Group Transfer Polymerization of *n*-Butyl Acrylate with Lewis Acid Catalysts. 2.[†] Kinetic Investigation Using the HgI_2/Me_3SiI Catalyst System in Toluene and Methylene Chloride

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ABSTRACT: In the presence of trimethylsilyl iodide (TMSI) the group transfer polymerization (GTP) of *n*–butyl acrylate (*n*-BuA) using 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS) as an initiator and mercuric iodide (HgI_2) as a catalyst in toluene is drastically accelerated. The rate of polymerization is comparable to that of the nucleophilic catalyzed GTP with half-lives in the range of seconds to minutes. The induction periods which characterize the GTP in the absence of TMSI completely disappear. A very slight curvature in the first-order time–conversion plots is attributed to some "back-biting" termination. Kinetic investigations show that the polymerization follows first-order kinetics with respect to catalyst and TMSI concentrations. The rate of polymerization strongly depends on the polarity of the reaction medium. An external reaction order of 1.52 with respect to the monomer concentration is due to the higher polarity of the reaction medium at higher monomer concentrations. The rate of polymerization is increased by 2 orders of magnitude in CH_2Cl_2/toluene mixtures. The Arrhenius plot displays a maximum at ∼−60 °C, indicating a negative apparent activation energy in the temperature range from +40 to −40 °C, and a positive one at temperatures <−70 °C. The kinetic results support a mechanism in which mercuric iodide and TMSI form an active complex which acts as a nucleophilic catalyst. At lower temperatures the concentration of active species increases, overriding the decrease of the rate constant of propagation. The molecular weight is controlled by the ratio $[M]_0/[I]_0$, and the molecular weight distributions of the polymers formed are very narrow and are not effected by TMSI.

Introduction

The group transfer polymerization (GTP) of *n*-butyl acrylate (*n*-BuA) using 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS) as an initiator and mercuric iodide (HgI_2) as a catalyst in toluene at room temperature gives a very good control of molecular weight and narrow molecular weight distribution ($M_w/M_n < 1.2$). Kinetic studies in this system[1] revealed that this reaction is rather slow, half-lives being in the range of minutes to hours. The reaction orders of propagation with respect to initiator and catalyst concentrations were found to be near unity, similar to the GTP of MMA with nucleophilic catalysts (oxyanions) in THF, indicating that HgI_2 rather acts like a nucleophilic than an electrophilic catalyst. However, the first-order time–conversion plots exhibit considerable induction periods. We proposed that the induction periods are due to the formation of trimethylsilyl iodide (TMSI) from MTS and HgI_2 (Scheme 1) which activates the catalyst. Initiator and activated catalyst in turn form the active species of polymerization (Scheme 2, *vide infra*).

In this paper we wish to present experimental evidence for this assumption by studying the effect of TMSI on the kinetics of polymerization of *n*-BuA using MTS as an initiator and HgI_2 as a catalyst in toluene as well as in mixtures of toluene and methylene chloride.

Experimental Part

Trimethylsilyl iodide (Aldrich 97%) was used without further treatment. The other reagents such as *n*–butyl acrylate (*n*-BuA), 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS), mercuric iodide (HgI_2), toluene, *n*-decane (internal standard), and argon were purified and dried as described in our previous paper.[1]

Methylene chloride (CH_2Cl_2) was fractionated over a 2 m column and then refluxed for more than 48 h over CaH_2. After degassing, it was stirred for several days over CaH_2 and distilled under vacuum into a flask with CaH_2, where it was stored. Before use it was distilled from the flask to a glass ampule equipped with a Teflon valve.

The experimental procedure was similar to that in our previous paper. First the HgI_2 solution was introduced into the reactor, then the monomer solution, and finally the solutions of TMSI and initiator were mixed in the mixing chamber, and the mixture was added.

Results and Discussion

Role of Trimethylsilyl Iodide in Polymerization. Figure 1 clearly shows that in the presence of TMSI the polymerization proceeds without any induction period and is much faster, half-lives being in the range of minutes, i.e., 2 orders of magnitude faster than in the absence of TMSI. The first-order time–conversion plots are very slightly curved downward at higher conversions (cf. Figure 1), indicating a small amount of termination. Two methods were used in order to determine the apparent rate constant of polymerization. First, the time–conversion plots were regarded as approximately linear and the slope was taken as the apparent rate constant, k_{app}. As a refinement, the effect of unimolecular termination (with rate constant k_t) was taken into consideration. By using a nonlinear regression procedure, k_{app} and k_t can be determined from eq 1,

$$\ln\frac{[M]_0}{[M]_t} = \frac{k_{app}}{k_t}\{1 - \exp(-k_t t)\} \qquad (1)$$

where $k_{app} = k_p[P^*]$, k_p and k_t are the rate constants of polymerization and termination, respectively, and $[P^*]$ is the concentration of active species. The curves in Figure 1 were calculated using rate constants obtained from such fits.

[†] Part 1, see ref 1.

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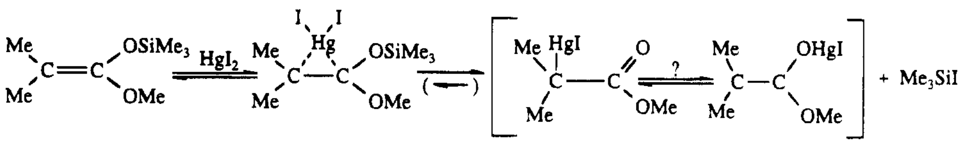
Scheme 1. Formation of TMSI



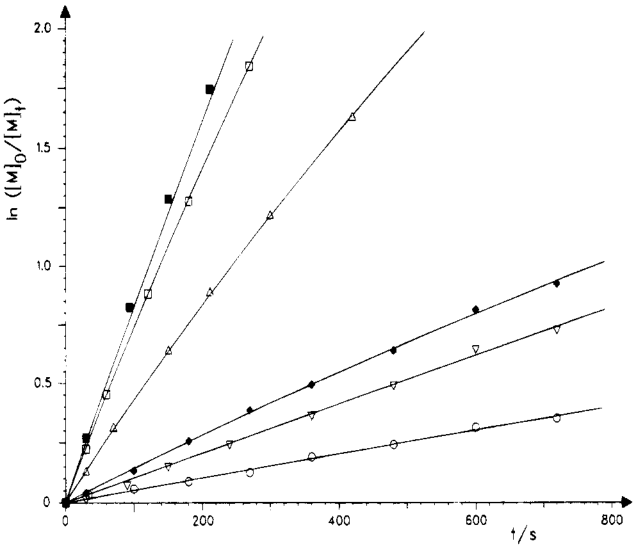


Figure 1. First-order time–conversion plots for the group transfer polymerization of *n*-BuA with MTS, HgI_2 and TMSI in toluene at 20 °C as a function of TMSI concentration. Symbols, cf. Table 1.

