

Kinetic Study on the Capping Reaction of Living Polyisobutylene with 1,1-Diphenylethylene. 1. Effect of Temperature and Comparison to the Model Compound 2-Chloro-2,4,4-trimethylpentane

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Received June 22, 1998; Revised Manuscript Received September 15, 1998

ABSTRACT: The addition reaction of 1,1-diphenylethylene to polymeric and dimeric isobutylene living chain ends in the presence of TiCl_4 was investigated in hexane/MeCl 60/40 (v/v) at -80 to -40 °C using on-line UV–vis spectroscopy. The apparent equilibrium constants of capping/decapping, K_e , and the apparent rate constants of capping, $k_c K_i$, were directly measured, and from these values, the corresponding rate constants of decapping, k_d , were calculated. The activation energy is found to be apparently negative for the capping reaction ($k_c K_i$) and positive for the decapping reaction (k_d). However, the respective activation parameters for the polyisobutylene differ significantly from those of the dimer; i.e., the chain length affects the kinetics of the capping/decapping reaction.

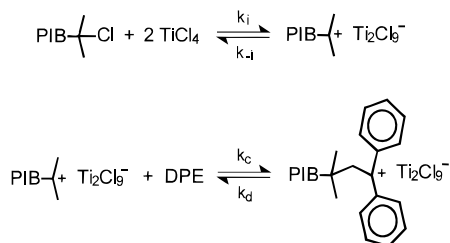
Introduction

The recent success of carbocationic macromolecular engineering in the synthesis of polyisobutylene-based functional polymers and block copolymers with high structural integrity is attributed to the intermediate capping of the living polyisobutylene (PIB) with non-homopolymerizable monomers such as 1,1-diphenylethylene (DPE) or its derivatives. By this process, a stable carbenium ion is formed, which is well suited for the quantitative end-functionalization of PIBs with π -nucleophiles, e.g., silyl ketene acetals¹ or allylsilanes,² and for the controlled initiation of a second monomer such as *p*-methylstyrene³, α -methylstyrene,⁴ isobutyl vinyl ether,⁵ and methyl vinyl ether.⁶ Also, DPE-capped PIBs can be quantitatively metalated and then used as macroinitiators for the anionic polymerization of methacrylates.⁷ Recently, bis-DPE compounds have been successfully used as “living” coupling agents⁸ for the synthesis of A_2B_2 star block copolymers.⁹

In any case, the synthesis of these polymers requires the quantitative addition of a single DPE unit to the living PIB chains. It has been shown that even for a large excess of DPE exclusively monoaddition occurs¹ but that the capping reaction is quantitative only under selected conditions. In fact, one has to consider a capping/decapping equilibrium that shifts toward the DPE-capped PIB with decreasing temperature and increasing Lewis acidity, solvent polarity, electron-donating ability of *p*-substituents, and concentrations of the reactants.^{10,11} In those works, the capping reaction of a chloro-terminated PIB (=PIBCl) with DPE and the decapping reaction of a methoxy-terminated DPE-capped PIB (=PIB-DPE-OMe) were monitored by

conductivity measurements and NMR spectroscopy. Using conductivity measurements, the reactions could be followed *on-line*, but since the dissociation equilibrium constant was not known, neither rates nor equilibrium constants could be calculated. These values were determined by NMR, but only *off-line*, so that the number of experimental data points was rather limited.

Since the cation of the DPE-capped dimer of isobutylene (TMP-DPE^+) shows a maximum absorption in the visible range ($\lambda_{\text{max}} = 444$ nm) with a very high molar absorption coefficient ($\epsilon_{\text{max}} = 37\,000\text{ M}^{-1}\cdot\text{cm}^{-1}$ in CH_2Cl_2),¹² visible spectroscopy is well suited to follow the capping and the decapping reaction *on-line*. In contrast to conductivity measurements, this method provides the total concentration of the diphenyl-substituted carbenium ions (ion-pairs and free ions exhibit practically identical λ_{max} and ϵ_{max})¹³ and thus the rate and equilibrium constants. However, PIB is sparingly soluble in CH_2Cl_2 at low temperatures, and above -60 °C termination of the PIB cation via β -proton elimination occurs.¹¹ In hexane/methyl chloride (Hex/MeCl) solvent mixtures instead, PIBs are better soluble and the decomposition of the cation is considerably slow even at -40 °C.¹⁴ In the present work, we report on the rate and equilibrium constants of the capping reaction of PIBCl with DPE in the presence of TiCl_4 at -80 to -40 °C in Hex/MeCl 60/40 (v/v) using on-line visible spectroscopy. The apparent rate constant of capping and the equilibrium constant of the capping/decapping reaction could directly be measured, and the effects of chain length ($\text{DP}_n = 2$ and $\text{DP}_n \approx 36$) and temperature were investigated.

