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Group Transfer Polymerization of *n*-Butyl Acrylate with Lewis Acid Catalysts. 1. Kinetic Investigation Using HgI_2 as a Catalyst in Toluene

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ABSTRACT: The group transfer polymerization (GTP) of *n*-butyl acrylate using 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene as an initiator and HgI_2 as a catalyst in toluene is much slower compared to nucleophilic-catalyzed GTP; half-lives are in the range of minutes to hours. Induction periods are observed which are attributed to the formation of trimethylsilyl iodide (TMSI). The polymerization follows first-order kinetics with respect to the concentrations of initiator and catalyst. With respect to concentration of monomer the reaction is of first-order internally but follows an external reaction order of 1.52 due to the higher polarity of the reaction medium at higher monomer concentrations. The degree of polymerization is controlled by the ratio $[M]_0/[I]_0$, and the molecular weight distribution is narrow and can be described by a modified Poisson distribution. Generally, $M_w/M_n \le 1.2$. It is proposed that the active species are formed from initiator, catalyst, and TMSI.

Introduction

Group transfer polymerization (GTP) is a convenient method to prepare methacrylate and acrylate polymers with narrow molecular weight distributions (MWD's) at room temperature.[1,2] For the GTP of methacrylates polar solvents and nucleophilic catalysts (e.g. bifluorides or benzoates) are most suitable for obtaining a living polymerization. The mechanism of GTP with nucleophilic catalysts is presently under dispute. However, in all mechanisms discussed so far, the first step is the reaction of the catalyst with an inactive silyl ketene acetal, either to form a species with pentacoordinate silicon[2–5] or to form an active ester enolate anion[6–8] (Scheme 1).

In the GTP of acrylates, the use of nucleophilic catalysts and polar solvents leads to broad MWD's.[9–11] In order to obtain narrow MWD's, Lewis acid catalysts (e.g. $ZnCl_2$, i–Bu_2AlCl) and nonpolar solvents (e.g. toluene, CH_2Cl_2) are more favorable.[12,13] The mechanism of GTP using Lewis acid catalysts is not clear. It has been suggested that the monomer is activated by forming a complex with the Lewis acid.[12] This mechanism is supported by many experiments in which the formation of a monomer/Lewis acid complex accelerates radical polymerization.[14–17] Another argument put forward in favor of this mechanism is that more than 10 mol % of the Lewis acid (e.g. $ZnCl_2$) based on *monomer* concentration was reported to be necessary for the polymerization reaction.[12]

On the other hand, when HgI_2 is used as a catalyst, only ca. 10 mol % of the Lewis acid based on *initiator* concentration is needed.[18–20] Dicker et al. have suggested that HgI_2 activates the initiator, i.e. acts like a nucleophilic catalyst[21] (Scheme 2). This mechanism is corroborated by the ability of HgI_2 to catalyze the *E*/*Z*[22,23] and O/C-silyl isomerization[24,25] of silyl ketene acetals in the absence of monomer.

In order to gain more insight into the mechanism of Lewis acid-catalyzed GTP we undertook a kinetic investigation of the polymerization of *n*-butyl acrylate using MTS as an initiator and HgI_2 as a catalyst in toluene.

Experimental Part

Reagents. Solvent. Toluene (BASF) was fractionated over a 2 m column and then refluxed for more than 48 h over potassium. After degassing, it was stirred for more than 24 h over potassium/sodium alloy and some benzophenone, and distilled under high vacuum into a flask with K/Na alloy, where it was stored. Before use it was distilled from the flask to a glass ampule equipped with a Teflon valve.

Inert Gas. Argon (99.996% Linde) was cleaned with an Oxisorb system (Messer Griesheim) which is able to reduce the concentration of O_2 and H_2O to less than 0.1 and 0.5 ppm, respectively, and then bubbled through two bottles filled with toluene with some benzophenone and K/Na alloy.

Internal Standard. *n*-Decane (Aldrich) was fractionated over a 2 m column. After degassing, it was stirred for more than 24 h over the K/Na alloy and distilled under high vacuum to a glass ampule before use.

Initiator. 1-Methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS; Petrarch Systems Inc.) was distilled under reduced pressure and stored under dry argon in a glass ampule.

Catalyst. Mercuric iodide (HgI_2; Aldrich 99.999%) was dried in vacuo 15 h at room temperature before use.

Monomer. *n*-Butyl acrylate (BASF: free from inhibitor) was stirred over CaH_2 at 0 °C for 12 h and then fractionated at reduced pressure over a 1 m column filled with Sulzer packing. After it was degassed and Irganox 1010 (Ciba-Geigy) was added as an inhibitor, the distillate was stirred twice over CaH_2 for 24 h and distilled under high vacuum into a glass ampule where it was stored under dry argon at ca. −30 °C. The level of impurities was less than 0.01% (by GC). Additional purification with $AlEt_3$ or $Al(i\text{-}Bu)_3$ did not improve the results.

