722 *Macromolecules* **1997,** *30,* 722−725

Living Oligomerization of Isobutylene Using Di- and Triisobutylene Hydrochlorides as Initiators

Michael Roth,[‡] Matthias Patz,[‡] Heidelore Freter,[‡] and Herbert Mayr*,[†]

Institut für Organische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 22, 64287 Darmstadt, Germany, and Institut für Organische Chemie, Ludwig-Maximilians-Universität, Karlstrasse 23, 80333 München, Germany

Received September 24, 1996; Revised Manuscript Received December 4, 1996[⊗]

ABSTRACT: The living isobutylene oligomerization initiated by diisobutylene hydrochloride (**1**) or triisobutylene hydrochloride (**2**) in the presence of BCl_3 and benzyltriethylammonium tetrachloroborate has been studied by gas chromatography which allowed the detection of the individual oligomers **2**, **3**, **4**, etc. The reactions followed second-order kinetics, first-order with respect to initiator (**1** or **2**), first-order with respect to BCl_3, and zeroth-order with respect to isobutylene. A kinetic model has been derived which explains these phenomena.

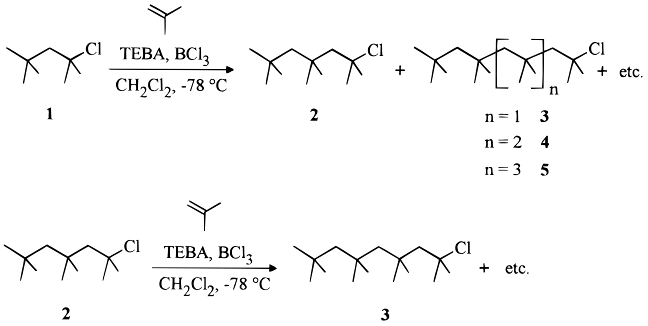
Introduction

On the basis of pioneering studies of Kennedy and co-workers in the early 1980s,[1−7] the living polymerization of isobutylene has become an active field of research. Whereas the treatment of isobutylene with Brönsted acids, Lewis acids, and Lewis acid/alkyl halide mixtures in nonnucleophilic solvents yielded polymers with broad molecular weight distribution,[1−12] the addition of Lewis bases as amines, amides, sulfides, esters, etc., has been found to reduce the polydispersity of the polymer.[8,13−19] Mixtures of alkyl halides, Lewis acids, and tetraalkylammonium halides, which are characterized by well-defined Lewis acid/base coordination equilibria, have also been found to be efficient initiators for living isobutylene polymerization.[20−25] In previous investigations on the Lewis acid promoted reactions of alkyl halides with alkenes, we have shown that the information derived from low molecular weight compounds provides valuable information on the rates of initiation, propagation, and transfer steps in carbocationic polymerization.[14,26,27] We have now extended this method for studying some aspects of the living carbocationic polymerization of isobutylene by investigating the initial steps of these reactions where the individual oligomers can be detected separately. Because of the backstrain-enhanced ionization rates[28−30] of diisobutylene hydrochloride (**1**) and triisobutylene hydrochloride (**2**), these compounds are more efficient initiators for carbocationic polymerization than *tert*-butyl chloride.[4,6,8−10,13,14,18,19,21,22,31] We have, therefore, used **1** and **2** in combination with boron trichloride for initiating the oligomerizations of isobutylene.

