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Kinetic Study on the Capping Reaction of Living Polyisobutylene with 1,1-Diarylethylenes. 2. Effect of Chain Length[†]

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ABSTRACT: The addition of 1,1-diphenylethylene (DPE) and 1,1-bis(4-methylphenyl)ethylene (DTE) to hydrochlorinated isobutylene (IB) *n*-mers, H−[IB]$_n$−Cl ($n = 2, 3, 4, 36$), in the presence of $TiCl_4$, was investigated in hexane (Hex)/methyl chloride (MeCl) 60/40 (v/v) at −80 °C using on-line visible spectroscopy. The apparent equilibrium constants of capping/decapping, K_e, and the apparent rate constants of capping, k_cK_i, have been determined. The K_e value was found to be similar for the capping reaction of all investigated IB *n*-mers with DPE, and they were about 10 times higher for DTE but independent of the chain length *n*. The value of k_cK_i increased with increasing *n* for the capping with both DPE and DTE: For $n = 3$, 4, and 36, it was approximately three, four, and five times higher, respectively, than for $n = 2$. The capping reaction of IB *n*-mers was approximately fifteen times faster with DTE than with DPE, which could be ascribed to a higher reactivity of DTE compared to DPE. The capping reaction was found to be first order in [diarylethylene] at $[DPE] < 2 \times 10^{-2}$ M and at $[DTE] < 3 \times 10^{-3}$ M. At higher than 3×10^{-3} M DTE concentrations, the order in [DTE] was lower than unity, and the apparent initial rate of addition became independent of DTE concentration at $[DTE] > 10^{-1}$ M. The change in the reaction order from unity to zero was attributed to a change in the rate-determining step from addition of DTE to the H−[IB]$_n^+$ cation to ionization of H−[IB]$_n$−Cl. The rate constant of ionization, $k_i = 6$, 11, and 15 $M^{-2}\ s^{-1}$, could then be calculated for the hydrochlorinated IB 2-, 3-, and 36-mers, respectively. Comparison of these k_i values with the corresponding k_cK_i values indicated that the observed increase of the apparent rate constant of capping with increasing chain length can be mainly ascribed to a similar increase in k_i and K_i.

Introduction

Low molecular weight model compounds resembling the structure of a growing chain end are often used in the elucidation of polymerization mechanisms and in kinetic studies.[1] However, the model compound should have chemical properties very similar to those of the polymer chain end; i.e., the choice of the right model compound is of utmost importance. For example, *tert*-butyl chloride (tBuCl) is a poor model of a dormant polyisobutylene chain end, PIBCl, in living cationic polymerization because of very large differences in *back-strain*, i.e., the release of steric strain during the rehybridization from sp^3 to sp^2 in the course of ionization.[2] Thus, the hydrochlorinated isobutylene (IB) dimer, TMPCl, thought to suitably mimic the PIB chain, has been extensively used in the past in model experiments.[3] Mayr et al.[4] reported that the electrophilic reactivities of the 1,1-diphenyl-substituted carbenium ions H−[IB]$_n$−DPE$^+$ depend little on the chain length *n*.[4a] On the other hand, the reactivities of H−[IB]$_n$−Cl in the presence of $TiCl_4$ were found to depend on *n*, but the origin of this dependence remained unclear.[4b]

We recently reported on the addition reaction of the non(homo)polymerizable monomer 1,1-diphenylethylene (DPE) to living dimeric and polymeric isobutylene chain ends in the presence of $TiCl_4$ (see Scheme 1; $n = 2, 36$).[5a] The capping reaction of living PIB with DPE or its derivatives such as 1,1-bis(4-methylphenyl)ethylene (1,1-bis(*p*-tolyl)ethylene, DTE) comprises two consecutive reactions (see Scheme 1): The first step is the ionization of PIBCl by $TiCl_4$ which is followed by the addition reaction of DPE to the polymer cation PIB$^+$. This capping reaction yields a stable and fully ionized product, PIB−DPE$^+$ but is quantitative under selected reaction conditions only. It has been found that the capping of living PIB with DPE is an equilibrium reaction shifted toward the right-hand side with decreasing temperature or with increasing Lewis acidity, solvent polarity, electron-donating ability of *p*-substituents, or concentration of reactants.[5b]