Kinetic Experiments and MWD Determination. The experiments were performed at 20 °C. A reactor was used which included a stirrer, glass ampules for monomer, initiator, and solvent, a mixing chamber, and a glass tube fitted with a Teflon valve for drawing samples. Mercuric iodide was introduced into the reactor 1 day before the experiment was carried out, and the reactor was evacuated for more than 15 h. Toluene was added and stirred with mercuric iodide for 15 min. Then, the initiator solution was added, and after the initiator was premixed with catalyst for 15 min, the monomer solution was added under argon pressure (ca. 70 mbar). After predetermined times samples were drawn and terminated with methanol. Monomer conversion was determined by GC using *n*-decane as the internal standard. The solvent and unreacted monomer were stripped in vacuo. The molecular weight distribution of the polymers was determined by GPC, using 2 × 5μm 100 Å and 1 × 5 μm 500 Å, 60 cm PL gel columns and THF as the eluent. The calibration curve was established by

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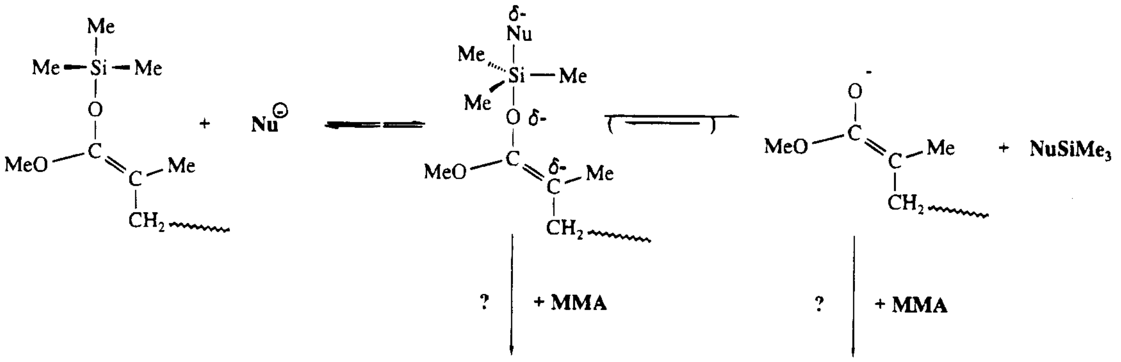
Scheme 1. Activation of Initiator in Nucleophilic Catalysis of GTP



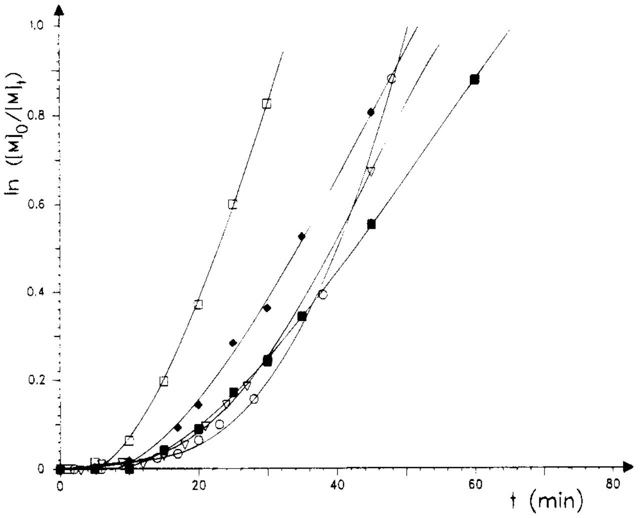
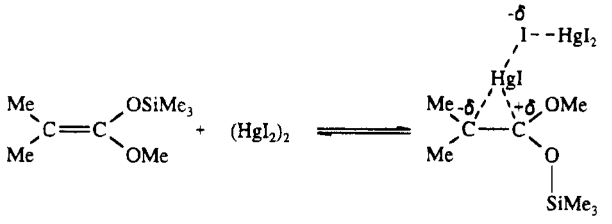


Figure 1. First-order time−conversion plots for the group transfer polymerization of nBuA with MTS and HgI_2 in toluene at 20 °C as a function of HgI_2 concentration: symbols, cf. Table 1.

Scheme 2. Activation of Initiator by HgI_2 According to Dicker[21]



using oligomers of *n*-BuA and PMMA standards. The difference in hydrodynamic volume between P*n*-BuA and PMMA appears to be small.

Results and Discussion

Dependence of Propagation Rate on Catalyst Concentration. Figure 1 shows first-order plots of monomer conversion versus time. All polymerizations exhibit a distinct induction period. The intercepts of the straight lines obtained from the final linear part of time−conversion plots with the abscissa were taken as induction periods (t_{ind}). The nature of the induction period will be discussed later. First, we wish to discuss the apparent rate constants of propagation, $k_{app} = k_p[P^*]$ of polymerization, which were taken as the slope of the final linear part of the time−conversion plots. Here, k_p is the propagation rate constant and $[P^*]$ is the concentration of active chain ends. k_{app} is determined as the maximum slope of the first-order time−conversion plot.

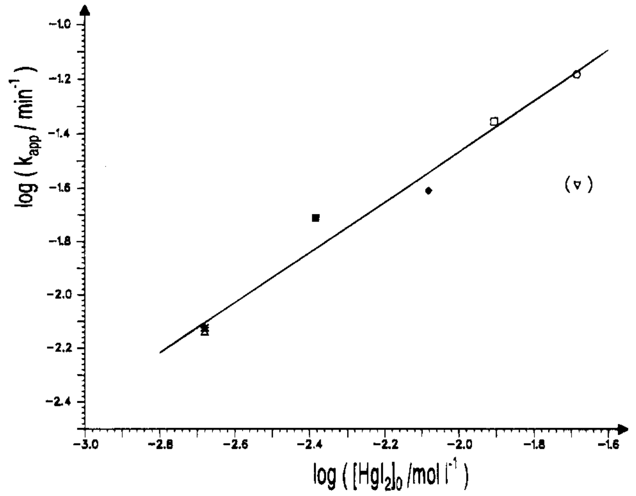


Figure 2. Determination of the reaction order with respect to catalyst concentration for the group transfer polymerization of nBuA with MTS and HgI_2 in toluene at 20 °C. Slope = 0.92 ± 0.05.