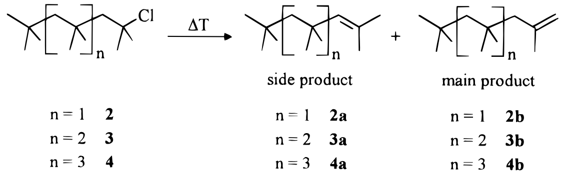
Oligomerization Products

Treatment of a mixture of diisobutylene hydrochloride (**1**) and isobutylene (7.4−33.1 equiv) with BCl_3 (0.44−0.77 equiv) in the presence of 0.10−0.17 equiv of benzyltriethylammonium chloride (TEBA) resulted in oligomerization to give the tertiary chlorides **2**, **3**, **4**, etc., as shown in Scheme 1. A complete identification of **2** and **3** has been given recently.[14] In contrast to the corresponding reaction in the absence of TEBA, this reaction is slow, and the continuous growth of the molecular weight can be followed by gas chromatography as shown in Figure 1. The double peaks observed for each oligomer in the chromatograms refer to the Hofmann (**2b**, **3b**, **4b**, etc.) and Saytzeff (**2a**, **3a**, **4a**, etc.) products that are formed by thermal HCl elimination from the tertiary chlorides **2−4** in the injector of the gas chromatograph (Scheme 2). Analogous experiments using triisobutylene hydrochloride (**2**) instead of **1** as initiator (Scheme 1) gave rise to analogous chromatograms.

Scheme 1



Scheme 2



Kinetics

In the CH_2Cl_2 solutions containing monomer, R-Cl, BCl_3, and $BnNEt_3^+BCl_4^-$ ion pairing can be assumed to be almost complete. Since paired and nonpaired carbocations have previously been shown to possess identical reactivities toward alkenes,[26,32,33] the small percentage of nonpaired carbocations in these solutions is neglected, and the chain growth can be described by Scheme 3.

From the continuous growth of the oligomers shown in Figure 1, one can derive that the reaction of the tertiary carbocations with BCl_4^- to give the tertiary chlorides is faster than their reaction with isobutylene, i.e., the ionization step in Scheme 3 is involved in a fast

---

* Corresponding author. Fax: 49-89-5902 254.

[†] Ludwig-Maximilians-Universität.

[‡] Technische Hochschule Darmstadt.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1997.

S0024-9297(96)01415-5 CCC: $14.00

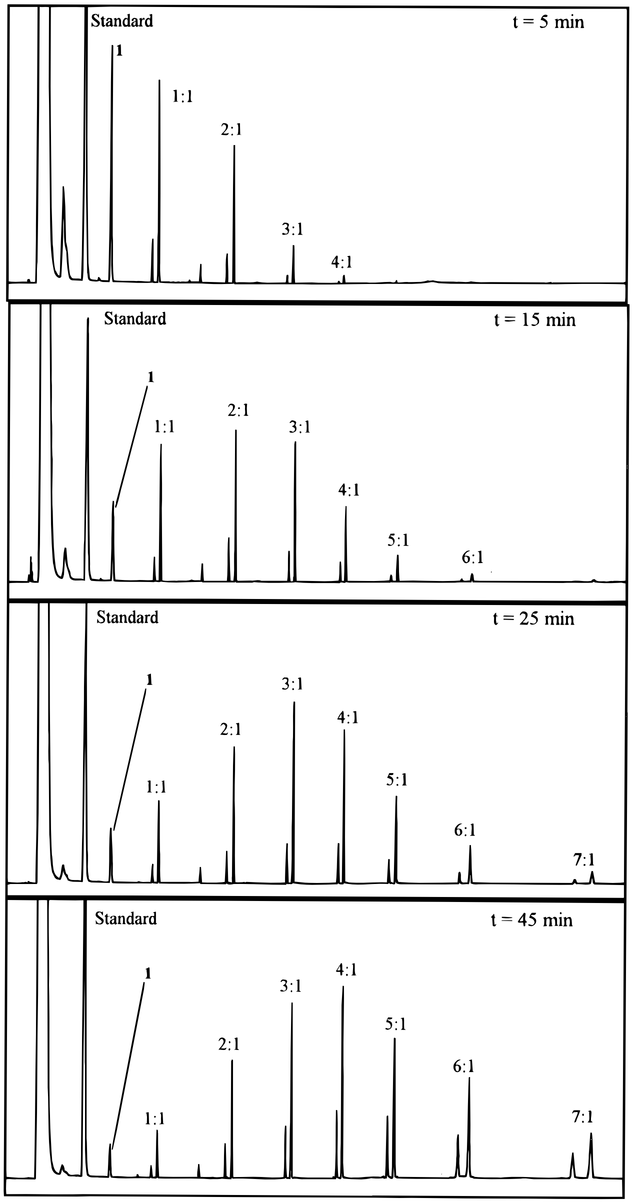
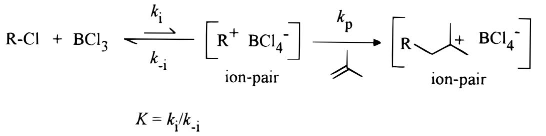