Scheme 1. Ionization of PIBCl with TiCl₄ (above) and Subsequent Capping of PIB⁺Ti₂Cl₉[−] with DPE (below)

Experimental Part

Materials. All chemicals and solvents were purified as described previously^{3–6} or used as received.

Visible Spectroscopy. For the visible spectroscopy 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).

Reaction Procedures. All reactions were carried out under a dry nitrogen atmosphere using [TMPCl] = 2.0×10^{-3} M (TMPCl = 2-chloro-2,4,4-trimethylpentane), [DPE] = 2.0×10^{-3} M, and [DTBP] = 3.0×10^{-3} M (DTBP = 2,6-di-*tert*-butylpyridine) unless otherwise noted. The concentration of TiCl₄ was increased with increasing temperature in order to obtain 30–70% DPE-capped cations in the equilibrium state: [TiCl₄] = 1.64×10^{-2} M (−80 °C), 7.8×10^{-2} M (−70 °C), 0.146 M (−60 °C), 0.473 M (−50 °C), 0.800 M (−40 °C). **Capping of TMPCl:** The solution of TiCl₄ and DTBP in Hex/MeCl 60/40 (v/v) was kept for ~1 h allowing complex inorganic salts to precipitate.¹⁵ After TMPCl was added, the solution was filtered at low temperature under vacuum, and the reference spectrum was taken. Then, DPE was added, and the visible spectroscopy measurement was started. **Capping of PIBCl** ($M_n \approx 2000$, $M_w/M_n \approx 1.2$): Isobutylene, DTBP, and TMPCl were mixed in Hex/MeCl 60/40 (v/v) at −80 °C, and the polymerization was initiated by adding TiCl₄, [TiCl₄] = 1.64×10^{-2} or 3.6×10^{-2} M. After ~1 h, more TiCl₄ was added to reach the desired final concentration. The reaction mixture was filtered, the temperature was raised to the capping temperature, and the reference spectrum was taken. Then, DPE was added, and the visible spectroscopy measurement was started.

Results and Discussion

Kinetic Scheme of the Capping/Decapping Reaction. Scheme 1 shows the general chemical reactions that correspond to the capping reaction of PIBCl.¹¹

Considering that the concentration of free ions is negligible compared to that of ion pairs in Hex/MeCl 60/40 (v/v),¹⁶ the equilibrium constant of ionization of PIBCl is expressed as

$$K_i = \frac{k_i}{k_{-i}} = \frac{[\text{PIB}^+\text{Ti}_2\text{Cl}_9^-]}{[\text{PIBCl}][\text{TiCl}_4]^2} \quad (1)$$

and the equilibrium constant of the capping/decapping equilibrium as

$$K_{cd} = \frac{k_c}{k_d} = \frac{[\text{PIB-DPE}^+\text{Ti}_2\text{Cl}_9^-]}{[\text{PIB}^+\text{Ti}_2\text{Cl}_9^-][\text{DPE}]} \quad (2)$$

The apparent equilibrium constant, which is the only experimentally accessible parameter, is given by

$$K_e = K_{cd}K_i = \frac{k_c K_i}{k_d} = \frac{[\text{PIB-DPE}^+\text{Ti}_2\text{Cl}_9^-]}{[\text{PIBCl}][\text{DPE}][\text{TiCl}_4]^2} \quad (3)$$

The evolution of [PIB-DPE⁺Ti₂Cl₉[−]] with time is described by

$$\frac{d}{dt}[\text{PIB-DPE}^+\text{Ti}_2\text{Cl}_9^-] = k_c[\text{PIB}^+\text{Ti}_2\text{Cl}_9^-][\text{DPE}] - k_d[\text{PIB-DPE}^+\text{Ti}_2\text{Cl}_9^-] \quad (4)$$