It can be seen from Table 1 that increasing HgI_2 concentrations lead to increased rates of polymerization and decreased induction periods. Figure 2 shows a bilogarithmic plot of the apparent rate constants of propagation, k_{app}, vs initial catalyst concentrations, $[C]_0$, resulting in a straight line with a slope of 0.92 ± 0.05. This indicates that the reaction is of first-order with respect to catalyst concentration.

Table 1. Experimental Conditions and Kinetic Results for Group Transfer Polymerization of nBuA (M) with MTS (I) and HgI_2 (C) in Toluene at 20 °C for Different Catalyst Concentrations

run	symbol	$[M]_0$, mol/L	$10^3[C]_0$, mol/L	$10^2[I]_0$, mol/L	$10^2[C]_0/[I]_0$	$[M]_0/[I]_0$	10^3k_{app},[a] min^{-1}	t_{ind},[b] min
K3	△	1.28	2.09	5.02	4.16	25.5	7.99	111.8
K7	*	1.40	2.09	6.16	4.16	22.7	7.30	145.0
K1	■	1.19	4.14	5.02	8.23	23.7	19.5	16.5
K4	◆	1.28	8.29	5.02	16.5	25.5	27.0	13.7
K2	□	1.28	12.4	5.02	24.7	25.5	45.8	11.0
K5	▽	1.28	20.7	5.02	41.2	25.5	28.5	15.5
K6	○	1.28	20.6	4.65	44.3	27.5	70.4	16.5

[a] Final slope of the time−conversion plot. [b] Induction period.

Table 2. Experimental Conditions and Kinetic Results for Group Transfer Polymerization of nBuA with MTS and HgI$_2$ in Toluene at 20 °C for Different Initiator Concentrations: $[M]_0 = 1.28$ mol/L, $[C]_0 = 4.15 \times 10^{-3}$ mol/L

run	symbol	$10^2[I]_0$, mol/L	$10^2[C]_0/[I]_0$	$[M]_0/[I]_0$	10^3k_{app},[a] min^{-1}	t_{ind},[b] min
K36	■	1.09	38.4	117.8	1.39	200
K35	□	2.28	18.2	56.1	7.96	150
K11	△	2.52	16.5	50.8	17.3	101
K1	◆	5.02	8.23	23.7	19.5	16.5
K9	▽	7.57	5.51	16.9	27.4	16.0
K10	○	10.1	4.13	12.7	60.3	17.0
K13	*	15.1	2.75	8.48	99.7	15.0

[a] Slope of the time–conversion curve. [b] Induction period.

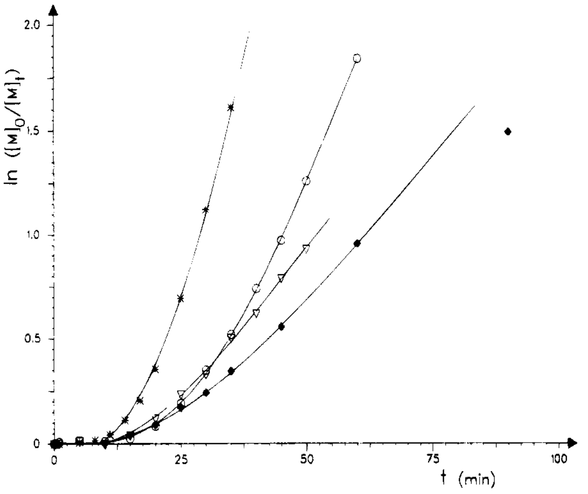


Figure 3. First-order time–conversion plots for the group transfer polymerization of nBuA with MTS and HgI$_2$ in toluene at 20 °C as a function of MTS concentration: symbols cf. Table 2.

Dependence of Propagation Rate on Initiator Concentration. Table 2 collects the experimental conditions and results for the dependence of polymerization rate on initial concentration of initiator. The first-order time–conversion plots are shown in Figure 3. Again, with increasing initiator concentration, the rates of polymerization increase and the induction periods decrease.

The bilogarithmic plot for the apparent rate constants, k_{app}, vs initiator concentrations $[I]_0$ (Figure 4) gives a slope of 1.13 ± 0.18. This indicates that the kinetic order with respect to initiator concentration is approximately unity, although a higher order cannot be excluded.

The reaction orders for both catalyst and initiator are similar to those obtained for the GTP of MMA in THF using tris(dimethylamino)sulfonium (TAS) benzoate as a nucleophilic catalyst.[5] This may be a first indication that the mechanisms of both reactions are similar.