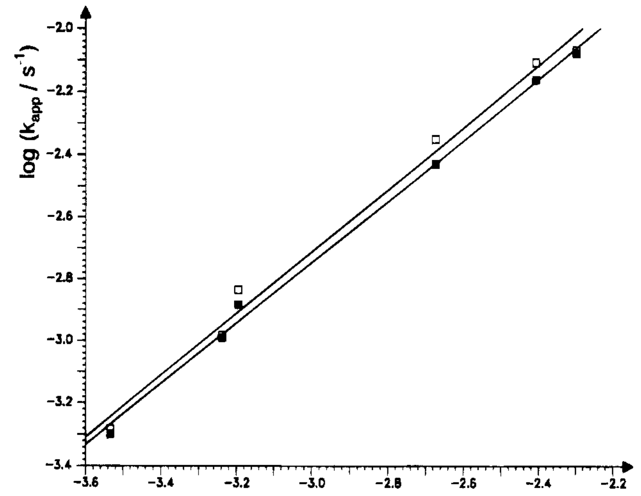


Figure 2. Determination of the reaction order with respect to TMSI concentration for the group transfer polymerization of *n*-BuA with MTS, HgI_2, and TMSI in toluene at 20 °C: (■) considering time–conversion plots as linear, slope = 0.97 ± 0.03; (□) fitted according to eq 1, slope = 0.99 ± 0.03.

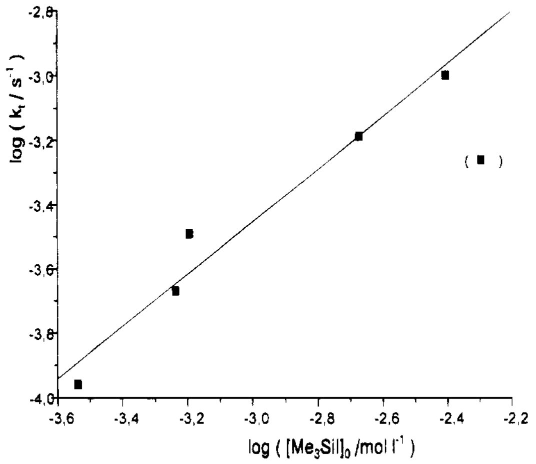


Figure 3. Bilogarithmic plot of apparent termination rate constant, k_t, fitted according to eq 1, vs initial concentration of TMSI for the group transfer polymerization of *n*-BuA with MTS, HgI_2, and TMSI in toluene at 20 °C. Slope = 0.81 ± 0.09.

Evidently, the rate of polymerization increases with increasing concentration of TMSI (cf. Table 1). A bilogarithmic plot of k_{app}, versus initial TMSI concentration, $[TMSI]_0$, results in a straight line with slopes of 0.97 ± 0.03, considering the time–conversion plots as linear, and 0.99 ± 0.03 for the results of the fit according to eq 1 (cf. Figure 2). This indicates that TMSI really takes part in the polymerization with first-order kinetics.

Extrapolating log k_{app} to the value obtained without TMSI (experiment K1), we can estimate that $[TMSI]_0 \cdot [HgI_2]_0 = 4.6 \times 10^{-8}$ for that experiment. It is impossible to separately estimate the concentrations of TMSI and HgI_2, because part of HgI_2 is consumed in the formation of TMSI. The concentrations are between the extreme values $[TMSI]_0 = 2.97 \times 10^{-5}$ and $[HgI_2]_0 = 1.55 \times 10^{-3}$ or $[TMSI]_0 = 1.55 \times 10^{-3}$ and $[HgI_2]_0 = 2.97 \times 10^{-5}$ mol/L.

Figure 3 shows a bilogarithmic plot of the termination rate constant k_t, vs initial concentration of TMSI. The slope is 0.81 ± 0.09. This means that chain propagation and termination reactions are equally accelerated by TMSI. On the basis of the UV signal at $\lambda = 260$ nm in the GPC eluograms, it was pointed out in part 1 of this series that the termination reaction most probably is "back-biting" (i.e. formation of cyclic β-keto ester end groups).

Table 1. Experimental Conditions and Kinetic Results for Group Transfer Polymerization of *n*-BuA (M) with MTS (I), HgI_2 (C), and Trimethylsilyl Iodide (S) in Toluene at 20 °C for Different Trimethylsilyl Iodide Concentrations: $[M]_0 = 0.81$ mol/L, $[C]_0 = 1.55 \times 10^{-3}$ mol/L, $[I]_0 = 3.0 \times 10^{-2}$ mol/L, $[M]_0/[I]_0 = 26$, $[C]_0/[I]_0 = 5.2\%$

run	symbol	10^3 $[S]_0$, mol/L	$[S]_0/[I]_0$, %	$[S]_0/[C]_0$	$10^3 k_{app}$,[a] s^{-1}	$10^3 k_{app}$,[b] s^{-1}	$10^4 k_t$,[b] s^{-1}
k91	■	5.05	16.9	3.26	8.32	8.51	5.48
k92	□	3.93	12.7	2.54	6.85	7.80	9.98
k93	△	2.13	6.87	1.37	3.72	4.45	6.51
k94	◆	0.64	1.99	0.41	1.31	1.46	3.23
k95	▽	0.58	1.89	0.389	1.02	1.04	2.14
k96	◇	0.29	0.94	0.197	0.51	0.52	1.10
K1[c]					0.060		

[a] Considering time–conversion curves as linear. [b] Fitted according to eq 1. k_t = rate constant of unimolecular termination. [c] In the absence of TMSI. $[M]_0 = 1.19$ mol/L. $[C]_0 = 4.14 \times 10^{-3}$ mol/L, $[I]_0 = 5.02 \times 10^{-2}$ mol/L. k_{app} recalculated to standard concentrations according to $k_{app} \propto [M]_0^{0.5}[I]_0[C]_0$.

Table 2. Experimental Conditions and Kinetic Results for Group Transfer Polymerization of *n*-BuA with MTS, HgI_2, and TMSI in Toluene at 20 °C for Different Catalyst Concentrations: $[I]_0 = 3.2 \times 10^{-2}$ mol/L, $[S]_0 = 2.2 \times 10^{-3}$ mol/L, $[M]_0 = 0.80$ mol/L, $[S]_0/[I]_0 = 7\%$

run	$10^3[C]_0$, mol/L	$[C]_0/[I]_0$, %	$[S]_0/[C]_0$	10^3k_{app},[a] s^{-1}	10^3k_{app},[b] s^{-1}	10^4k_t,[b] s^{-1}
k93	1.55	4.99	1.37	3.72	4.45	6.50
k97	0.93	2.89	2.38	2.51	2.54	2.99
k98	0.51	1.61	4.35	1.17	1.33	1.90
k99	0.23	0.73	9.44	0.43		
k100	0.061	0.19	35.7	0.087[c]		

[a] Considering time−conversion plots as linear. [b] Fitted according to eq 1. [c] After an induction period of ca. 90 min.