Figure 1. Gas chromatographic analysis of the living oligomerization of isobutylene initiated by diisobutylene hydrochloride (**1**) (BCl_3, $BnNEt_3^+Cl^-$, CH_2Cl_2, −78 °C).

Scheme 3



preequilibrium. The consumption of the initiator R-Cl is given by eq 1, and with the steady state assumption (eqs 2, 3) one obtains expression 4:

$$-\frac{d[\text{R-Cl}]}{dt} = k_p[R^+BCl_4^-][C_4H_8] \quad (1)$$

$$\frac{d[R^+BCl_4^-]}{dt} = k_i[\text{R-Cl}][BCl_3] - k_{-i}[R^+BCl_4^-] - k_p[R^+BCl_4^-][C_4H_8] \approx 0 \quad (2)$$

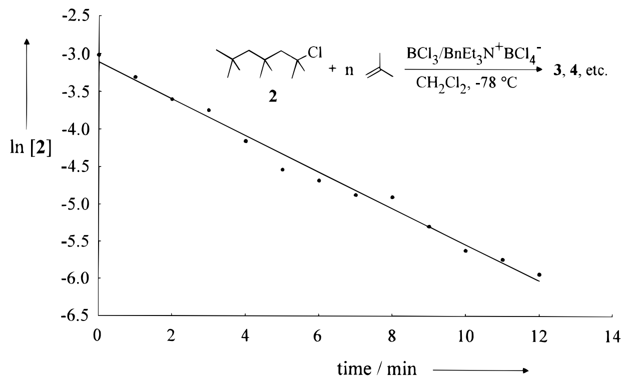


Figure 2. Pseudo-first-order consumption of the initiator **2** in the living oligomerization of isobutylene (BCl_3, $BnNEt_3^+Cl^-$, CH_2Cl_2, −78 °C).

$$[R^+BCl_4^-] = \frac{k_i}{k_{-i} + k_p[C_4H_8]}[\text{R-Cl}][BCl_3] \quad (3)$$

$$-\frac{d[\text{R-Cl}]}{dt} = \frac{k_p k_i}{k_{-i} + k_p[C_4H_8]}[\text{R-Cl}][BCl_3][C_4H_8] \quad (4)$$

Since $k_{-i} \gg k_p[C_4H_8]$ (rapid preequilibrium $K = k_i/k_{-i}$, see above), one obtains eq 5, a third-order kinetic expression, linear with respect to each [R-Cl], $[BCl_3]$, and $[C_4H_8]$.

$$-\frac{d[\text{R-Cl}]}{dt} = Kk_p[\text{R-Cl}][BCl_3][C_4H_8] \quad (5)$$

Because the concentration of BCl_3 is constant, and isobutylene is used in large excess (7.4−33.1 equiv) over the initiator R-Cl, pseudo-first-order kinetics are expected (eq 6). Integration of eq 6 yields eq 7, and as a consequence, a linear correlation between ln [R-Cl] versus time must result, in accord with the experimental findings shown in Figure 2.