Dependence of Propagation Rate on Monomer Concentration. The good linearity of the final part of the first-order time–conversion plots indicates that the internal order with respect to monomer concentration is unity. In order to determine the external reaction order, the initial monomer concentration, $[M]_0$, was varied. Table 3 shows that with increasing $[M]_0$, the apparent propagation rate constants, k_{app}, somewhat increase whereas the induction period is not significantly affected. A bilogarithmic plot of k_{app} vs $[M]_0$ results in a slope of 0.52 ± 0.19 (Figure 5) which leads to an external reaction order of 1.52 with respect to monomer concentration.

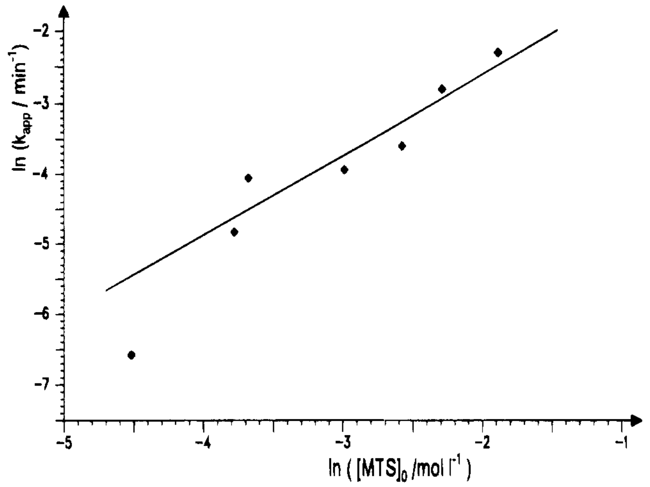


Figure 4. Determination of reaction order with respect to initiator concentration for the group transfer polymerization of nBuA with MTS and HgI$_2$ in toluene at 20 °C. Slope = 1.13 ± 0.18.

Table 3. Experimental Conditions and Kinetic Results for Group Transfer Polymerization of nBuA with MTS and HgI$_2$ in Toluene at 20 °C for Different Monomer Concentrations: $[C]_0 = 4.17 \times 10^{-3}$ mol/L, $[I]_0 = 0.051$ mol/L, $[C]_0/[I]_0 = 8.2\%$

run	$[M]_0$, mol/L	$[M]_0/[I]_0$	10^3k_{app},[a] min^{-1}	t_{ind},[b] min
K18	0.33	6.45	10.6	38
K26	0.38	7.44	18.3	40
K17	0.69	13.5	15.2	40
K27	0.70	13.6	25.7	75
K1	1.19	23.7	19.5	16.5
K14	1.85	36.3	64.4	28
K16	2.64	51.8	23.7	20
K25	2.94	57.1	59.2	40

[a] Final slope of the time–conversion plot. [b] Induction period.

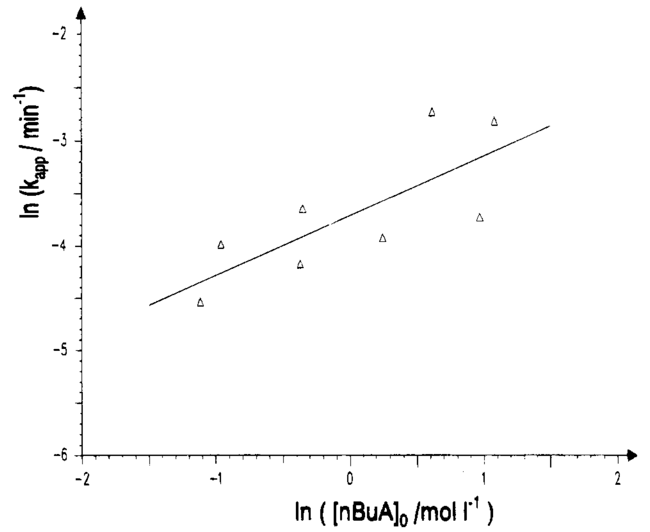


Figure 5. Determination of external reaction order with respect to monomer concentration for the group transfer polymerization of nBuA with MTS and HgI$_2$ in toluene at 20 °C. Slope = 0.52 ± 0.19.

The reason for the higher external reaction order is that the reaction is very sensitive toward the polarity of the reaction medium. It is well-known that polar solvents accelerate reactions involving a charge-separated transition state. In fact, the group transfer polymerization of n-BuA catalyzed by HgI$_2$ is reported to be faster in polar solvents.[21,26] Since the monomer is more polar than toluene, increasing the monomer concentration raises the polarity of the medium and

Table 4. Experimental Conditions and Kinetic Results for Group Transfer Polymerization of nBuA with MTS and HgI_2 in Toluene for Different Temperatures

run	temp, °C	$[M]_0$, mol/L	$10^3[C]_0$ mol/L	$10^2[I]_0$, mol/L	10^3k_{app},^{a} min^{-1}	$10^{3k}{}_{app}$,^{c} min^{-1}	t_{ind},^{b} min
K20	0	1.28	4.17	5.07	3.3		66
K22	10	1.28	4.17	5.07	78.7		75
K1	20	1.19	4.14	5.02	19.5		16.5
K19	40	1.28	4.16	5.07	21.4		18
K29	0	1.63	5.22	6.46	2.2	1.2	145
K31	10	1.63	5.22	6.46	4.1	2.2	72
K30	30	1.63	5.22	6.46	24.0	12.9	22
K32	40	1.63	5.22	6.46	29.8	16.1	27

^{a} Final slope of the time–conversion plot. ^{b} Induction period. ^{c} Recalculated to standard concentrations, according to $k_{app} \propto [C]_0[I]_0[M]_0^{0.53}$.

thus accelerates the polymerization. This indicates also that the polymerization involves a charge-separated transition state. Since a polar polymer is formed during the reaction, the polarity of the medium will not change considerably with conversion. A quantitative treatment will be given in part 2 of this series.