Equilibrium ($K_e = K_{cd}K_i$) and rate (k_cK_i and k_d) constants of the capping/decapping reaction have been determined using spectroscopic methods (NMR and UV/visible) in the temperature range from −80 to −40 °C.[5] The value of the apparent equilibrium constant, K_e, was found to decrease by approximately 4 orders of magnitude and that of the apparent rate constant, k_cK_i, by 2 orders of magnitude upon increasing the temperature from −80 to −40 °C.[5a] According to the latter finding, the value of the activation energy of the capping reaction is apparently negative, which was attributed to a negative enthalpy of the ionization of PIBCl, already invoked to explain the negative apparent activation energy for the rate of propagation of IB.[6] Interestingly, it was found that the capping of PIBCl with DPE in

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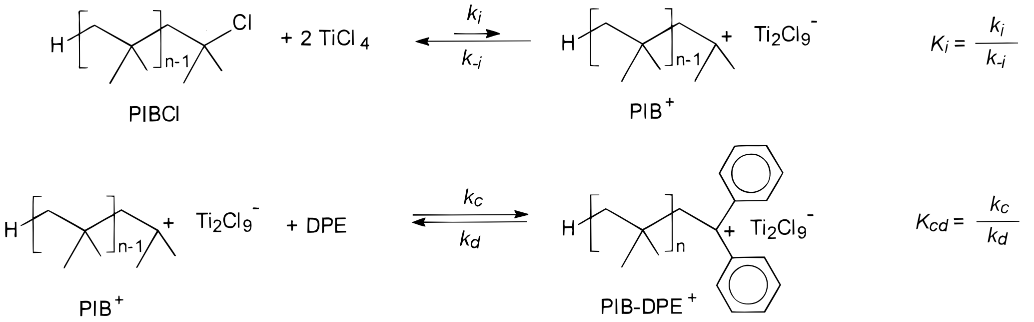
Scheme 1. Ionization of PIBCl with $TiCl_4$ and Subsequent Capping of $PIB^+Ti_2Cl_9^-$ with DPE.



the presence of $TiCl_4$ and 2,6-di-*tert*-butylpyridine (DTBP) in Hex/MeCl 60/40 (v/v) at −80 °C is approximately seven times faster than that of TMPCl. TMPCl can therefore hardly be regarded as an appropriate model compound for PIBCl, although the values of the corresponding apparent equilibrium constants (K_e) were very similar.[5a]

The chain length dependence of the apparent rate constant of capping (k_cK_i) may be explained by a constant rate (k_c) but an increased equilibrium constant of ionization (K_i) with increasing chain length. However, k_c and K_i could not be separately determined to confirm this hypothesis. A similar hypothesis was reported by Mayr et al.[4b] to explain the differences of the addition rates of IB to the hydrochlorinated IB dimer and trimer in the presence of BCl_3 at −78 °C. The apparent rate constant of IB addition (k_pK_i, where k_p is the rate constant of IB oligomerization) to the hydrochlorinated trimer was found to be three times higher than that obtained with the hydrochlorinated dimer. This was mainly ascribed to a somewhat higher degree of ionization (i.e., a higher value of K_i) of the trimer due to an increase of back-strain.[4b]

The large reactivity difference between IB dimers' and polymers' ends is assumed to gradually disappear with increasing chain length. In the present work, we report on kinetic and thermodynamic parameters of the reactions between hydrochlorinated IB *n*-mers ($n = 2, 3, 4, 36$) and DPE and DTE, to further elucidate the effect of chain length on capping/decapping kinetics.

Experimental Part

Visible Spectroscopy. For the visible spectroscopic measurements a quartz immersion probe 661.000-QX (Hellma, optical path: 0.02 cm) connected to a fiber optic Tungsten light source (Ocean Optics) and a Zeiss MMS 256 photodiode array detector was used. The latter was connected to a personal computer via a TEC5 interface, and the spectra were recorded using the "Aspect Plus" software (Zeiss).