$$-\frac{d[\text{R-Cl}]}{dt} = k_{obs}[\text{R-Cl}] \quad (6)$$

$$[\text{R-Cl}] = [\text{R-Cl}]_0 \exp\{-k_{obs}t\} \quad (7)$$

Table 1 shows the expected linear dependence of $k_{obs(\mathbf{2})}$ on the concentration of BCl_3 (constancy of $k_{obs(\mathbf{2})}/[BCl_3]$, see column 9) for the polymerization of isobutylene initiated by the tertiary chloride **2**. The constancy of $k_{obs(\mathbf{1})}/[BCl_3]$ is also found for the oligomerizations initiated by **1** (Table 2, column 9), but because of the small variation of $[BCl_3]$ in these experiments, this observation does not provide additional support for the linear dependence of the reaction rates on $[BCl_3]$. In accordance with literature reports,[15−17] both reaction series using either **1** or **2** as initiators show zeroth-order in isobutylene (Tables 1 and 2), in contrast to the expectations based on eq 5 and the experimental observations in ref 19.

Since our previous studies on the kinetics of the reactions of carbocations with alkenes[27,33] also showed first-order dependence on alkene concentration ([alkene] < 0.01 mol L^{-1}), we have now examined the kinetics at higher alkene concentrations. The reaction of the bis(*p*-methoxybenzhydryl) tetrachloroborate with isobutylene ($[C_4H_8] = 0.6$ mol L^{-1}, corresponding to the concentration in the oligomerization experiments) in CH_2Cl_2 again followed second-order kinetics, and the rate

Table 1. Rate Constants and Concentrations of the Living Isobutylene Oligomerization Initiated by Triisobutylene Hydrochloride 2 (≈1 mmol of 2, ≈0.1 mmol of $BnNEt_3^+Cl^-$, ≈20 mL of CH_2Cl_2, −78 °C)

[**2**] (mmol, mol L^{-1})	$[C_4H_8]_0$ (mmol, mol L^{-1})^a	$[BCl_3]_0$ (mL, mmol)	$[BCl_3]$ (mol L^{-1})^b	$BnNEt_3^+Cl^-$ (mmol)	*n*-octane (μL)	CH_2Cl_2 (mL)	$k_{obs(\mathbf{2})}$ (s^{-1})	$k_{obs(\mathbf{2})}/[BCl_3]$ (L mol^{-1} s^{-1})
1.20, 4.53×10^{-2}	24.4, 9.20×10^{-1}	12, 0.54	1.38×10^{-2}	0.168	175	24.6	8.05×10^{-4}	5.81×10^{-2}
1.29, 5.08×10^{-2}	27.3, 1.07	14, 0.62	1.79×10^{-2}	0.168	150	23.3	1.25×10^{-3}	6.96×10^{-2}
0.75, 3.31×10^{-2}	5.08, 2.24×10^{-1}	20, 0.89	3.19×10^{-2}	0.168	100	22.3	1.78×10^{-3}	5.59×10^{-2}
1.30, 5.26×10^{-2}	7.75, 3.14×10^{-1}	42, 1.87	6.90×10^{-2}	0.168	175	24.1	4.05×10^{-3}	5.87×10^{-2}
								$(6.06 \pm 0.53) \times 10^{-2}$

[a] $\rho_{isobutylene}(-78\ °C) = 0.707$ g cm^{-3} from ref 36. [b] $[BCl_3] = [BCl_3]_0 - [BnNEt_3^+BCl_4^-]$.

Table 2. Rate Constants and Concentrations of the Living Isobutylene Oligomerization Initiated by Diisobutylene Hydrochloride 1 (≈2 mmol of 1, ≈0.2 mmol of $BnNEt_3^+Cl^-$, ≈20 mL of CH_2Cl_2, −78 °C)