Dependence of Propagation Rate on Temperature. In two sets of experiments the effect of temperature on the rate of polymerization was studied (cf. Table 4). For the second set ca. 25% higher absolute concentrations of reagents were used than for the first one. Taking into account the reaction orders determined above, this should lead to a ca. 70% increase in rate for a given temperature. The data points for set 2 in Figure 6 were adjusted accordingly. As expected, the rate of polymerization increases with temperature and at the same time the induction periods decrease.

Figure 6 shows the Arrhenius plot from which the apparent activation energy $E_{a,app} = 42.5 \pm 9.6$ kJ/mol can be obtained.

Since k_{app} depends on catalyst, initiator, and monomer concentrations and may involve one or more equilibrium constants, the activation parameters are only apparent ones and it is difficult to compare them to other systems. Nevertheless, a comparison with GTP of MMA in THF catalyzed by TAS benzoate[5] yields the same activation energy ($E_{a,app} = 42.1$ kJ/mol). This is another indication that the mechanisms are similar.

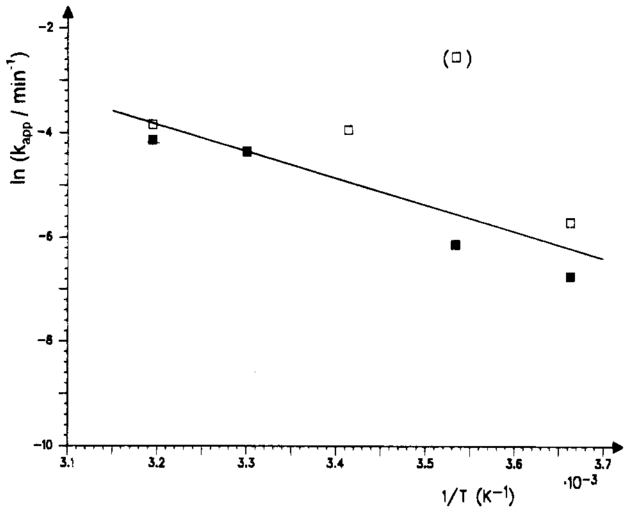


Figure 6. Arrhenius plot for the group transfer polymerization of nBuA with MTS and HgI_2 in toluene: (□) first set; (■) second set of experiments (recalculated to standard concentrations).

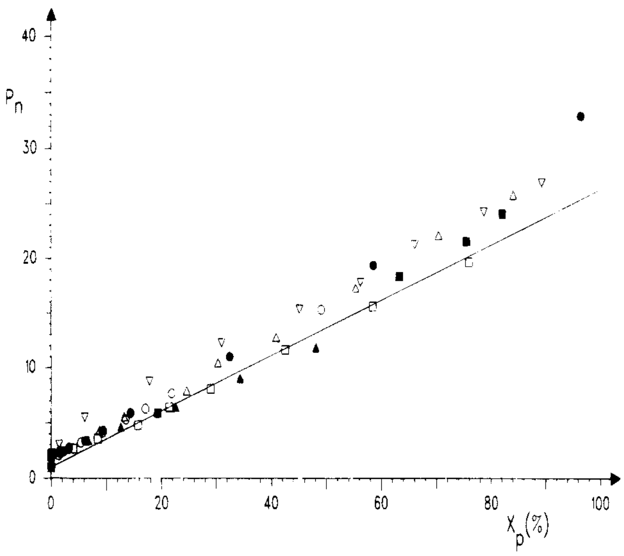
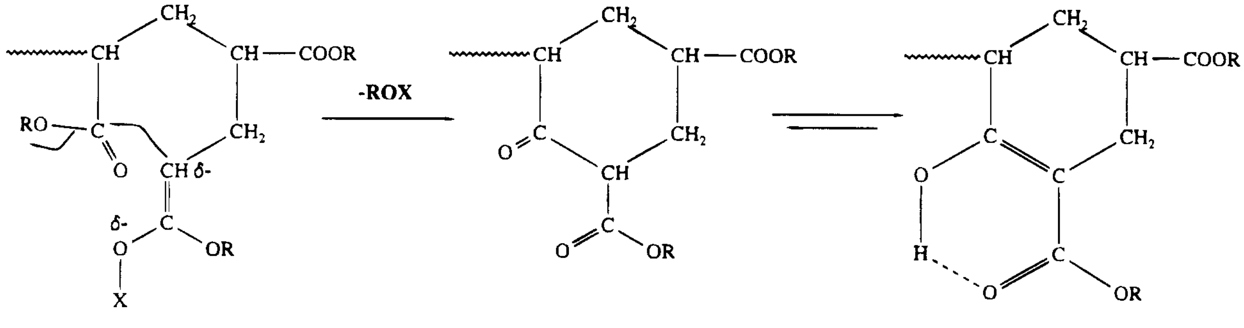


Figure 7. Plot of number-average degree of polymerization, P_n, vs monomer conversion, x_p, for the group transfer polymerization of nBuA with MTS and HgI_2 in toluene for different catalyst concentrations. (—) theoretical line; symbols, cf. Table 1.