Table 3. Experimental Conditions and Kinetic Results for Group Transfer Polymerization of *n*-BuA with MTS, HgI_2, and TMSI in Toluene at 20 °C for Different Initiator Concentrations: $[M]_0 = 0.80$ mol/L, $[C]_0 = 1.0 \times 10^{-3}$ mol/L, $[S]_0 = 2.2 \times 10^{-3}$ mol/L

run	$10^3[I]_0$, mol/L	$[C]_0/[I]_0$, %	$[S]_0/[I]_0$, %	$[M]_0/[I]_0$	10^3k_{app},[a] s^{-1}	10^3k_{app},[b] s^{-1}	10^4k_t,[b] s^{-1}
k108	72.1	1.40	3.37	11.1	4.59	4.64	2.74
k107	55.5	1.84	3.77	14.8	3.67	3.73	4.17
k97	32.3	2.89	6.87	26.0	2.51	2.54	2.99
k106	12.3	8.30	17.3	69.1	1.41	1.56	3.05
k105	6.23	16.41	35.3	130.2	0.859	0.935	2.50

[a] Considering time−conversion plots as linear. [b] Fitted according to eq 1.

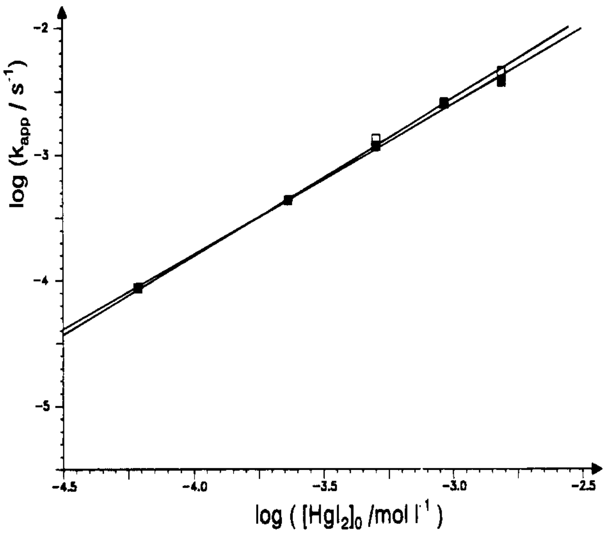
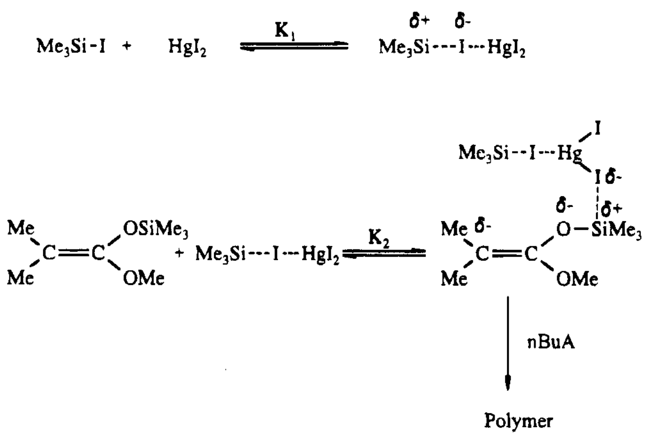


Figure 4. Determination of the reaction order with respect to catalyst concentration for the group transfer polymerization of *n*-BuA with MTS, HgI_2, and TMSI in toluene at 20 °C: (■) considering time−conversion curves as linear, slope = 1.19 ± 0.04; (□) fitted according to eq 1, slope = 1.25 ± 0.065.

Scheme 2. Formation of Active Species



Since the absence of induction periods considerably facilitates the determination of rate constants, we also undertook a reinvestigation of reaction orders with respect to catalyst, initiator, and monomer concentrations. In addition, the rate of termination was studied as a function of these parameters.

Dependence of Rates of Polymerization and Termination on Catalyst Concentration. Table 2 shows the experimental conditions and kinetic results for the dependence of the polymerization rate on the catalyst concentration in the presence of trimethylsilyl iodide. Except for one run at very low catalyst concentration ($[C]_0 \approx 6 \times 10^{-5}$ mol/L or 0.2% relative to $[I]_0$), the first-order time−conversion plots do not show induction periods. The bilogarithmic plots of the apparent rate constant, k_{app}, versus initial catalyst concentration give straight lines with slopes of 1.19 ± 0.04 and 1.25 ± 0.07, respectively (cf. Figure 4). This indicates that the reaction is first-order with respect to catalyst concentration. A similar slope was found in the absence of TMSI (slope = 0.94 ± 0.04).

Since the reaction order is also unity with respect to trimethylsilyl iodide concentration, the reaction relies on both HgI_2 and TMSI with the same weight. In the absence of TMSI the polymerization reaction is much slower, exhibiting induction periods. With TMSI alone the polymerization does not take place. Thus, it can be concluded that the catalytic effect is due to both HgI_2 and TMSI. It is reasonable to assume that HgI_2 and TMSI form a complex which catalyzes the polymerization reaction (Scheme 2).

A bilogarithmic plot of the termination rate constant, k_t, vs initial concentration of catalyst, $[HgI_2]_0$, has a slope of 1.09 ± 0.23. This indicates that only chains actived by the TMSI−HgI_2 adduct are capable of termination.

Dependence of Rates of Polymerization and Termination on Initiator Concentration. The experimental conditions and kinetic results for the investigation of the dependence of rates of polymerization and termination on initiator concentration are given in Table 3. It is seen clearly that the rate of polymerization increases with increasing initiator concentration. The reaction order with respect to initiator concentration is 0.67 ± 0.02 or 0.63 ± 0.03 determined from the bilogarithmic plot of k_{app} (as determined in two different ways) versus $[I]_0$ (Figure 5). It is considerably smaller than the value obtained in the absence of TMSI, where the reaction order is 1.29 ± 0.18. In that case, MTS is needed to form both TMSI and active species, so that the rate of polymerization more strongly depends on it. In the presence of TMSI, MTS is only needed to form active species.