[**1**] (mmol, mol L^{-1})	$[C_4H_8]_0$ (mmol, mol L^{-1})^a	$[BCl_3]_0$ (mL, mmol)	$[BCl_3]$ (mol L^{-1})^b	$BnNEt_3^+Cl^-$ (mmol)	*n*-octane (μL)	CH_2Cl_2 (mL)	$k_{obs(\mathbf{1})}$ (s^{-1})	$k_{obs(\mathbf{1})}/[BCl_3]$ (L mol^{-1} s^{-1})
1.51, 7.24×10^{-2}	11.2, 5.37×10^{-1}	15, 0.67	2.49×10^{-2}	0.150	150	20.0	5.57×10^{-4}	2.24×10^{-2}
1.04, 4.63×10^{-2}	34.4, 1.53	18, 0.80	2.85×10^{-2}	0.160	175	19.8	7.44×10^{-4}	2.61×10^{-2}
2.09, 9.43×10^{-2}	26.6, 1.20	20, 0.89	3.04×10^{-2}	0.220		20.0	6.41×10^{-4}	2.11×10^{-2}
2.12, 6.60×10^{-2}	26.7, 8.32×10^{-1}	22, 0.98	2.37×10^{-2}	0.220	175	30.0	5.89×10^{-4}	2.49×10^{-2}
1.61, 6.87×10^{-2}	12.6, 5.35×10^{-1}	26, 1.16	3.79×10^{-2}	0.270	125	22.5	8.14×10^{-4}	2.15×10^{-2}
								$(2.32 \pm 0.22) \times 10^{-2}$

[a] $\rho_{isobutylene}(-78\ °C) = 0.707$ g cm^{-3} from ref 36. [b] $[BCl_3] = [BCl_3]_0 - [BnNEt_3^+BCl_4^-]$.

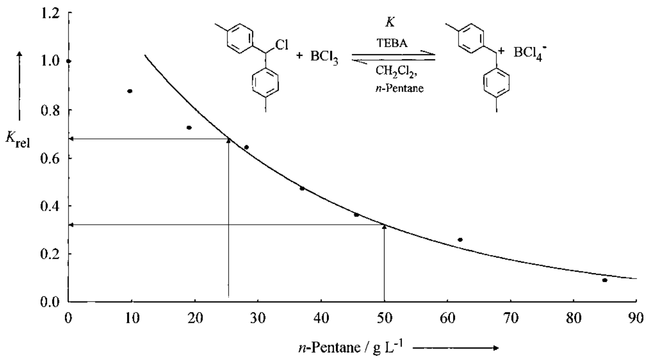


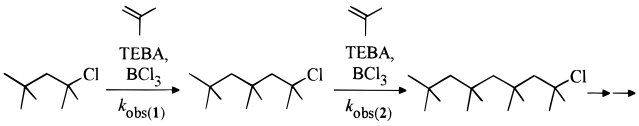
Figure 3. Dependence of the ionization constant *K* of bis(*p*-methylbenzhydryl) chloride on the solvent polarity in CH_2Cl_2/*n*-pentane mixtures (BCl_3, $BnNEt_3^+Cl^-$, −78 °C).

constant was the same as determined at low alkene concentrations.[34]

In accord with previous observations,[32] variation of the solvent polarity thus had an insignificant influence on the rate of attack of carbocations at alkenes. We, therefore, assumed that the observed zeroth-order in isobutylene concentration was due to a change of the ionization constant while altering the concentration of isobutylene. In order to examine this hypothesis we have studied the influence of solvent polarity on the ionization constant in a model system. Continuous addition of *n*-pentane (a nonreactive substitute for isobutylene) to a solution of partially ionized bis(*p*-methyl)benzhydryl chloride in $CH_2Cl_2/BCl_3/BnNEt_3^+$-BCl_4^- resulted in a decrease of the ionization constant as shown in Figure 3.

The almost hyperbolic relationship between the degree of ionization (K_{rel}) and the amount of added *n*-pentane in the range of 20−80 g of *n*-pentane/L shows that doubling of the hydrocarbon concentration results in halving of $[R^+BCl_4^-]$ due to decreasing solvent polarity. This observation may explain the apparent zeroth-order kinetics with respect to the concentration of isobutylene (eq 5). According to eq 1, d[R-Cl]/d*t* remains constant, when the increase of $[C_4H_8]$ is compensated by the decrease of $[R^+BCl_4^-]$. Since solvent polarity remains almost unaffected during the course of a polymerization reaction, this interpretation implies that the rate of polymerization decreases with decreasing $[C_4H_8]$ during one polymerization experiment. In contrast the rate of polymerization is independent of $[C_4H_8]_0$ when different experiments with variable concentrations of $[C_4H_8]_0$ are compared.