At steady state,

$$\begin{aligned} \frac{d}{dt}[\text{PIB}^+\text{Ti}_2\text{Cl}_9^-] &= k_i[\text{PIBCl}][\text{TiCl}_4]^2 - \\ &k_{-i}[\text{PIB}^+\text{Ti}_2\text{Cl}_9^-] - k_c[\text{PIB}^+\text{Ti}_2\text{Cl}_9^-][\text{DPE}] + \\ &k_d[\text{PIB-DPE}^+\text{Ti}_2\text{Cl}_9^-] = 0 \end{aligned} \quad (5)$$

the concentration of PIB⁺Ti₂Cl₉[−] is given as

$$[\text{PIB}^+\text{Ti}_2\text{Cl}_9^-] = \frac{k_i[\text{PIBCl}][\text{TiCl}_4]^2 + k_d[\text{PIB-DPE}^+\text{Ti}_2\text{Cl}_9^-]}{k_{-i} + k_c[\text{DPE}]} \quad (6)$$

If $k_{-i} \gg k_c[\text{DPE}]$, eq 4 can then be written as

$$\frac{d}{dt}[\text{PIB-DPE}^+\text{Ti}_2\text{Cl}_9^-] = k_c K_i [\text{PIBCl}][\text{DPE}][\text{TiCl}_4]^2 - k_d[\text{PIB-DPE}^+\text{Ti}_2\text{Cl}_9^-] \quad (7)$$

According to eq 7, the capping reaction should be first-order with respect to [DPE] when $k_{-i} \gg k_c[\text{DPE}]$ (it should be independent from [DPE] when $k_{-i} \ll k_c[\text{DPE}]$)—this was, in fact, found to be the case (see below).

Determination of the Rate and Equilibrium Constants via Visible Spectroscopy. The calculation of the rate and the equilibrium constants of the capping/decapping reaction requires the concentration of diphenylcarbenium ions:

$$[\text{PIB-DPE}^+\text{Ti}_2\text{Cl}_9^-] = \frac{\text{absorbance at } \lambda_{\max}}{\epsilon_{\max} d} \quad (8)$$

where ϵ_{\max} is the molar absorption coefficient at λ_{\max} (for both free ions and ion pairs)¹³ and d is the optical path length. Since TiCl₄ was always used in excess ([TiCl₄]/[PIBCl] > 8, cf. Experimental Part), ionization of the DPE-capped end is considered to be quantitative.¹²

To determine λ_{\max} and ϵ_{\max} of the diphenylcarbenium ion in Hex/MeCl 60/40 (v/v), the model compound TMP-DPE-OMe was ionized at −80 °C in the presence of a large excess of TiCl₄ ([TiCl₄]/[TMP-DPE-OMe] > 350). Under these conditions, ionization of TMP-DPE-OMe is complete and the decapping of the resulting TMP-DPE⁺cation is prevented.¹² The TMP-DPE⁺cation showed an absorption maximum at $\lambda_{\max} = 440$ nm (cf. Figure 1), and the molar absorption coefficient was found to be $\epsilon_{\max} = 45\,000 \text{ M}^{-1}\text{cm}^{-1}$. This value is somewhat different from that obtained in CH₂Cl₂ ($\epsilon_{\max} = 37\,000 \text{ M}^{-1}\text{cm}^{-1}$),¹² which might be attributed to different polarities of the media.¹⁷

Figures 1 and 2 show some selected UV-vis spectra and the time-dependent evolution of the absorbance at

