = 0$. If $[\mathbf{P}_n{}^*]$ is not neglected, the respective equation contains an additional term in comparison with eq 7, namely[18]

$$\log r_p = \log\{k_p(K_{da}/m)^{1/m}\} + (1/m)\log[\mathbf{I}]_0 + \log \mathbf{X} \qquad (12)$$

where the function $\mathbf{X}$ reads

$$\mathbf{X} = (K_{da}/8[\mathbf{I}]_0 + 1)^{1/2} - (K_{da}/8[\mathbf{I}]_0)^{1/2} \quad (\text{for } m = 2) \qquad (13)$$

Table 1. Anionic Polymerization with Reversible Aggregation of Active Centers: Comparison of Propagation Rate Constants (k_p) and Equilibrium Constants of Aggregation (K_a) Determined Numerically with Constants Determined by Means of Eq 8

active species	$\cdots\!-\!CH_2\bar{C}H[C_6H_4(OCH_3)],Li^+$	$\cdots\!-\!CH_2\bar{C}(CH_3)C(O)OCH_3,Li^+$	$\cdots\!-\!CH_2CH_2O^-,Li^+$	$\cdots\!-\!Si(CH_3)_2O^-,Li^+$
monomer	*o*-methoxystyrene	methyl methacrylate	oxirane	D_3
solvent, temp	toluene, 20 °C	THF, −65 °C	THF, 70 °C	THF, 22 °C
ref	7	9	11	14
aggregation deg (m)	2	2	3	4
$k_p/(mol^{-1}{\cdot}L{\cdot}s^{-1})$				
numerical curve fit	0.83	46.0	3.50	
present work (eq 8)	0.75	43.6	3.65	0.098
$K_a/(mol^{-1}{\cdot}L)^{m-1}$				
numerical curve fit	1000	2000	3.00×10^6	
present work (eq 8)	857	1670	1.99×10^6	1.37×10^8
linear regression coeff (r)	0.9912	0.9629	0.9957	0.9720

$$\mathbf{X} = \{{}^1/_2 + (K_{da}/81[\mathbf{I}]_0{}^2 + {}^1/_4)^{1/2}\}^{1/3} + \{{}^1/_2 - (K_{da}/81[\mathbf{I}]_0{}^2 + {}^1/_4)^{1/2}\}^{1/3} \quad (\text{for } m = 3) \quad (14)$$

where $[\mathbf{I}]_0 = [\mathbf{P}_n{}^*]_{tot} = [\mathbf{P}_n{}^*] + m[(\mathbf{P}_n{}^*)_m]$ and $K_{da} = 1/K_a$. For $m \geq 4$ the function $\mathbf{X}$ is to be evaluated only numerically.

Reconstruction of the Experimental Data with the Determined k_p and K_a. Finally, we used eqs 12–14 to check whether the k_p and K_a values determined in the preceding section allow the reconstruction of the dependence of $\log r_p$ on $\log[\mathbf{P}_n{}^*]_{tot}$ found experimentally. Plots for $m \geq 4$ had to be simulated numerically on the basis of eqs 5 and 15. The latter equation stems directly from the expression for the constant of the deaggregation equilibrium (1) ($K_{da} = [\mathbf{P}_n{}^*]^m/[(\mathbf{P}_n{}^*)_m]$)

$$[\mathbf{P}_n{}^*]^m + (K_{da}/m)[\mathbf{P}_n{}^*] - (K_{da}/m)[\mathbf{I}]_0 = 0 \qquad (15)$$

as described in ref 18.

In Figure 1 the result of these calculations is shown: the solid and the dashed lines were obtained using values of k_p and K_a determined by our method (linear analytical method, eq 8) and the numerical treatment, respectively.

The computed lines reproduce the original dependencies within the calculated error of the experimental work.

Conclusions

There are a number of chemical reactions in both low- and high-molecular-weight systems involving species that tend to aggregate. These systems can be described by the following scheme:

$$m\mathbf{P}_n{}^* \overset{K_{da}}{\rightleftharpoons} (\mathbf{P}_n{}^*)_m \qquad \mathbf{P}_n{}^*\text{: active}$$

$$\mathbf{P}_n{}^* + \mathbf{M} \xrightarrow{k_p} \mathbf{P}_{n+1}{}^* \qquad (\mathbf{P}_n{}^*)_m\text{: inactive } m\text{-aggregate} \qquad (16)$$

(a more general notation could have been used).

If no simplifying assumptions are made and if it is only assumed, as shown above, that the aggregated species do not react as such with $\mathbf{M}$, then this system can be solved analytically. Such a solution for the dimerizing active species was briefly outlined by Szwarc,[5] and we have given the full solution in our works,[17,18] allowing the analytical determination of both k_p and K_a in the polymerization of ϵ-caprolactone initiated with dialkylaluminum alkoxides.

In the present paper the same equation was applied to a few systems known to conform to the kinetic situation described above and treated by the involved authors numerically. These systems are anionic polymerizations of the following monomers: *o*-methoxystyrene with Li^+ counterion, methyl methacrylate with Li^+ counterion, oxirane with Cs^+ counterion, and hexamethylcyclotrisiloxane (D_3) with Li^+ counterion.

In all of the analyzed polymerizations a good agreement was found between the values of k_p and K_a determined previously numerically and analytically in this work. The respective data are collected in Table 1.

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