Materials. All chemicals and solvents were purified as described previously[7] or used as received. DTE and 1-methoxy-1,1-bis(4-methylphenyl)-3,3,5,5-tetramethylhexane (TMP−DTE−OMe) were synthesized following procedures reported elsewhere.[7a,e] Hydrochlorinated IB *n*-mers: 2-chloro-2-methylpropane (tBuCl, $n = 1$) was used as received from Aldrich; 2-chloro-2,4,4-trimethylpentane (TMPCl, $n = 2$), 2-chloro-2,4,4,6,6-pentamethylheptane ($n = 3$), and 2-chloro-2,4,4,6,6,8,8-heptamethylnonane ($n = 4$) were synthesized as described elsewhere;[8] PIBCl ($n_{\mathrm{average}} = 36$) was prepared in situ prior to capping.[5a]

General Reaction Procedure. All reactions were carried out at −80 °C under a dry nitrogen atmosphere using [IB *n*-mer] = 2.0×10^{-3} M, [diarylethylene] = 2.0×10^{-3} M, [$TiCl_4$] = 1.64×10^{-2} M, and [DTBP] = 3.0×10^{-3} M (unless otherwise noted). The solution of the IB *n*-mer, $TiCl_4$, and DTBP in Hex/MeCl 60/40 (v/v) was kept for ∼1 h to allow complex inorganic salts to precipitate. Then, the solution was filtered in a vacuum, and the reference spectrum taken. Finally, either DPE or DTE was added, and the accumulation of the visible spectra started.

Results and Discussion

Kinetic Scheme of the Capping/Decapping Reaction. As described earlier,[5] capping of PIBCl is a two-step process that involves the ionization of the chain end and the subsequent addition of DPE or its derivatives (Scheme 1). Considering that the concentration of free ions is negligible compared to that of ion pairs in Hex/MeCl 60/40 (v/v),[6a] the equilibrium constant of ionization of PIBCl is expressed as

$$K_i = \frac{k_i}{k_{-i}} = \frac{[\mathrm{PIB^+Ti_2Cl_9^-}]}{[\mathrm{PIBCl}][\mathrm{TiCl_4}]^2} \tag{1}$$

and the equilibrium constant of the capping/decapping equilibrium as

$$K_{cd} = \frac{k_c}{k_d} = \frac{[\mathrm{PIB{-}DPE^+Ti_2Cl_9^-}]}{[\mathrm{PIB^+Ti_2Cl_9^-}][\mathrm{DPE}]} \tag{2}$$

The apparent equilibrium constant is given by

$$K_e = K_{cd}K_i = \frac{k_cK_i}{k_d} = \frac{[\mathrm{PIB{-}DPE^+Ti_2Cl_9^-}]}{[\mathrm{PIBCl}][\mathrm{DPE}][\mathrm{TiCl_4}]^2} \tag{3}$$

The evolution of [$PIB{-}DPE^+\ Ti_2Cl_9^-$] with time is described by

$$\frac{d}{dt}[\mathrm{PIB{-}DPE^+Ti_2Cl_9^-}] = k_c[\mathrm{PIB^+Ti_2Cl_9^-}][\mathrm{DPE}] - k_d[\mathrm{PIB{-}DPE^+Ti_2Cl_9^-}] \tag{4}$$

Assuming steady state for $PIB^+\ Ti_2Cl_9^-$, i.e.

$$\frac{d}{dt}[\mathrm{PIB^+Ti_2Cl_9^-}] = k_i[\mathrm{PIBCl}][\mathrm{TiCl_4}]^2 - k_{-i}[\mathrm{PIB^+Ti_2Cl_9^-}] - k_c[\mathrm{PIB^+Ti_2Cl_9^-}][\mathrm{DPE}] + k_d[\mathrm{PIB{-}DPE^+Ti_2Cl_9^-}] = 0 \tag{5}$$

the concentration of $PIB^+\ Ti_2Cl_9^-$ is given as

$$[\mathrm{PIB^+Ti_2Cl_9^-}] = \frac{k_i[\mathrm{PIBCl}][\mathrm{TiCl_4}]^2 + k_d[\mathrm{PIB{-}DPE^+Ti_2Cl_9^-}]}{k_{-i} + k_c[\mathrm{DPE}]} \tag{6}$$

If $k_{-\mathrm{i}} \gg k_\mathrm{c}[\mathrm{DPE}]$, the second term in the denominator of eq 6 can be neglected and eq 4 can be written as

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{PIB{-}DPE^+Ti_2Cl_9^-}] = k_\mathrm{c}K_\mathrm{i}[\mathrm{PIBCl}][\mathrm{DPE}][\mathrm{TiCl_4}]^2 + k_\mathrm{d}\left(\frac{k_\mathrm{c}[\mathrm{DPE}]}{k_{-\mathrm{i}}} - 1\right)[\mathrm{PIB{-}DPE^+Ti_2Cl_9^-}] \quad (7)$$

According to eq 7, the capping reaction should be first-order with respect to [DPE] when $k_{-\mathrm{i}} \gg k_\mathrm{c}[\mathrm{DPE}]$, which has been found to be the case at $[\mathrm{DPE}] < 2 \times 10^{-2}$ M,[5a] and it should be independent of [DPE] (or [DTE]) when $k_{-\mathrm{i}} \ll k_\mathrm{c}[\mathrm{DPE}]$, e.g., at high diarylethylene concentrations (this case will be discussed below).