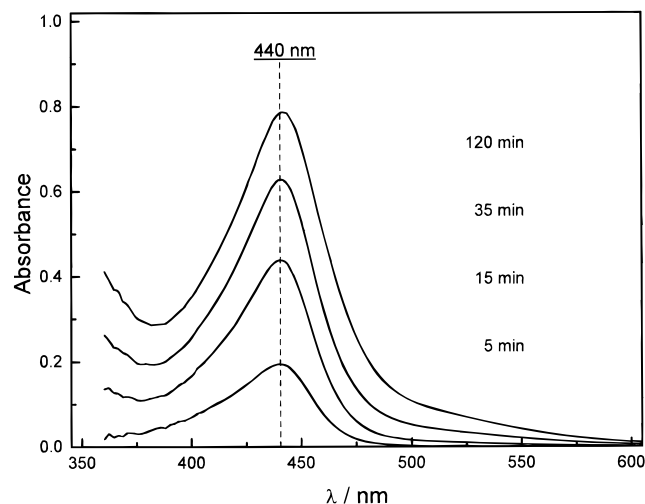


Figure 1. Selected visible spectra obtained during the capping of PIBCl with DPE in Hex/MeCl 60/40 (v/v) at $-70\text{ }^{\circ}\text{C}$ (see Experimental Part for reaction conditions).

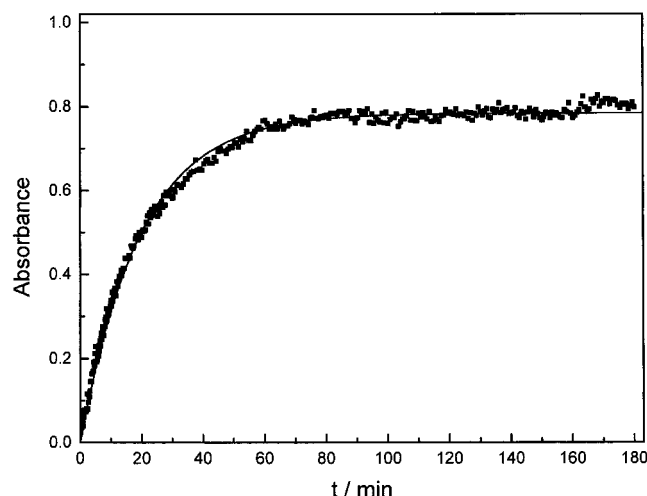


Figure 2. Plot of the absorbance at $\lambda_{\text{max}} = 440\text{ nm}$ versus time for the capping reaction of PIBCl with DPE in Hex/MeCl 60/40 (v/v) at $-70\text{ }^{\circ}\text{C}$, cf. Figure 1.

$\lambda_{\text{max}} = 440\text{ nm}$, respectively, which were obtained during the course of the capping reaction of PIBCl ($\text{DP}_n \approx 36$) with DPE in Hex/MeCl 60/40 (v/v) at $-70\text{ }^{\circ}\text{C}$. Similar plots were obtained for TMPCl ($\text{DP}_n = 2$) and at all temperatures investigated.

The capping reaction of TMPCl with DPE at $-80\text{ }^{\circ}\text{C}$ was found to follow first-order kinetics with respect to [DPE] (cf. Figure 3), and eq 7 is therefore valid under the chosen reaction conditions. Then, we can determine the respective values of the apparent rate constant of capping, $k_c K_i$, and the equilibrium constant, K_e , from the initial slope and the plateau of the plot in Figure 2, respectively, as follows:

(a) At $t \rightarrow 0$, the decapping reaction is negligible and, according to eq 7, the initial rate of formation of the PIB-DPE⁺ cation is given as

$$\left(\frac{d}{dt}[\text{PIB-DPE}^+\text{Ti}_2\text{Cl}_9^-]\right)_{t=0} = k_c[\text{PIB}^+\text{Ti}_2\text{Cl}_9^-][\text{DPE}] = k_c K_i c_0^2 [\text{TiCl}_4]^2 \quad (9)$$

with $c_0 = [\text{PIBCl}] = [\text{DPE}]$ (cf. Experimental Part). Considering eq 8, we obtain