Molecular Weights and Molecular Weight Distributions. Generally, the polymerization of *n*-BuA with MTS and HgI_2 in toluene exhibits a good control of molecular weight. The number-average degree of polymerization, P_n, increases linearly with increasing monomer conversion, and the molecular weight distribution is very narrow. Figure 7 shows a plot of P_n versus monomer conversion, x_p, for different catalyst concentrations. Similar plots are obtained for the variation of initiator and monomer concentrations and

Scheme 3. Back-Biting Reaction of Polyacrylates



X = Li$^+$, Na$^+$, -SiMe$_3$

λ_{max} = 220 nm

λ_{max} = 305 nm

λ_{max} = 260 nm

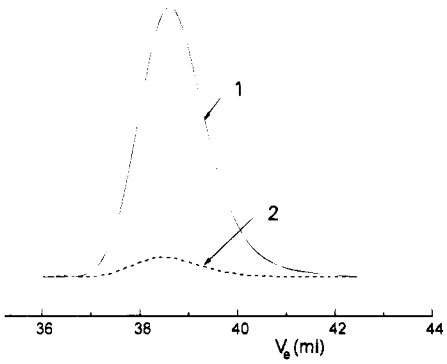
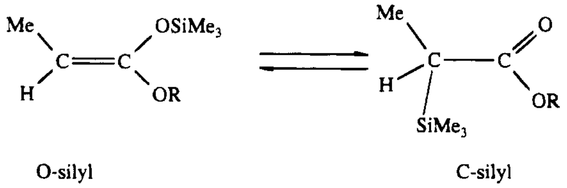


Figure 8. Typical GPC eluogram for the group transfer polymerization of nBuA with MTS and HgI_2 in toluene (M_n = 6600; D = 1.07): (1) RI; (2) UV(260 nm) × M.

Scheme 4. Isomerization of Silyl Ketene Acetals



temperature. It can be seen that the experimental data agree well with the expected values. A typical GPC eluogram is shown in Figure 8. Usually, the polydispersity index, M_w/M_n is smaller than 1.15. The good molecular weight control and the narrow MWD's strongly support that the GTP of n-BuA with MTS and HgI_2 in toluene is a living process.

However, inspection of the GPC eluograms reveals some peaks with a very slight UV absorption at 260 nm, which is typical for an enolized cyclic β-keto ester end group formed by the back-biting reaction observed in anionic polymerization of *tert*-butyl acrylate[27] and also in the GTP of MMA[28] (Scheme 3). Since the UV detector only detects the polymer end groups, the corresponding eluogram will show a frequency distribution, in contrast to the RI detector. Thus, for comparison to the RI signal, the UV signal was multiplied by the corresponding molecular weight for each slice of the eluogram.

Brittain and Dicker also reported that acrylate oligomers formed by HgI_2-catalyzed GTP self-terminate by cyclization, and in addition by O/C-silyl isomerization[28,29] (Scheme 4).

Under our experimental conditions, it seems that these termination reactions are so minimal that they do not significantly affect the molecular weight distribution. It is clearly seen from the plot of polydispersity index versus conversion (Figure 9) that polydispersity decreases with conversion whereas termination or transfer reactions would have resulted in an increase of polydispersity with conversion.

Interestingly, all plots of polydispersity index versus monomer conversion exhibit a maximum at low conversion. This conversion decreases with increasing $[M]_0/[I]_0$. The reason for this unfamiliar phenomenon stems from the fact that the rate of initiation is comparable to the rate of propagation ($k_i \approx k_p$), because the chemical structure of the initiator (MTS) is similar to that of the growing chain end. Thus, at low conversion, there is some residual unreacted initiator which is not taken into account in the determination of the MWD by GPC. This leads to an apparently narrower distribution than a Poisson distribution, where instantaneous initiation ($k_i \gg k_p$) is assumed. At higher conversions, all initiator molecules will have reacted and the distribution should approximate a Poisson distribution. For $k_i > k_p$ and $k_i < k_p$ the Gold distribution[30] describes the MWD. However, this distribution fails for $k_i = k_p$. For this case, Flory's derivation of the Poisson distribution[31] can be modified by subtracting the mole fraction of the initiator, $n(1)$

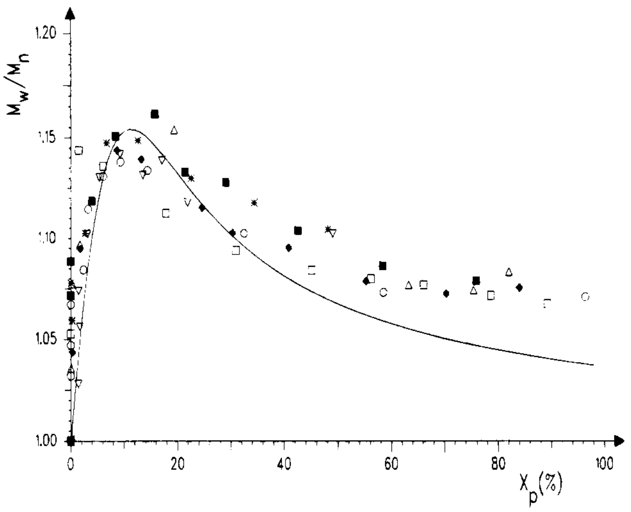


Figure 9. Plot of polydispersity index, M_w/M_n, vs monomer conversion, x_p, for the group transfer polymerization of nBuA with MTS and HgI_2 in toluene for different catalyst concentrations: symbols, cf. Table 1. (—) Calculated with $[M]_0/[I]_0$ = 25.5 according to eq 6.