Determination of the Rate and Equilibrium Constants via Visible Spectroscopy. For the calculation of the rate and the equilibrium constants of the capping/decapping reaction, the concentration of diarylcarbenium ions was derived from the measured absorbance at the absorption maximum λ_max and the corresponding molar adsorption coefficient ϵ_max, as described below. When capping is first order in diarylethylene concentration (which has been shown for DPE at low concentration but not for DTE), eq 7 is valid and the respective values of the apparent rate constant of capping, $k_\mathrm{c}K_\mathrm{i}$, and the equilibrium constant, K_e, can be determined from the initial slope and the plateau of the absorbance vs time plot, respectively, as follows:

(a) At $t \to 0$, the decapping reaction is negligible, and the initial rate of formation of the cation PIB−DPE$^+$ can be calculated according to

$$\left(\frac{\mathrm{d}}{\mathrm{d}t}[\mathrm{PIB{-}DPE^+Ti_2Cl_9^-}]\right)_{t\to 0} = k_\mathrm{c}[\mathrm{PIB^+Ti_2Cl_9^-}][\mathrm{DPE}] = k_\mathrm{c}K_\mathrm{i}c_0^{\,2}[\mathrm{TiCl_4}]^2 \quad (8)$$

where $c_0 = [\mathrm{PIBCl}] = [\mathrm{DPE}]$ (cf. Experimental Part).

(b) The value of the apparent equilibrium constant, K_e, can be calculated from the constant absorbance obtained at long reaction times ($t \to \infty$) (indicating that the thermodynamic equilibrium of the capping/decapping reaction has been established) using eq 3. A more detailed description of the procedure has been given.[5a]

For the 3,3,5,5-tetramethyl-1,1-diphenylhexyl cation (TMP−DPE$^+$) in Hex/MeCl 60/40 (v/v), $\epsilon_\mathrm{max} = 45\,000$ M^{-1} cm^{-1} at $\lambda_\mathrm{max} = 440$ nm has already been reported.[5a] To determine λ_max and ϵ_max of the bis(4-methylphenyl)carbenium ion (TMP−DTE$^+$) in Hex/MeCl 60/40 (v/v), the corresponding model compound TMP−DTE−OMe was ionized in the presence of a large excess of $\mathrm{TiCl_4}$ ($[\mathrm{TiCl_4}]/[\mathrm{TMP{-}DTE{-}OMe}] = 130$) at −80 °C—these reaction conditions ensure complete ionization and prevent decapping. TMP−DTE$^+$ showed an absorption maximum at $\lambda_\mathrm{max} = 464$ nm (cf. Figure 1), and the molar absorption coefficient was found to be $\epsilon_\mathrm{max} = 44\,000$ M^{-1} cm^{-1}. These values are virtually identical to that found for the DTE-capped dimeric styryl end in $\mathrm{CHCl_3/CH_2Cl_2}$ 70/30 (v/v) ($\lambda_\mathrm{max} = 467$ nm, $\epsilon_\mathrm{max} = 44\,000$ M^{-1} cm^{-1})[9] and are similar to those determined for TMP−DPE$^+$ under identical conditions.

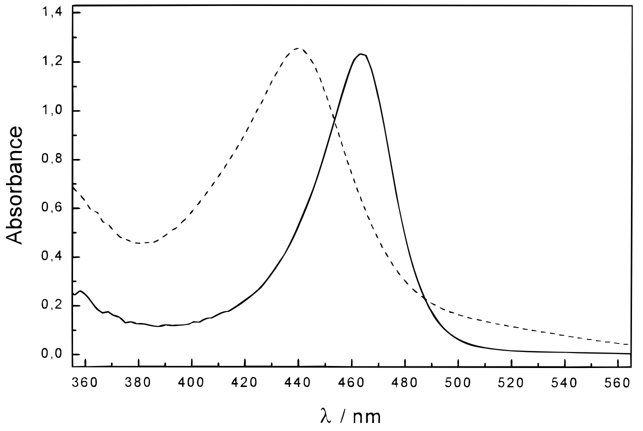


Figure 1. UV/visible spectrum of TMP−DPE$^+$ (- - -) and TMP−DTE$^+$ (—) (both at 1.4×10^{-3} M) in Hex/MeCl 60/40 (v/v) at −80 °C.