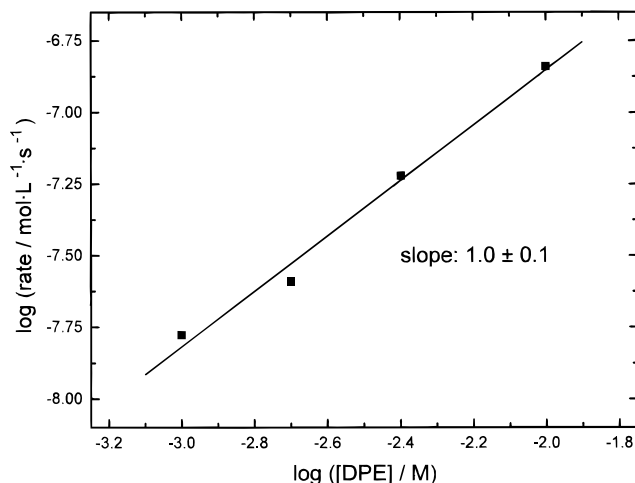


Figure 3. Determination of the reaction order with respect to [DPE] for the capping reaction of TMPCl with DPE in Hex/MeCl 60/40 (v/v) at $-80\text{ }^{\circ}\text{C}$. $[\text{TMPCl}] = 2.0 \times 10^{-3}\text{ M}$, $[\text{TiCl}_4] = 1.64 \times 10^{-2}\text{ M}$, $[\text{DTBP}] = 3.0 \times 10^{-3}\text{ M}$, $[\text{DPE}] = (1.0\text{--}10.0) \times 10^{-3}\text{ M}$.

$$k_c K_i = \frac{\text{initial slope (absorbance unit}\cdot\text{s}^{-1})}{\epsilon_{\text{max}} d c_0^2 [\text{TiCl}_4]^2} \quad (10)$$

(b) The constant absorbance obtained at long reaction times ($t \rightarrow \infty$) indicates that the thermodynamic equilibrium of the capping/decapping reaction has been established. The value of the apparent equilibrium constant K_e can then be calculated using eqs 3 and 8:

$$K_e = \frac{(\text{absorbance})_{t \rightarrow \infty} \epsilon_{\text{max}} d}{(c_0 \epsilon_{\text{max}} d - (\text{absorbance})_{t \rightarrow \infty})^2 [\text{TiCl}_4]^2} \quad (11)$$

It is noteworthy that the mixture of DPE and TiCl_4 exhibits an absorption at $\lambda_{\text{max}} = 440\text{ nm}$ even in the absence of PIBCl or TMPCl, which might be due to some addition products of TiCl_4 to DPE.¹⁸ However, this side reaction is significantly slower than the capping of TMPCl with DPE (see Figure 4), and the experimental error due to this additional absorption at 440 nm on the values of $k_c K_i$ and K_e can therefore be regarded as negligible in the investigated temperature range. Further corroborating this assumption, virtually the same values for $k_c K_i$ and K_e were obtained when using different concentrations of TiCl_4 for capping.

From $k_c K_i$ and K_e , the rate constant of decapping, k_d , can be calculated according to eq 3:

$$k_d = \frac{k_c K_i}{K_e} \quad (12)$$

Basically, k_d could be directly measured by following the decapping reaction of PIB-DPE-OMe in the presence of TiCl_4 . This approach requires a considerably fast and complete ionization, which is achieved in CH_2Cl_2 ¹¹ but not in a Hex/MeCl 60/40 (v/v) mixture.¹⁹ Therefore, we can only refer to calculated values of k_d derived from eq 12 at present.

Capping of TMPCl and PIBCl with DPE. The values of the apparent equilibrium constant K_e and the rate constants $k_c K_i$ and k_d , which were obtained for the capping reaction of TMPCl and PIBCl with DPE in Hex/MeCl 60/40 (v/v) at -80 to $-40\text{ }^{\circ}\text{C}$, are summarized in

Table 1. Equilibrium Constant K_e and Rate Constants $k_c K_i$ and k_d for the Capping/Decapping Reaction of TMPCl and PIBCl with DPE at -80 to -40 °C^a

$T/^\circ\text{C}$	TMPCl ($\text{DP}_n = 2$)			PIBCl ($\text{DP}_n \approx 36$)		
	K_e/M^{-3}	$k_c K_i/\text{M}^{-3}\cdot\text{s}^{-1}$	k_d/s^{-1}	K_e/M^{-3}	$k_c K_i/\text{M}^{-3}\cdot\text{s}^{-1}$	k_d/s^{-1}
-80	4.9×10^6	24.0	4.9×10^{-6}	5.2×10^6	170	32.7×10^{-6}
-70	7.4×10^5	13.9	1.9×10^{-5}	7.7×10^6 ^b	430 ^b	120.0×10^{-6} ^b
-60	9.2×10^4	7.0	0.8×10^{-4}	1.2×10^5	35.8	29.8×10^{-5}
-50	0.7×10^3	5.0	7.7×10^{-3}	3.0×10^5 ^b		
-40	1.4×10^2	2.1	1.5×10^{-2}	2.4×10^4	18.4	7.7×10^{-4}
				6.0×10^4 ^b		
				2.0×10^3	3.0	1.5×10^{-3}
				2.2×10^2	1.1	0.5×10^{-2}
				8.0×10^2 ^b		