In the GTP with nucleophilic catalysts the reaction order with respect to initiator concentration is between

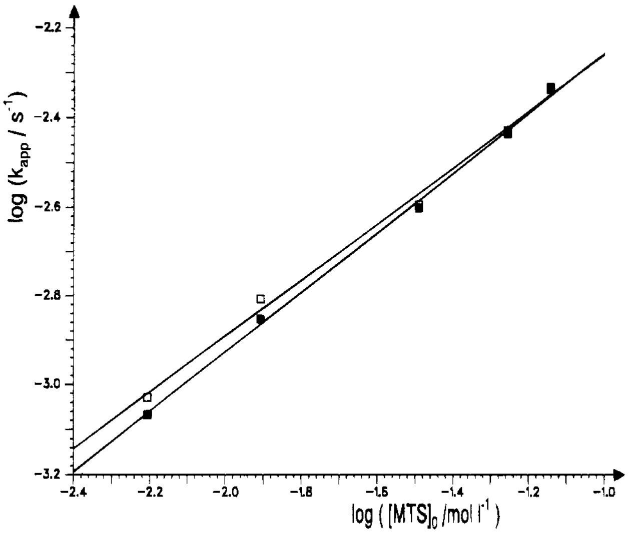


Figure 5. Determination of the reaction order with respect to initiator concentration for the group transfer polymerization of n-BuA with MTS, HgI_2, and TMSI in toluene at 20 °C: (■) considering time−conversion plots as linear, slope = 0.67 ± 0.02; (□) fitted according to eq 1, slope = 0.63 ● 0.03.

Table 4. Reaction Orders with Respect to the Concentrations of Reagents for GTP of *n*-BuA with MTS, HgI_2, and TMSI in Toluene at 20 °C

	reacn order of polymzn	
reagents	with TMSI[a]	without TMSI
initiator	0.67 ± 0.02	1.13 ± 0.18
catalyst	1.12 ± 0.04	0.92 ± 0.05
TMSI	0.97 ± 0.03	

[a] Considering the time−conversion plots as linear.

Scheme 3. Kinetic Scheme for GTP with HgI_2 and TMSI

$$\mathrm{C} + \mathrm{S} \overset{K_1}{\rightleftharpoons} \mathrm{X}$$

$$\mathrm{X} + \mathrm{P}'_i \overset{K_2}{\rightleftharpoons} \mathrm{P}^*_i$$

$$\mathrm{P}^*_i + \mathrm{M} \xrightarrow{k_p} \mathrm{P}^*_{i+1}$$

0 and unity, depending on the position of the equilibrium between dormant and active species. For the limiting case that the equilibrium is shifted to the dormant species side, the reaction order is unity. In contrast if the equilibrium is shifted to the active species side, the reaction order is 0. The fractional reaction order with respect to initiator concentration in this system may indicate that the position of the equilibrium is between these extreme cases. A more detailed analysis will be given below.

A bilogarithmic plot of the termination rate constant, k_t, vs initial concentration of initiator, $[MTS]_0$, has a slope of 0.1 ± 0.1, indicating that k_t does not depend on $[I]_0$. This is reasonable, because first-order kinetics with respect to the concentration of active species have already been assumed for the determination of k_t. This means that the estimation of k_t according to eq 1 is correct.

Concentration of Active Species. The reaction orders of polymerization with respect to the concentration of initiator, catalyst, TMSI, and monomer obtained from kinetic experiments are collected in Table 4.

The mechanism in Scheme 2 is represented by the kinetic Scheme 3. Here, C, S, and M represent HgI_2, TMSI, and n-BuA, respectively, P′ and P* represent dormant and active chains, respectively, with i monomeric units ($i = 1$: initiator), and X represents the complex between HgI_2 and TMSI.

From this scheme the relationships of concentrations of reagents can be expressed as

$$\begin{aligned} [\mathrm{X}] &= K_1[\mathrm{C}][\mathrm{S}] \\ [\mathrm{P}^*] &= K_2[\mathrm{X}][\mathrm{P}'] \\ [\mathrm{C}] &= [\mathrm{C}]_0 - [\mathrm{X}] - [\mathrm{P}^*] \\ [\mathrm{S}] &= [\mathrm{S}]_0 - [\mathrm{X}] - [\mathrm{P}^*] \\ [\mathrm{P}'] &= [\mathrm{I}]_0 - [\mathrm{P}^*] \end{aligned} \qquad (2)$$

Here, [P*] and [P′] represent the total concentration of active and dormant chains, respectively (including initiator), i.e. $[\mathrm{P}^*] = \Sigma[\mathrm{P}^*_i]$ and $[\mathrm{P}'] = \Sigma[\mathrm{P}'_i]$.

From eq 2 the concentration of active species can be expressed in a way similar to that given in ref 2:

$$\frac{[\mathrm{P}^*]}{K_1K_2} = \left([\mathrm{C}]_0 - \frac{[\mathrm{P}^*]}{K_2([\mathrm{I}]_0 - [\mathrm{P}^*])} - [\mathrm{P}^*]\right) \times \left([\mathrm{S}]_0 - \frac{[\mathrm{P}^*]}{K_2([\mathrm{I}]_0 - [\mathrm{P}^*])} - [\mathrm{P}^*]\right)([\mathrm{I}]_0 - [\mathrm{P}^*]) \qquad (3)$$

Generally, the concentration of catalyst is ca. 5% of the initiator or less. For this case $[\mathrm{P}'] \approx [\mathrm{I}]_0$.

Thus, eq 3 can be simplified to

$$\frac{[\mathrm{P}^*]}{K_1K_2} = \left([\mathrm{C}]_0 - \frac{K_2[\mathrm{I}]_0 + 1}{K_2[\mathrm{I}]_0}[\mathrm{P}^*]\right) \times \left([\mathrm{S}]_0 - \frac{K_2[\mathrm{I}]_0 + 1}{K_2[\mathrm{I}]_0}[\mathrm{P}^*]\right)[\mathrm{I}]_0 \qquad (3a)$$

The general solution for eq 3a is

$$[\mathrm{P}^*] = \frac{K_2[\mathrm{I}]_0}{2(K_2[\mathrm{I}]_0 + 1)}\left\{[\mathrm{S}]_0 + [\mathrm{C}]_0 + \frac{1}{K_1(K_2[\mathrm{I}]_0 + 1)} \pm \sqrt{\left([\mathrm{S}]_0 + [\mathrm{C}]_0 + \frac{1}{K_1(K_2[\mathrm{I}]_0 + 1)}\right)^2 - 4[\mathrm{S}]_0[\mathrm{C}]_0}\right\} \qquad (4)$$

This is the general expression for the concentration of active species under the condition of $[\mathrm{I}]_0 \gg [\mathrm{C}]_0$. On the basis of this expression two limiting cases can be discussed.