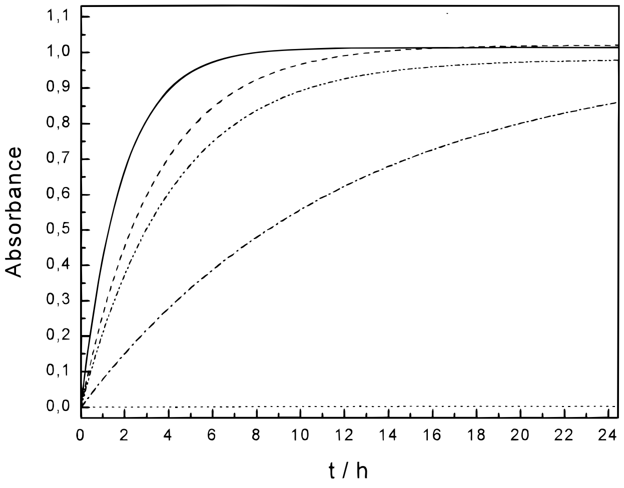
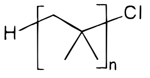


Figure 2. Plot of the absorbance at $\lambda = 440$ nm vs time for the capping reaction of hydrochlorinated IB *n*-mers with DPE in Hex/MeCl 60/40 (v/v) at −80 °C: *n* = 1 (···), 2 (− · −), 3 (− · · −), 4 (- - -), 36 (—).

Table 1. Equilibrium Constant, K_e, and Rate Constants, $k_\mathrm{c}K_\mathrm{i}$ and k_d, for the Capping/Decapping Reaction of Hydrochlorinated IB *n*-mers (*n* = 1−4, 36) with DPE in the Presence of $\mathrm{TiCl_4}$ and DTBP at −80 °C[a]

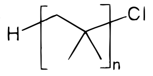
	$K_\mathrm{e}/10^6$ M^{-3}	$k_\mathrm{c}K_\mathrm{i}$/M^{-3} s^{-1}	$k_\mathrm{d}/10^{-5}$ s^{-1}
n = 1	0.1	0.3	0.2
2	4.9	24	0.5
3	4.9	69	1.3
4	5.5	85	1.6
36	5.2	170	3.2

[a] For reaction conditions, see Experimental Part; $[\mathrm{TiCl_4}] = 0.146$ M was used for the capping of *tert*-butyl chloride (*n* = 1).

Capping with DPE. Figure 2 shows the absorbance vs time plots and Table 1 shows the thermodynamic and kinetic constants determined from these plots for the capping of hydrochlorinated IB oligomers with *n* = 1−4 and PIBCl with DPE in the presence of $\mathrm{TiCl_4}$ and DTBP in Hex/MeCl 60/40 (v/v) at −80 °C.

According to Figure 2, the initial rate of formation of PIB−DPE$^+$ (→ initial slope) and thus $k_\mathrm{c}K_\mathrm{i}$ increases with increasing chain length. The absorbance at $t \to \infty$ however is similar for every $n \geq 2$, which suggests that the apparent equilibrium constants K_e are comparable. Compared to the $k_\mathrm{c}K_\mathrm{i}$ and K_e values obtained for the capping of the higher oligomers (Table 1), those for the hydrochlorinated IB (tBuCl) are significantly lower. Similar results have been reported by Mayr et al.,[4b] who found that the addition of trimethylallylsilane to *tert*-

Table 2. Equilibrium Constant, K_e, and Rate Constants, k_cK_i and k_d, for the Capping/Decapping Reaction of Hydrochlorinated IB n-mers ($n = 2-4, 36$) with DTE in the Presence of $TiCl_4$ and DTBP at −80 °C[a]

	$K_e/10^6\ M^{-3}$	$k_cK_i/M^{-3}\ s^{-1}$	$k_d/10^{-5}\ s^{-1}$
$n = 2$	43	350	0.8
3	58	1060	1.8
4	58	1290	2.2
36	48	1730	3.6

[a] For reaction conditions, see Experimental Part.