^a [TMPCl] = [DPE] = 2.0×10^{-3} M, [TiCl₄] = $(1.6\text{--}80) \times 10^{-2}$ M, [DTBP] = 3.0×10^{-3} M, K_e and $k_c K_i$ were obtained via visible spectroscopy, k_d was calculated according to eq 12. ^b Determined by NMR; see ref 11.

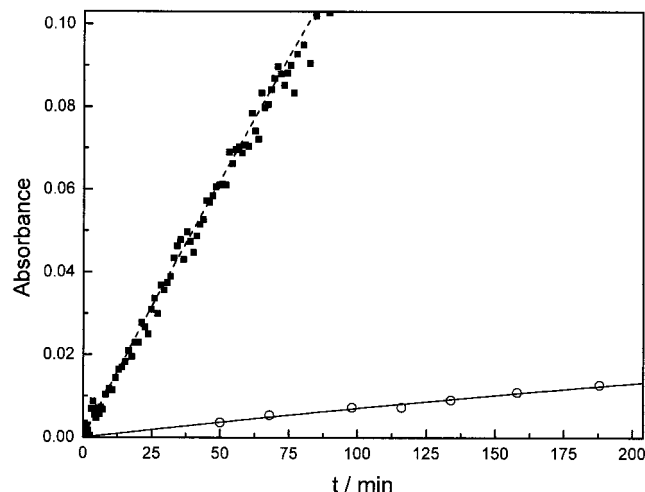


Figure 4. Plot of the absorbance at $\lambda_{\text{max}} = 440$ nm versus time for the reaction of DPE with TiCl₄ in Hex/MeCl 60/40 (v/v) at -80 °C (○); [DPE] = 2.0×10^{-3} M, [TiCl₄] = 1.64×10^{-2} M, [DTBP] = 3.0×10^{-3} M. ■ Capping of TMPCl with DPE under otherwise identical conditions, [TMPCl] = 2.0×10^{-3} M.

Table 1. Virtually identical values of K_e were also derived from decapping experiments with TMP-DPE-OMe. It appears that the results obtained from UV-vis measurements are in quite good agreement with those previously determined by NMR spectroscopy.¹¹

The value of the apparent equilibrium constant K_e strongly depends on temperature—it decreases approximately 4 orders of magnitude upon raising the temperature from -80 to -40 °C. Although the experimental error is quite large, K_e does not appear to be significantly different for TMPCl and PIBCl (cf. Figure 5), which indicates that the polyisobutylene chain length has no effect on the thermodynamics of the capping/decapping reaction.

The apparent rate constant of capping, $k_c K_i$, and the rate constant of decapping, k_d , are also drastically affected by temperature. The value of $k_c K_i$ decreases and that of k_d increases with increasing temperature (cf. Figures 6 and 7), which means that the value of the apparent activation energy, E_a , is negative for the capping reaction and positive for the decapping reaction (see Table 2). However, the respective activation energies as well as the frequency factors, $\log A$, are different for TMPCl and PIBCl (see Table 2); i.e., the chain length seems to influence the kinetics of the capping and the decapping reaction. At -80 °C, PIBCl reacts 7 times faster with DPE than with TMPCl. It appears therefore that TMPCl cannot be regarded as a suitable model

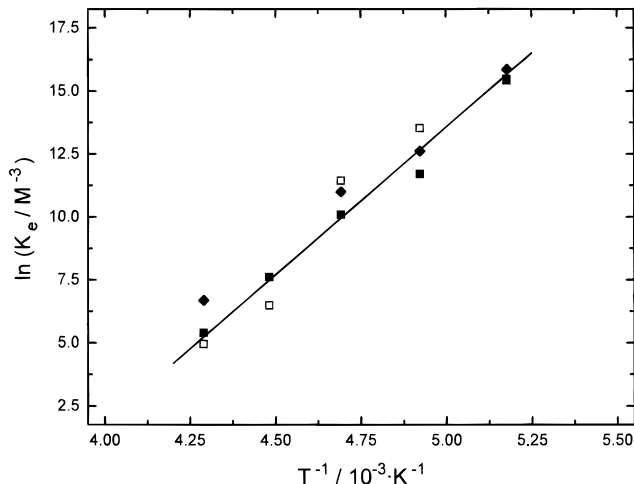


Figure 5. Van't Hoff plot of the apparent equilibrium constant of the capping/decapping equilibrium, K_e , for TMPCl (□) and PIBCl (■). (◆) K_e values for PIBCl obtained by NMR; see ref 11.