$$n(1) = e^{-\nu} \quad \text{with} \quad \nu = [M]_0 x_p/[I]_0 \tag{1}$$

Accordingly, for the derivation of the averages of the distribution, summations start at $P = 2$ instead of $P = 1$:

$$M_n = \frac{\sum_{P=2}^{\infty} P\, n(P)}{\sum_{P=2}^{\infty} n(P)} \tag{2}$$

$$M_w = \frac{\sum_{P=2}^{\infty} P^2\, n(P)}{\sum_{P=2}^{\infty} P\, n(P)} \tag{3}$$

Since for the Poisson distribution the summations start from $P = 1$, the mole fraction of the unimer has to be subtracted from the moments of the Poisson distribution:

$$M_n = \frac{\sum_{P=1}^{\infty} P\, n(P) - n(1)}{\sum_{P=1}^{\infty} n(P) - n(1)} = \frac{\nu + 1 - e^{-\nu}}{1 - e^{-\nu}} \tag{4}$$

$$M_w = \frac{\sum_{P=1}^{\infty} P^2\, n(P) - n(1)}{\sum_{P=1}^{\infty} P\, n(P) - n(1)} = \frac{\nu^2 + 3\nu + 1 - e^{-\nu}}{\nu + 1 - e^{-\nu}} \tag{5}$$

Table 5. Effect of Premixing Times of MTS and HgI_2 on the Rate of Polymerization and Induction period: $T = 20$ °C, $[M]_0 = 1.28$ mol/L, $[I]_0 = 0.052$ mol/L, $[C]_0 = 4.1 \times 10^{-3}$ mol/L

run	mixing time, (h)	$10^3 k_{app}$,[a] min^{-1}	t_{ind},[b] min
K42	0.07	12.1	70
K1	0.25	19.5	17
K43	0.25	14.7	18
K44	0.5	14.9	64
K12	1.0	39.0	11
K70/K71	1.0	14.7	18
K75	3.0	16.1	16
K45	3.0	14.4	12
K73	4.0	36.1	8
K72	5.0	60.2	0
K76	10.0	15.0	5
K48	18.0	43.7	7
K74	23.0	60.8	0
K78/K79[c]	0.5	30.4	17
K80[c]	1.0	21.9	9

[a] Final slope of the time–conversion plot. [b] Induction period. [c] $T = 40$ °C.

Table 6. Effect of Premixing Times of Monomer and Catalyst on the Rate of Polymerization and Induction Period at 20 °C, Concentrations Same as in Table 5

run	mixing time, (h)	$10^3 k_{app}$,[a] min^{-1}	t_{ind},[b] min
K8	0.25	19.2	17.4
K38	0.25	13.0	61.6
K39	1.0	15.0	14.8
K47	2.0	14.3	24.0

[a] Final slope of the time–conversion plot. [b] Induction period.

Table 7. Reaction Orders and Apparent Activation Energies, $E_{a,app}$ for the Propagation and Induction in the Group Transfer Polymerization of nBuA with MTS and HgI_2 in Toluene at 20 °C

	propagation (k_{app})	induction ($1/t_{ind}$)
catalyst	0.92 ± 0.05	0.91 ± 0.36
initiator	1.13 ± 0.18	1.01 ± 0.25
monomer	1.52 ± 0.19	≈0
$E_{a,app}$/kJ mol^{-1}	42.5 ± 9.6	29.2 ± 8.8

The polydispersity index is given by

$$D = \frac{M_w}{M_n} = \frac{(\nu^2 + 3\nu + 1 - e^{-\nu})(1 - e^{-\nu})}{(\nu + 1 - e^{-\nu})^2} \qquad (6)$$

The maximum of the plot of D vs x_p is found for $dD/d\nu = 0$, corresponding to $\nu_{max} \approx 2.9$ and $x_p^{max} \approx 2.9[I]_0/[M]_0$. At this point the fraction of residual initiator $n(1) = e^{-\nu_{max}} \approx 0.06$ becomes unimportant. At $\nu \geq 4.6$ (corresponding to $n(1) \leq 0.01$) the modified distribution merges with the original Poisson distribution. It can be seen from Figure 9 that the calculated results agree well with the experimental data.

Since the concentration of catalyst is much smaller than that of the initiator, only a small fraction of chains is active. Consequently, the catalyst has to be exchanged between the polymer chains in order to activate all of the chains. The broader MWD's in GTP with nucleophilic catalysts were attributed to a slow rate of exchange relative to the rate of propagation.[5,32] The narrower MWD's in our case might be explained by the much lower rate of propagation as compared to the MMA/THF system.

Nature of the Induction Periods. The time–conversion plots shown above are characterized by considerable induction periods (t_{ind}), and various possibilities can be discussed in order to understand the nature of these.