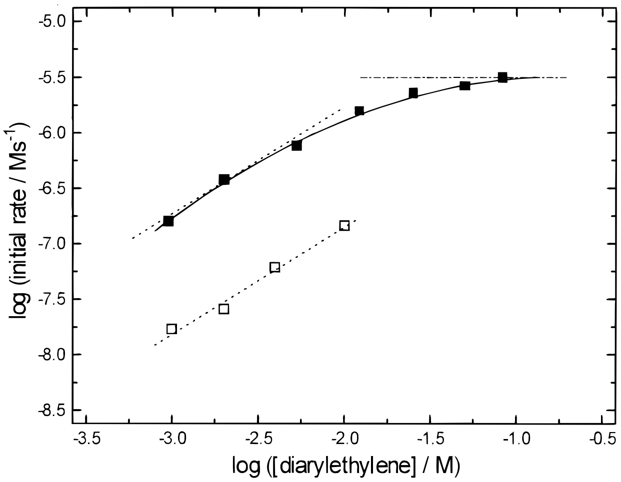


Figure 3. Bilogarithmic plot of the initial rate of capping vs the concentration of diarylethylene for the capping of TMPCl with DPE (□) and DTE (■) in Hex/MeCl 60/40 (v/v) at −80 °C. Zero-order (— • • —) and first-order (- - -) kinetics in [diarylethylene] are indicated.

butyl cation is much slower than that to the dimeric cation ($n = 2$). This difference in rate was attributed to the back-strain effect, which is assumed to affect the rate and extent of ionization.

The finding that the rate constant k_cK_i (and k_d) for $n = 3$ is three times higher than that for $n = 2$ is in accordance with that of Mayr et al.[4b] Surprisingly, the capping/decapping of the hydrochlorinated IB tetramer is still two times slower than that of PIBCl.

Capping with DTE. Table 2 shows the thermodynamic and kinetic constants for the capping of the hydrochlorinated IB oligomers with $n = 2-4$ and PIBCl with DTE ([DTE] = 2.0×10^{-3} M; i.e., the same concentration which was used for DPE in Table 1) in the presence of $TiCl_4$ and DTBP in Hex/MeCl 60/40 (v/v) at −80 °C.

Similar to the results with DPE, the value of K_e remains virtually unchanged while that of k_cK_i increases with increasing chain length. For $n = 3$, 4, and 36, k_cK_i is three, four, and five times higher, respectively, than that for $n = 2$. Interestingly, capping with DTE is approximately 15 times faster than capping with DPE.

Since k_c is 15 times higher for DTE compared to DPE, the question arises whether $k_{-i} \gg k_c$[DTE], a necessary condition to use eq 7, is valid or not at [DTE] = 2.0×10^{-3} M. To investigate this point, the capping reaction of TMPCl with DTE was also carried out with increasing concentration of DTE from 1.0×10^{-3} to 8.3×10^{-2} M. Figure 3 shows the log(initial rate)s as a function of log[diarylethylene] for DTE and, for comparison, those for DPE.[5a]

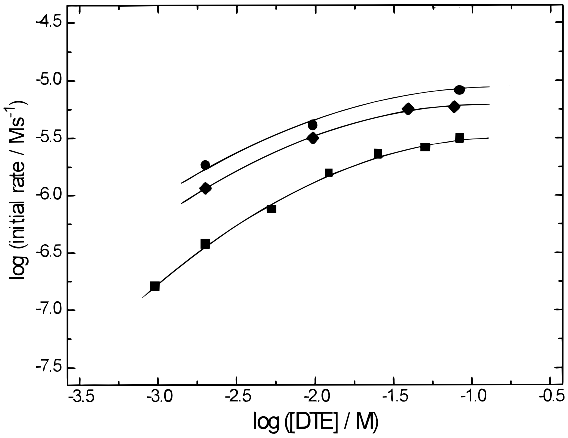


Figure 4. Bilogarithmic plot of the initial rate of capping vs the concentration of DTE for the capping reaction of hydrochlorinated IB n-mers with DTE in Hex/MeCl 60/40 (v/v) at −80 °C: $n = 2$ (■), 3 (◆), and 36 (●).

It is clearly shown that the capping of TMPCl with DTE follows first-order kinetics at [DTE] < 3×10^{-3} M, i.e., $k_{-i} \gg k_c$[DTE] and thus the use of eq 7 is justified at [DTE] = 2.0×10^{-3} M.