(1) For the case that equilibrium 2 in Scheme 3 is shifted to the right hand side ($K_2[\mathrm{I}]_0 \gg 1$), eq 4 can be simplified to

$$[\mathrm{P}^*] = \frac{1}{2}\left\{[\mathrm{S}]_0 + [\mathrm{C}]_0 + \frac{1}{K_1K_2[\mathrm{I}]_0} \pm \sqrt{\left([\mathrm{S}]_0 + [\mathrm{C}]_0 + \frac{1}{K_1K_2[\mathrm{I}]_0}\right)^2 - 4[\mathrm{S}]_0[\mathrm{C}]_0}\right\} \qquad (4a)$$

Here, we can discuss two more limiting cases:

(1a) If the first equilibrium is also shifted to the right hand side, i.e., $([\mathrm{C}]_0 + [\mathrm{S}]_0) \gg 1/K_1K_2[\mathrm{I}]_0$, eq 4a can be

Table 5. Dependence of Reaction Orders on the Concentration of Reagents and Magnitude of Equilibrium Constants According to Scheme 2 and Eqs 4–7

reagent		$K_1K_2[I]_0 \gg 1/([S]_0 + [Cl]_0)$ reacn order (case 1a)	$K_1K_2[I]_0 \ll 1/([S]_0 + [C]_0)$ reacn order (case 1b)
initiator	$K_2[I]_0 \gg 1$	**0**	**1**
catalyst		0/1 ($[S]_0 \lesssim [C]_0$)	1
TMSI		1/0 ($[S]_0 \lesssim [C]_0$)	1

reagent		$K_1 \gg 1/([S]_0 + [C]_0)$ reacn order (case 2a)	$K_1 \ll 1/([S]_0 + [C]_0)$ reacn order (case 2b)
initiator	$K_2[I]_0 \ll 1$	**1**	**1**
catalyst		0/1 ($[S]_0 \lesssim [C]_0$)	1
TMSI		1/0 ($[S]_0 \lesssim [C]_0$)	1

simplified to

$$[P^*] \approx \frac{1}{2}\left\{[C]_0 + [S]_0 \pm \sqrt{([C]_0 + [S]_0)^2 - 4[C]_0[S]_0}\right\} = \begin{cases}[C]_0 & \text{for } [C]_0 < [S]_0 \\ [S]_0 & \text{for } [C]_0 > [S]_0\end{cases} \tag{5}$$

Thus, the reaction order with respect to initiator concentration should be equal to zero. However, the reaction order with respect to $[C]_0$ and $[S]_0$ depends on the reagent in excess. If $[C]_0 > [S]_0$, the reaction order is 0 for $[C]_0$ and 1 for $[S]_0$, and vice versa.

(1b) On the other hand, if $([C]_0 + [S]_0) \ll 1/K_1K_2[I]_0$, eq 4a can be simplified to

$$[P^*] \approx K_1K_2[I]_0[C]_0[S]_0 \tag{6}$$

which results in first-order kinetics for initiator, catalyst, and TMSI.

(2) For the case that equilibrium 2 is shifted to the left hand side ($K_2[I]_0 \ll 1$), eq 4 can be simplified to

$$[P^*] = \frac{K_2[I]_0}{2}\left\{[S]_0 + [C]_0 + \frac{1}{K_1} \pm \sqrt{\left([S]_0 + [C]_0 + \frac{1}{K_1}\right)^2 - 4[S]_0[C]_0}\right\} \tag{4b}$$

which results in first-order kinetics with respect to initiator. Similarly, there are also two limiting cases.

(2a) If K_1 is high enough, i.e. $([C]_0 + [S]_0) \gg 1/K_1$, eq 4b can be simplified to

$$[P^*] = \frac{1}{2}K_2[I]_0\left\{[S]_0 + [C]_0 \pm \sqrt{([S]_0 + [C]_0)^2 - 4[S]_0[C]_0}\right\} = \begin{cases}K_2[I]_0[S]_0 & \text{for } [C]_0 > [S]_0 \\ K_2[I]_0[C]_0 & \text{for } [C]_0 < [S]_0\end{cases} \tag{7}$$

(2b) On the other hand, if K_1 is small, i.e. $([C]_0 + [S]_0) \ll 1/K_1$, eq 4b can be simplified to eq 6.

Another special case deserves interest. For $([C]_0 + [S]_0 + 1/[K_1(K_2[I]_0 + 1)])^2 \gg 4[C]_0[S]_0$ (i.e. both K_1 and K_2 not very large), eq 4 can be simplified to

$$[P^*] \approx \frac{K_1K_2[C]_0[S]_0[I]_0}{K_1(K_2[I]_0 + 1)([C]_0 + [S]_0) + 1} \tag{8}$$

This equation can be transformed into three linear equations with respect to $[I]_0$, $[C]_0$, and $[S]_0$. However, the corresponding plots are not linear, indicating that this condition is not well fulfilled.

It can be seen from the above discussion that the reaction order with respect to initiator concentration is in the range from 0 to 1 depending on the equilibrium constants, and on the relative concentration of reagents (cf. Table 5). The reaction order of 0.67 indicates that in this system the equilibrium is lying between the four extreme cases (cf. Figure 6). Some possible combinations are discussed below.

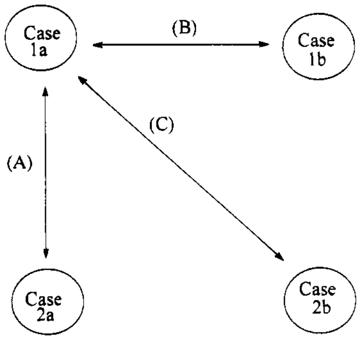


Figure 6. Limiting cases for fractional reaction orders with respect to initiator.

A. Between the extreme cases **1a** and **2a**: i.e., $K_2[I]_0$ is comparable to unity, and $K_1 \gg 1/([S]_0 + [C]_0)$. For this case a change of reaction order with respect to $[C]_0$ and $[S]_0$ should be observed, when $[S]_0$ is greater or smaller than $[C]_0$. Since, according to Table 1, where $[C]_0$ is both larger and smaller than $[S]_0$, no change of reaction order with respect to TMSI concentration was observed, this case can be excluded.

B. $K_2[I]_0 \gg 1$, and $K_1K_2[I]_0$ is comparable to $1/([S]_0 + [C]_0)$ (i.e., between cases **1a** and **1b**). This leads to the condition $K_2[I]_0 \approx 1/K_1([S]_0 + [C]_0) \gg 1$. As a consequence K_2 should be much higher than 10^2 mol/L and K_1 much smaller than 10^2 mol/L.

C. Between the extreme cases **1a** and **2b**: i.e., $K_2[I]_0 \gg 1$, $K_1K_2[I]_0 \gg 1/([S]_0 + [C]_0)$ and $K_2[I]_0 \ll 1$, $K_1 \ll 1/([S]_0 + [C]_0)$. It shows that $K_2[I]_0$ is comparable to unity and K_1 is not very small.