Scheme 4



1 **2** **3**

The observed rate constants $k_{obs(\mathbf{1})}$ and $k_{obs(\mathbf{2})}$ of the oligomerizations initiated by **1** and **2** (Scheme 4) show that the initiator **2** reacts nearly 3 times faster than **1**, probably because of the higher degree of ionization of **2** due to the increase of backstrain[28−30] (Tables 1 and 2).

Conclusion

We have shown that the living oligomerization of isobutylene initiated by R-Cl/BCl_3 in the presence of benzyltriethylammonium tetrachloroborate can be explained by Scheme 3, in which a rapid reversible ionization step is followed by the rate-determining propagation step. Instead of the third-order kinetics (eq 5) derived from Scheme 3, second-order kinetics, linear with respect to [R-Cl] and $[BCl_3]$, were observed. It has been shown that the zeroth-order with respect to $[C_4H_8]$ can be explained by the decreasing ionization constants associated with increasing isobutylene concentration (reduction of solvent polarity).

Experimental Section

Dichloromethane (Merck, pa) was stirred with sulfuric acid for 3 days, then washed with water, aqueous $NaHCO_3$ solution, and again with water, dried with $CaCl_2$, and distilled from CaH_2 before use. Boron trichloride (Messer Griesheim, 99.9%) was taken from a steel cylinder using gas-tight syringes; isobutylene (Fluka, >99%), *n*-octane (Fluka, pa), and benzyltriethylammonium chloride (Fluka) were used without further purification. The tertiary chlorides **1** and **2** were prepared as described previously.[14]

The GC analyses were carried out on Carlo Erba Instruments GC 6000 Vega Series 2 (capillary column: 25 m × 0.27 mm, SE54). The chromatograms were evaluated using an APEX chromatography workstation from Autochrom.

Oligomerization Experiments. General Procedure. The alkyl chloride **1** or **2**, benzyltriethylammonium chloride, and *n*-octane (internal standard) were dissolved in dry CH_2Cl_2 and cooled in a dry ice bath. Isobutylene was condensed into the precooled solution before adding boron trichloride. After definite intervals 1-mL samples were taken from the reaction solution and hydrolyzed with aqueous ammonium chloride solution (2 mL). After drying with $MgSO_4$ the samples were analyzed by GC without further purification. The calibration constants for evaluation of the gas chromatograms are based on the relative ratios of carbon atoms.[35] Details of these experiments are listed in Tables 1 and 2.

Acknowledgment. We thank Bayer AG, Leverkusen, for financial support.