At [DTE] > 3×10^{-3} M, the reaction order in [DTE] is lower than unity, and it is zero at [DTE] > 10^{-1} M—eq 7 is therefore not valid. The independence of the rate of capping from [DTE] at [DTE] > 10^{-1} M indicates that the ionization of TMPCl (first step in Scheme 1) has become the rate-determining step. Then, k_{-i} in the denominator of eq 6 can be neglected, and when decapping is negligible, eq 4 can be written as

$$\frac{d}{dt}[\text{PIB}-\text{DTE}^+\text{Ti}_2\text{Cl}_9^-] = k_i[\text{PIBCl}][\text{TiCl}_4]^2 \qquad (9)$$

Importantly, from eq 9 the value of the rate constant of ionization, k_i, can be calculated for the first time. From the limiting initial rate of capping (cf. Figures 3 and 4), $k_i = 6\ M^{-2}\ s^{-1}$ was obtained for TMPCl.

As already mentioned, the chain length dependence of the apparent rate constant of capping, k_cK_i, may be explained by a constant reactivity, k_c, but an increased equilibrium constant of ionization, K_i, with increasing chain length due to the effect of back-strain. However, k_c and K_i could not be separately determined to confirm this hypothesis. Considering $K_i = k_i/k_{-i}$ (cf. eq 1), it is likely that any increase with increasing chain length would be due to an increase of k_i and not to a decrease of k_{-i}. The proof of the hypothesis of an increasing K_i with increasing n may be obtained by determining the k_i values—as was shown for TMPCl—for the higher IB n-mers. Comparison of the relative ratios of the k_i values with the relative values of k_cK_i will allow the separation of the effect of k_c and K_i. Therefore, the log(initial rates) of the capping reaction of the IB trimer and PIBCl ($n = 36$) with DTE were measured as a function of DTE concentration. Figure 4 shows the corresponding plots for $n = 2$, 3, and 36.

The general tendency of the plots are similar: $n = 3$ runs higher but almost parallel to the plot for $n = 2$, and $n = 36$ is placed at the top. From these plots, the k_i values were calculated from the limiting initial rates: $k_i = 6$, 11, and 15 $M^{-2}\ s^{-1}$ for $n = 2$, 3, and 36, respectively. Comparison of these values with the corresponding k_cK_i values listed in Tables 1 and 2 indicates that the increase of the apparent rate constant of capping with increasing chain length can in fact be ascribed to a similar increase in k_i and K_i.

Conclusions

On the basis of a kinetic investigation of the addition reaction of DPE and DTE to hydrochlorinated IB n-mers, H−[IB]$_n$−Cl ($n = 2, 3, 4, 36$), in the presence of $TiCl_4$ in Hex/MeCl 60/40 (v/v) at −80 °C, we conclude that the hydrochlorinated dimer TMPCl is not an appropriate model for the dormant polyisobutylene chain end, PIBCl, in living cationic polymerization. Although the value of the apparent equilibrium constant of capping/decapping, K_e, was found to be independent of chain length, that of the apparent rate constant of capping, k_cK_i increased with increasing n for both DPE and DTE. For $n = 3$, 4, and 36, k_cK_i is approximately three, four, and five times higher, respectively, than that for $n = 2$. Capping with DTE was approximately 15 times faster than with DPE indicating a much higher reactivity of DTE.

The capping reaction is first order in [diarylethylene] at [DPE] $< 2 \times 10^{-2}$ M and at [DTE] $< 3 \times 10^{-3}$ M. At higher than 3×10^{-3} M DTE concentrations, the order in [DTE] is lower than unity and the apparent initial rate of addition becomes independent of DTE concentration at [DTE] $> 10^{-1}$ M. The change in the reaction order from unity to zero is attributed to a change in the rate-determining step from addition of DTE to the H−[IB]$_n^+$ cation to ionization of H−[IB]$_n$−Cl. From the limiting initial rate of capping with DTE at [DTE] > 10^{-1} M, the rate constant of ionization, k_i could be calculated for the first time—for the hydrochlorinated IB 2-, 3-, and 36-mers, $k_i = 6$, 11, and 15 $M^{-2}\,s^{-1}$ were obtained, respectively. Comparison of these k_i values with the corresponding k_cK_i values indicates that the observed chain length dependence of the latter could be mainly ascribed to a similar increase in k_i and K_i, due to an increase in back-strain with increasing n.

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