Dependence of Rates of Polymerization and Termination on Monomer Concentration. The near linearity of the time–conversion plots (Figure 1) indicates that the reaction is of internal first-order with respect to monomer concentration. However, it can be clearly seen from Table 6 that with increasing initial monomer concentration the rate of polymerization increases. The bilogarithmic plots of the apparent rate constants versus initial monomer concentration (Figure 7) yield straight lines with slopes of 0.52 ± 0.03 and 0.57 ± 0.03 depending on the method with which the k_{app} is determined. This indicates that the external reaction order with respect to monomer concentration is 1.52, similar to the value found in the absence of TMSI.

Table 6. Experimental Conditions and Kinetic Results for Group Transfer Polymerization of n-BuA with MTS, HgI$_2$, and TMSI in Toluene at 20 °C for Different Monomer Concentrations: $[C]_0 = 1.0 \times 10^{-3}$ mol/L, $[I]_0 = 3.1 \times 10^{-2}$ mol/L, $[S]_0 = 2.2 \times 10^{-3}$ mol/L

run	$[M]_0$, mol/L	$[M]_0/[I]_0$	10^3k_{app},[a] s^{-1}	10^3k_{app},[b] s^{-1}	10^4k_t,[b] s^{-1}
k102	2.02	64.1	4.21	4.66	6.13
k101	1.31	41.1	3.35	3.53	4.60
k97	0.84	26.0	2.51	2.54	2.99
k103	0.52	16.9	1.96	2.06	1.98
k014	0.27	8.84	1.50		

[a] Considering time–conversion plots as linear. [b] Fitted according to eq 1.

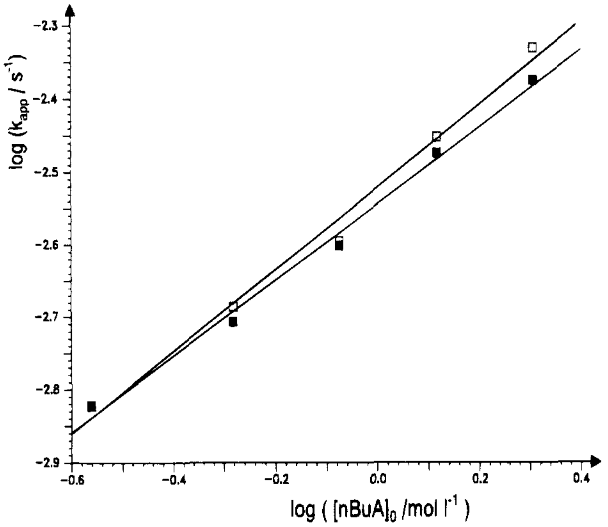


Figure 7. Determination of the reaction order with respect to monomer concentration for the group transfer polymerization of n-BuA with MTS, HgI$_2$, and TMSI in toluene at 20 °C: (■) considering time–conversion plots as linear, slope = 0.52 ± 0.03; (□) fitted according to eq 1, slope = 0.57 ± 0.03.

In the first paper of this series[1] we proposed that the reason for the high external reaction order is the increasing polarity of the reaction medium with increasing monomer concentration. The dependence of the reaction rate on the dielectric constant, ϵ, of the reaction medium, can be expressed by an equation derived by Kirkwood[3]

$$\ln k = A + B\frac{\epsilon - 1}{2\epsilon + 1} \tag{9}$$

where A and B are constants.

In our case, the dielectric constant of the reaction medium can be approximated by

$$\begin{aligned}\epsilon &= \epsilon_{tol} + (\epsilon_{mon} - \epsilon_{tol})w_{mon} \\ &\approx \epsilon_{tol} + (\epsilon_{mon} - \epsilon_{tol})\frac{M_{mon}}{\rho_{tol}\,1000}[M]_0 \\ &\approx 2.39 + 0.49[M]_0\end{aligned} \tag{10}$$

Here, w_{mon} is the weight fraction and M_{mon} is the molecular weight of the monomer; ρ_{tol} is the density of toluene. We assume that ϵ_{mon} is approximately equal to the dielectric constant of methyl isobutyrate[4] ($\epsilon = 5.7$); ϵ_{tol} is 2.39.[5]

A plot of the apparent rate constant according to eq 9 (Figure 8) results in an approximately linear correlation, with the slope of 18.8 ± 1.7. A bilogarithmic plot of the rate constant of termination, k_t, vs initial concentration of monomer, results in a slope of 0.85 ± 0.04. The slope of the corresponding Kirkwood plot is 24.9 ± 3.4. This indicates that termination depends more strongly on the polarity of the reaction medium than propagation, due to a stronger charge separation in the transition state.

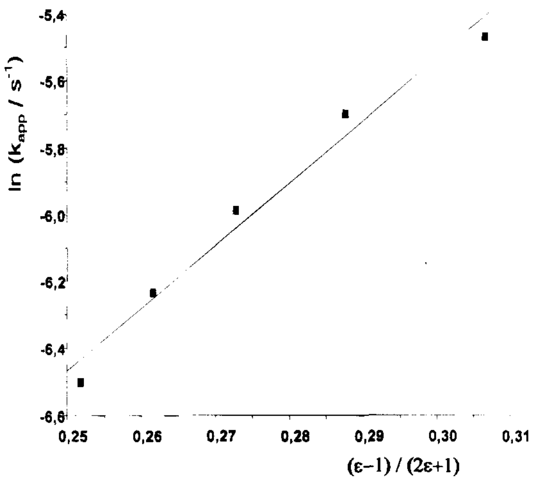


Figure 8. Correlation between ln k_{app} and the dielectric constant of the reaction medium for group transfer polymerization of n-BuA with MTS, HgI$_2$, and TMSI at 20 °C. Slope = 18.8 ± 1.7 (taking maximal slopes of time–conversion plot as k_{app}).

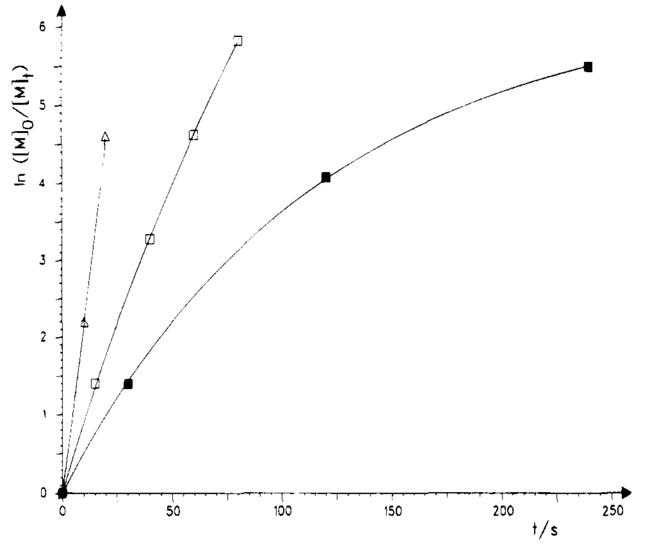


Figure 9. First-order time–conversion plots for the group transfer polymerization of n-BuA with MTS, HgI$_2$, and TMSI in methylene chloride (toluene = 10%) as a function of temperature. Symbols, cf. Table 7.