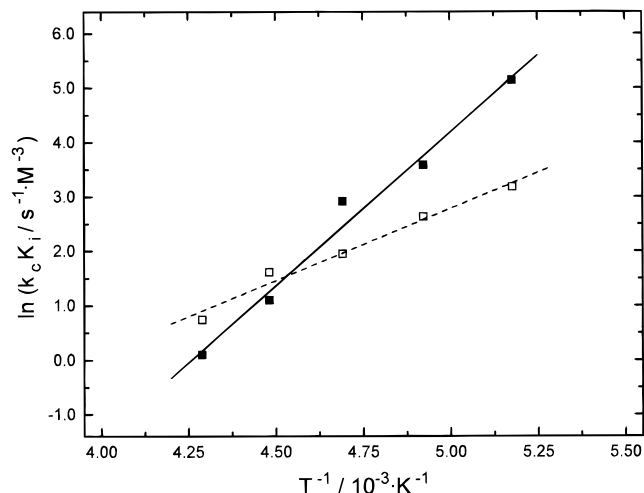


Figure 6. Arrhenius plot of the apparent rate constant of capping, $k_c K_i$, for TMPCl (□) and PIBCl (■).

compound to reflect the capping/decapping reaction of PIBCl with DPE.

Since only the apparent rate constant $k_c K_i$ could be obtained, one cannot distinguish between the contributions of kinetics (k_c) and thermodynamics (K_i) on its value. The effects of temperature and chain length on the rate of capping might be, however, predominantly explained in terms of K_i :

(a) The negative apparent activation energy, E_a , of the capping reaction might result from some negative

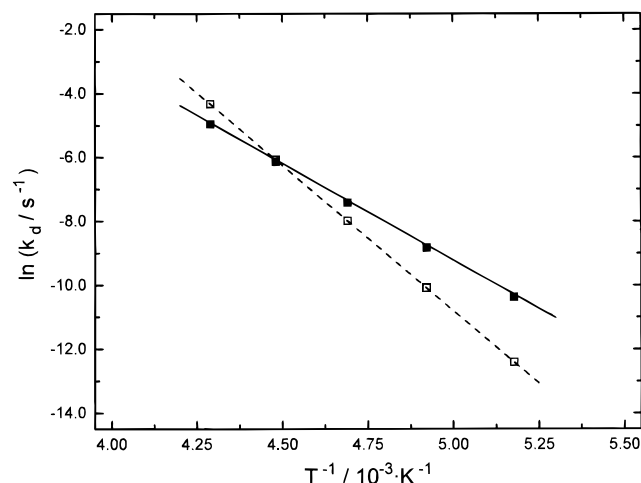


Figure 7. Arrhenius plot of the rate constant of decapping, k_d , for TMPCl (\square) and PIBCl (\blacksquare) calculated by eq 12 using K_e and $k_c K_i$ values that were reobtained from the linear plots in Figures 5 and 6, respectively.

Table 2. Activation Energies, E_a , and Frequency Exponents, $\log A$, for the Apparent Rate Constant of Capping, $k_c K_i$, and the Rate Constant of Decapping, k_d , for TMPCl and PIBCl (Calculated from the Slopes and the Intercepts of the Arrhenius Plots in Figures 6 and 7)

	TMPCl ($DP_n = 2$)		PIBCl ($DP_n \approx 36$)	
	$E_a/kJ \cdot mol^{-1}$ ($E_a/kcal \cdot mol^{-1}$)	$\log A$	$E_a/kJ \cdot mol^{-1}$ ($E_a/kcal \cdot mol^{-1}$)	$\log A$
$k_c K_i$	-21.6 (-5.2)	-4.5	-46.6 (-11.1)	-10.4
k_d	75.7 (18.1)	15.1	50.7 (12.1)	9.2

enthalpy ΔH_i of ionization of PIBCl (cf. Scheme 1),^{14,16} which overcompensates any positive activation energy E_a^c for the addition of DPE to the carbenium ion: $E_a = E_a^c + \Delta H_i$.