References and Notes

(1) Kennedy, J. P.; Smith, R. A. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1523–1537.
(2) Iván, B.; Kennedy, J. P.; Chang, V. S. C. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 3177–3191.
(3) Kennedy, J. P.; Chang, V. S. C.; Smith, R. A.; Iván, B. *Polym. Bull.* **1979**, *1*, 575–580.
(4) Faust, R.; Kennedy, J. P. *Polym. Bull.* **1986**, *15*, 317–323.
(5) Nagy, A.; Faust, R.; Kennedy, J. P. *Polym. Bull.* **1986**, *15*, 411–416.
(6) Faust, R.; Kennedy, J. P. *J. Polym. Sci., Polym. Chem.* **1987**, *A25*, 1847–1869.
(7) Kennedy, J. P.; Iván, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Carl Hanser Verlag: Munich, 1992.
(8) Majoros, I.; Nagy, A.; Kennedy, J. P. *Adv. Polym. Sci.* **1994**, *112*, 1–114.
(9) (a) Nuyken, O.; Pask, S. D.; Vischer, A.; Walter, M. *Makromol. Chem.* **1985**, *186*, 173–190. (b) Freyer, C. V.; Mühlbauer, H. P.; Nuyken, O. *Angew. Makromol. Chem.* **1986**, *145/146*, 69–87. (c) Freyer, C. V.; Nuyken, O. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 319–335. (d) Freyer, C. V.; Manz, J.; Nuyken, O. *Macromol. Theory Simul.* **1994**, *3*, 845–854.
(10) Mishra, M. K.; Kennedy, J. P. *J. Macromol. Sci. Chem.* **1987**, *A24*, 933–948.
(11) Fehérvári, A.; Kennedy, J. P.; Tüdos, F. *J. Macromol. Sci. Chem.* **1981**, *A15*, 215–230.
(12) Toman, L.; Pokorny, S.; Spevacek, J.; Danhelka, J. *Polymer* **1986**, *27*, 1121–1127.
(13) Kaszas, G.; Puskas, J. E.; Kennedy, J. P.; Chen, C. C. *J. Macromol. Sci. Chem.* **1989**, *A26*, 1099–1114.
(14) Roth, M.; Mayr, H. *Macromolecules* **1996**, *29*, 6104–6109.
(15) Kaszás, G.; Puskás, J.; Kennedy, J. P. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 473–493.
(16) Zsuga, M.; Kelen, T.; Balogh, L.; Majoros, I. *Polym. Bull.* **1992**, *29*, 127–134.
(17) Zsuga, M.; Kennedy, J. P. *Polym. Bull.* **1989**, *21*, 5–12.
(18) Kaszas, G.; Puskas, J. *Polym. React. Eng.* **1994**, *2*, 251–273.
(19) Balogh, L.; Faust, R. *Polym. Bull.* **1992**, *28*, 367–374.
(20) Deák, G.; Zsuga, M.; Kelen, T. *Polym. Bull.* **1992**, *29*, 239–246.
(21) Kelen, T.; Zsuga, M.; Balogh, L.; Majoros, I.; Deak, G. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 325–338.
(22) Pernecker, T.; Kelen, T.; Kennedy, J. P. *J. Makromol. Sci., Pure Appl. Chem.* **1993**, *A30*, 399–412.
(23) Matyjaszewski, K.; Lin, C.-H.; Bon, A.; Xiang, J. S. *Macromol. Symp.* **1994**, *85*, 65–78.
(24) Szymanski, R.; Matyjaszewski, K. *Macromol. Theory Simul.* **1995**, *4*, 335–345.
(25) Matyjaszewski, K.; Szymanski, R.; Teodorescu, M. *Macromolecules* **1994**, *27*, 7565–7574.
(26) Mayr, H.; Schneider, R.; Schade, C. *Makromol. Chem., Macromol. Symp.* **1988**, *13/14*, 43–59.
(27) Mayr, H. In *Cationic Polymerization: Mechanisms, Synthesis, and Applications*; Matyjaszewski, K., Ed.; Marcel Dekker: New York, 1996; pp 51–136.
(28) Brown, H. C.; Fletcher, R. S. *J. Am. Chem. Soc.* **1949**, *71*, 1845–1854.
(29) Brown, H. C.; Stern, A. *J. Am. Chem. Soc.* **1950**, *72*, 5068–5070.
(30) Brown, H. C.; Berneis, H. L. *J. Am. Chem. Soc.* **1953**, *75*, 10–14.
(31) Faust, R.; Iván, B.; Kennedy, J. P. *J. Macromol. Sci. Chem.* **1991**, *28*, 1–13.
(32) Mayr, H.; Schneider, R.; Schade, C.; Bartl, J.; Bederke, R. *J. Am. Chem. Soc.* **1990**, *112*, 4446–4454.
(33) Mayr, H. *Angew. Chem.* **1990**, *102*, 1415–1428; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1371–1384.
(34) Mayr, H.; Schneider, R.; Grabis, U. *J. Am. Chem. Soc.* **1990**, *112*, 4460–4467.
(35) Schomburg, G. *Gaschromatographie*; VCH: Weinheim, 1987.
(36) Taylor, R. B.; Williams, F. *J. Am. Chem. Soc.* **1969**, *91*, 3728–3732.

MA9614151