Polymerization in Methylene Chloride/Toluene Mixtures. Methylene chloride ($\epsilon = 9.08$ at 20 °C[5]) is much more polar than toluene. According to the above considerations the polymerization should run much faster in this solvent.

Table 7 and Figure 9 show the experimental conditions and results for some orientational experiments in methylene chloride/toluene mixtures. The rates of propagation and termination are ca. 2 orders of magnitude higher than those in toluene. The fraction of toluene has a strong influence on the polarity of the reaction medium. With decreasing toluene fraction, the polarity of the reaction medium and rate of the polymerization increase. Run DD (30% toluene v/v, $\epsilon \approx 7.6$) is much slower relative to run K150, which was performed in a more polar solvent (only 10% toluene v/v, $\epsilon \approx 8.6$). These results indicate that the polarity of the reaction medium has indeed a very strong effect on the

Table 7. Experimental Conditions and Kinetic Results for Group Transfer Polymerization of *n*-BuA with MTS, HgI_2, and TMSI in Toluene/Methylene Chloride Mixture (Toluene = 10% v/v)

run		T, °C	ϵ	$10^2[I]_0$, mol/L	$10^4[C]_0$, mol/L	$10^3[S]_0$, mol/L	$[M]_0$, mol/L	10^2k_{app},[a] s^{-1}	10^2k_{app},[b] s^{-1}
k98[c]		20	2.8	3.1	5.2	2.2	0.83	0.133	0.133
DD[d]		20	7.6	2.3	5.1	3.5	0.70	7.38	5.79
k150	■	20	8.6	1.1	2.0	1.0	0.31	5.43	69.8
k151	□	0	9.4	1.1	2.1	1.0	0.32	9.45	115
k152	△	−20	10.3	1.1	2.0	1.0	0.31	20.6	256

[a] Fitted according to eq 1. [b] Recalculated to the concentrations of run k98. [c] Pure toluene. [d] Toluene = 30%.

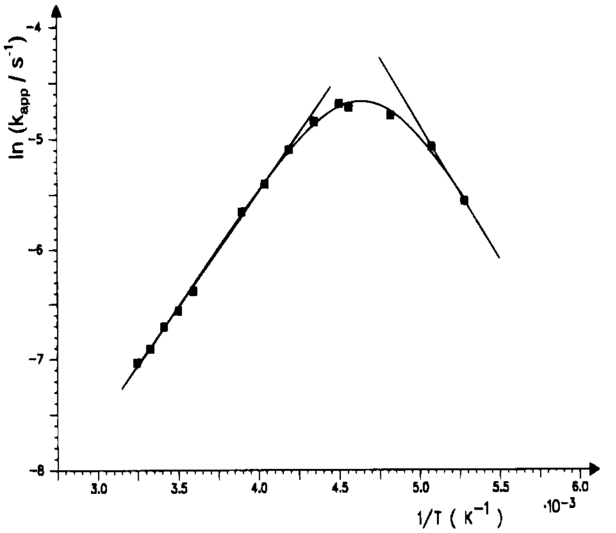


Figure 10. Arrhenius plot for GTP of n-BuA with MTS, HgI_2, and TMSI in toluene (assuming linear time−conversion plots). The curved line was calculated with the fitted parameters in Scheme 3.

Table 8. Experimental Conditions and Kinetic Results for Group Transfer Polymerization of *n*-BuA with MTS, HgI_2, and TMSI in Toluene for Different Temperatures (Initial Concentrations (at 20 °C): $[M]_0$ = 0.83 mol/L, $[C]_0$ = 5.2 × 10^{-4} mol/L, $[I]_0$ = 3.1 × 10^{-2} mol/L, $[S]_0$ = 2.2 × 10^{-3} mol/L)

run	T, °C	10^3k_{app},[a] s^{-1}	10^3k_{app},[b] s^{-1}	10^3k_{app},[c] s^{-1}	10^4k_t,[c] s^{-1}	k_t/k_{app}
k138	−83.8	3.84	3.84			
k136	−76.2	6.28	6.28			
k135	−65.6	8.28	8.28			
k137	−53.9	8.91	8.91			
k130	−51.0	12.11	9.20			
k131	−43.0	9.99	7.86			
k132	−34.5	7.54	6.13	7.79	1.48	0.019
k133	−25.7	5.35	4.50	5.64	2.43	0.043
k134	−16.5	4.03	3.50	4.48	3.91	0.087
k111	5.0	1.80	1.70	2.00	2.98	0.15
k112	12.5	1.46	1.42	1.51	2.34	0.16
k98	20.0	1.17	1.23	1.33	1.90	0.14
k109	27.5	0.975	1.00	1.06	3.84	0.36
k110	35.0	0.835	0.884	0.96	6.08	0.63

[a] Considering time−conversion plots as linear. [b] Calculated to standard concentrations according to eq 11 in order to consider the volume changes with the temperature. [c] Fitted according to eq 1.

rate of polymerization and strongly support the interpretation for the higher external reaction order with respect to the concentration of monomer, confirming that charge separation in the transition state is involved in the polymerization. Due to the very high conversions, the determination of k_t is not reliable.

It can be also seen from Table 7 and Figure 9 that in the experimental temperature range from +20 to −20 °C the rate of polymerization increases with decreasing temperature; the apparent activation energy is negative ($E_{a,app}$ = −17.6 kJ/mol). This effect might be attributed in part to the increase of the dielectric constant of the reaction medium, but it also occurs in pure toluene and is discussed below.