(b) Mayr et al.²⁰ found that isobutylene adds 3 times faster to triisobutylene hydrochloride than to TMPCl in the presence of BCl_3 at $-78^\circ C$, and this was mainly ascribed to a higher degree of ionization for the trimer due to the increase of back strain.

However, any shift of the ionization equilibrium of PIBCl with temperature or chain length can only affect the value of the apparent rate constant $k_c K_i$ but certainly not that of the absolute rate constant k_d . The effects of temperature and chain length on the kinetics of the decapping reaction are considered to result from different reactivities/stabilities of the dimeric and polymeric cationic species—the reason for this difference in

reactivity or stability is not fully understood yet and will be the subject of further investigations.

Conclusions

UV-vis measurements enable the determination of thermodynamic (K_e) and kinetic parameters ($k_c K_i$, k_d) of the capping/decapping reaction of living polyisobutylene ($DP_n = 2, 36$). It was found that the kinetics of this reaction is significantly affected by the temperature and the chain length. While the effects on $k_c K_i$ might be attributed to different positions of the ionization equilibrium, those on k_d indicate that the dimeric and polymeric cations have substantially different reactivities/stabilities. Thus, the dimeric model compound (TMPCl) cannot reflect the polymer chain end in the capping/decapping reaction.

Acknowledgment. NSF (DMR-9502777 and INT-9512834) and CNRS are gratefully acknowledged for financial support.

References and Notes

- (1) Hadjikyriacou, S.; Fodor, Zs.; Faust, R. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, *A32* (6), 1137.
- (2) Mayr, H.; Roth, M.; Faust, R. *Macromolecules* **1996**, *29*, 6110.
- (3) Fodor, Zs.; Faust, R. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, *A31* (12), 1985.
- (4) Li, D.; Faust, R. *Macromolecules* **1995**, *28*, 1383.
- (5) Hadjikyriacou, S.; Faust, R. *Macromolecules* **1995**, *28*, 7893.
- (6) Hadjikyriacou, S.; Faust, R. *Macromolecules* **1996**, *29*, 5261.
- (7) Feldthusen, J.; Iván, B.; Müller, A. H. E. *Macromolecules* **1998**, *31*, 578.
- (8) Bae, Y. C.; Fodor, Zs.; Faust, R. *Macromolecules* **1997**, *30*, 198.
- (9) Bae, Y. C.; Faust, R. *Macromolecules* **1998**, *31*, 2480.
- (10) Bae, Y. C.; Fodor, Zs.; Faust, R. *Polym. Prepr.* **1996**, *37* (1), 801.
- (11) Bae, Y. C.; Fodor, Zs.; Faust, R. *ACS Symp. Ser.* **1997**, *665*, 168.
- (12) Charleux, B.; Moreau, M.; Vairon, J. P.; Hadjikyriacou, S.; Faust, R. *Macromol. Symp.* **1998**, *132*, 25.
- (13) Schneider, R.; Mayr, H.; Plesch, P. H. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 1369.
- (14) Fodor, Zs.; Bae, Y. C.; Faust, R. *Macromolecules* **1998**, *31*, 4439.
- (15) Gyor, M.; Wang, H.-C.; Faust, R. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29* (8), 639.
- (16) Storey, R. F.; Choate, K. R., Jr. *Macromolecules* **1997**, *30*, 4799.
- (17) Rao, C. N. R. *Ultra-violet and Visible Spectroscopy*; Plenum Press: New York, 1967; p 4.
- (18) Sauvet, G.; Vairon, J.-P.; Sigwalt, P. *J. Polym. Sci., Polym. Chem.* **1978**, *16*, 3047.
- (19) Schlaad, H.; Faust, R. Unpublished results.
- (20) Roth, M.; Patz, M.; Freter, H.; Mayr, H. *Macromolecules* **1997**, *30*, 722.

MA9809738