Dependence of Rates of Polymerization and Termination on Temperature. The dependence of the polymerization rate on temperature was studied in the temperature range from −84 to +35 °C in pure toluene. Table 5 shows the experimental conditions and kinetic results, and Figure 10 shows an Arrhenius plot of the apparent rate constants. In consideration of the change of volume with temperature the apparent rate constants were recalculated to standard concentrations at 20 °C according to the reaction orders

$$k_{app} \propto [I]_0^{0.67}[M]_0^{0.52}[C]_0^{1.12}[S]_0 \qquad (11)$$

The Arrhenius plot shows a distinct maximum at $T \approx$ −60 °C. Above ca. −40 °C the activation energy is apparently negative ($E_{a,app} \approx -17.6 \pm 0.7$ kJ/mol) similar to that in the toluene/methylene chloride mixture; i.e. the rate of polymerization increases with decreasing temperature. Only at temperatures below ca. −70 °C does the rate of the polymerization decrease with decreasing temperature; the activation energy is $E_{a,app} \geq +20$ kJ/mol (in the absence of TMSI: $E_{a,app} \approx$ 46 kJ/mol). This value is comparable to those found in many anionic polymerizations.[6]

In order to explain these results, one has to consider that the apparent rate constant of polymerization, k_{app}, is equal to the product of the rate constant, k_p, and the concentration of active species, [P*]:

$$k_{app} = k_p[P^*] \qquad (12)$$

The rate constant of polymerization, k_p, must decrease with decreasing temperature according to the Arrhenius relation. The concentration of active species will also depend on temperature if the active species are formed in an equilibrium. If this reaction is exothermic, it will lead to a decrease of concentration of active species with increasing temperature. The rate of polymerization depending on the activation energy of monomer addition and on the enthalpy of active species formation can lead to a curved Arrhenius plot including an apparent negative activation energy. A similar phenomenon was found in the anionic polymerization of styrene in THF.[7] If the temperature is low enough to allow for a complete shift of the equilibrium to the side of the active species, only the activation energy will determine the temperature dependence.

The rate constants of termination show a large scatter. The activation energy can be estimated to $E_{a,t} \approx 6.0 \pm 3.6$ kJ/mol, which is higher than that of propagation by ca. 24 kJ/mol. In the anionic polymerization of MMA with the Na^+ conterion the activation energy of termination was found to be higher than that of propagation by 30 kJ/mol.[8]

As discussed above, if K_1 and K_2 are not very great, the concentration of active species [P*] can be approximately expressed by eq 8 and, because k_p =

Table 9. Fitting Results for Activation and Thermodynamic Parameters of GTP of *n*-BuA

log A	E_a, kJ mol^{-1}	ΔH_1, kJ mol^{-1}	ΔS_1, J mol^{-1} K^{-1}	ΔH_2, kJ mol^{-1}	ΔS_2, J mol^{-1} K^{-1}
6.73	20.8	−23.5	−81.7	−15.6	−23.5

T, °C	$10^{-2}k_p$, L mol^{-1} s^{-1}	K_1, L mol^{-1}	10^2K_2, L mol^{-1}	[P*]/[C]$_0$, %	[P*]/[I]$_0$, %
40	18.2	0.446	0.240	0.0778	0.00128
20	10.5	0.825	0.362	0.216	0.00356
0	5.64	1.67	0.580	0.691	0.0114
−60	0.427	30.7	4.04	41.0	0.676
−90	0.0622	270	17.2	77.6	1.28

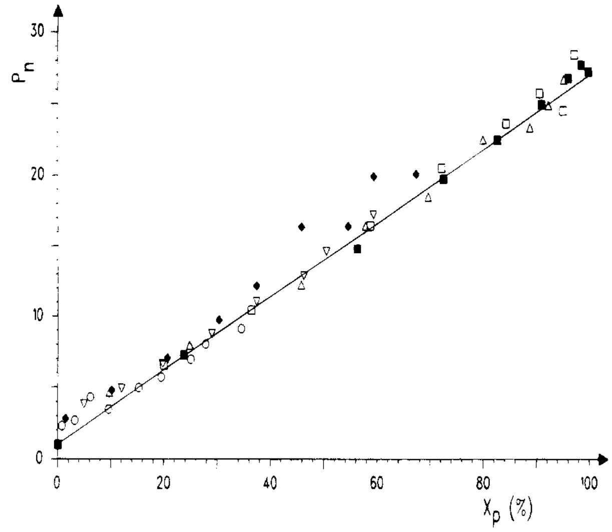


Figure 11. Plot of number-average degree of polymerization, P_n, vs monomer conversion, x_p, for the group transfer polymerization of *n*-BuA with MTS and HgI$_2$/TMSI in toluene for different TMSI concentrations in toluene at 20 °C: (—) theoretical line.

$A \exp(-E_a/RT)$ and $-RT \ln K = \Delta H - T\Delta S$, we can fit K_1, K_2, and k_p to the Arrhenius data in Table 8. A possible combination of parameters and the corresponding values of [P*] given as an example in Table 9. Other combinations are possible.

Molecular Weight and Molecular Weight Distribution. In the absence of TMSI we obtained a good molecular weight control and narrow molecular weight distributions. The presence of TMSI changes neither the molecular weight control nor the molecular weight distribution. The molecular weights of the polymers increase with increasing monomer conversion, as theoretically expected (Figure 11). The molecular weight distribution is also very narrow, generally, the polydispersity index $M_w/M_n \leq 1.15$, similar to the case without TMSI, and a maximum of polydispersity index can also be observed at low monomer conversions (Figure 12). The deviation of the experimental points from the modified Poisson distribution[1] can be attributed to termination, the products of which lead to a small UV signal at $\lambda = 260$ nm (cf. part 1).

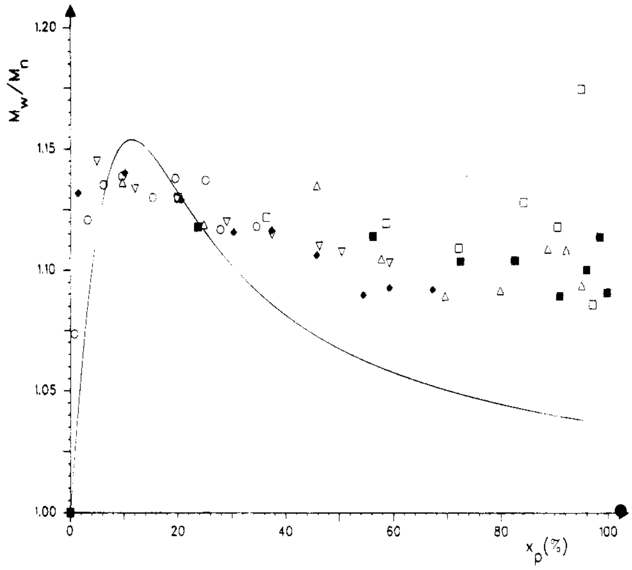


Figure 12. Plot of polydispersity index versus monomer conversion for the group transfer polymerization of *n*-BuA with MTS and HgI$_2$/TMSI in toluene for different TMSI concentrations in toluene at 20 °C. (—) calculated with $[M]_0/[I]_0 = 25.5$ according to the modified Poisson distribution.[1]

The good control of molecular weight by the ratio [*n*-BuA]$_0$/[MTS]$_0$ and the narrow molecular weight distributions indicate that the polymer chains are initiated by MTS molecules and not by TMSI and, in conjunction with the linear first-order time−conversion plots, confirm that this polymerization system can be considered as living.

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