- A slow initiation reaction can lead to an induction period. Since the number of polymer chains increases during that period, the plot of P_n vs x_p should be nonlinear. In addition, broader molecular weight distributions are expected. According to Gold's calculation[30] for slow initiation ($k_i \ll k_p$) $M_w/M_n \leq 1.35$. GTP's of MMA[33,34] and *n*-BuA[11] using nucleophilic catalysts (TAS benzoate) are reported to exhibit slow initiation processes and broader distributions. However, as shown above, in our case the plots of P_n vs conversion are linear and the distribution is very narrow. This indicates that the rate of initiation is comparable to propagation ($k_i \approx k_p$) and the induction periods are not due to slow initiation.
- HgI_2 is not very soluble in toluene; especially at higher catalyst concentrations the solutions are turbid. A slow dissolution of catalyst might cause induction periods. Thus, it can be argued that the presence of monomer increases the solubility and changes a colloidal to a molecularly disperse solution. However, an increase of monomer concentration has no significant effect on the induction periods (cf. Table 3). Thus, it can be deduced that the slow dissolution of catalyst is not an essential reason for the induction periods.
- A third possibility is the slow formation of the active species from initiator and catalyst. In some experiments (cf. Table 5) the time of premixing initiator and catalyst solution was varied. It is clearly seen that the apparent rate constants of polymerization increase and the induction periods decrease with increasing premixing time. For premixing times of more than 4 h the induction periods disappear. Table 6 gives the results of experiments where the premixing time of monomer and catalyst (prior to initiator addition) was changed. As can be seen, there is not a significant effect on the apparent rate constant of polymerization and on the induction periods.

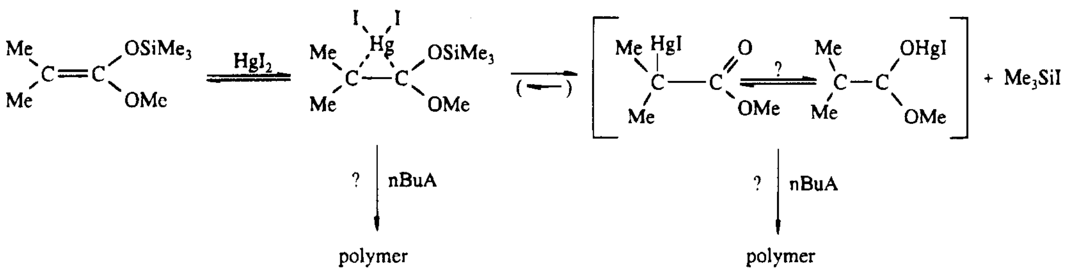
Bilogarithmic plots of t_{ind} vs $[C]_0$, $[I]_0$, and $[M]_0$, respectively, show that the rate of formation of active species which is proportional to $1/t_{ind}$ is of first-order with respect to catalyst and initiator concentrations, but does not significantly depend on $[M]_0$ (cf. Table 7). This corroborates the assumption of a slow formation of active species.

Tentative Reaction Mechanism. Dicker suggested that a complex between silyl ketene acetal and HgI_2 is the intermediate in GTP as well as in *E*/*Z* and O/C-silyl isomerization of silyl ketene acetals.[21] This mechanism agrees with the observed reaction orders of polymerization. However, it does not explain the induction periods.

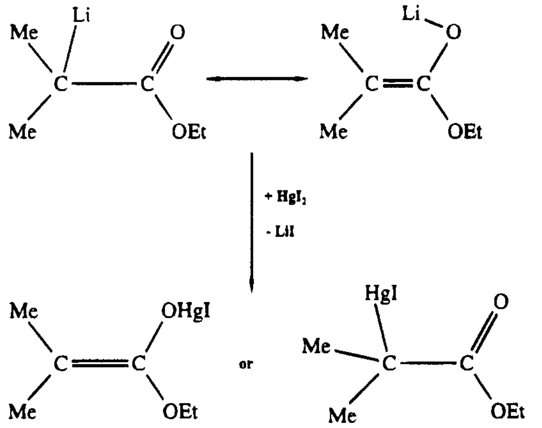
It is possible that MTS reacts with HgI_2 to form a mercuric enolate or the corresponding α-mercuro ester and trimethylsilyl iodide (TMSI) through an adduct (Scheme 5). The MTS–HgI_2 adduct may be too stable to initiate the polymerization. It was reported that mercury predominatly forms C–Hg instead of O–Hg bonds.[35–37]

Evidently, TMSI is not the active species of polymerization. It is open as to whether α-mercuro esters or mercuric enolates are active at all. When a lithium enolate (ethyl α-lithioisobutyrate) is mixed with HgI_2 in toluene at room temperature, a metal exchange reaction should take place to form an α-mercuro ester or a mercuric enolate (cf. Scheme 6). If these are active species, the polymerization should run much faster and

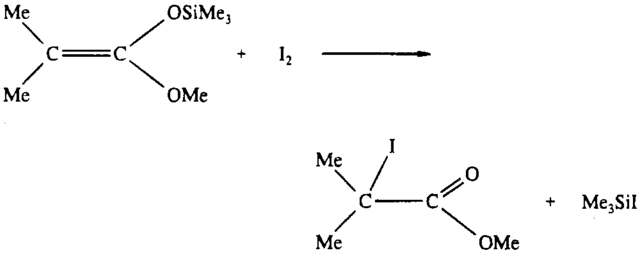
Scheme 5. Formation of TMSI from Initiator and Catalyst



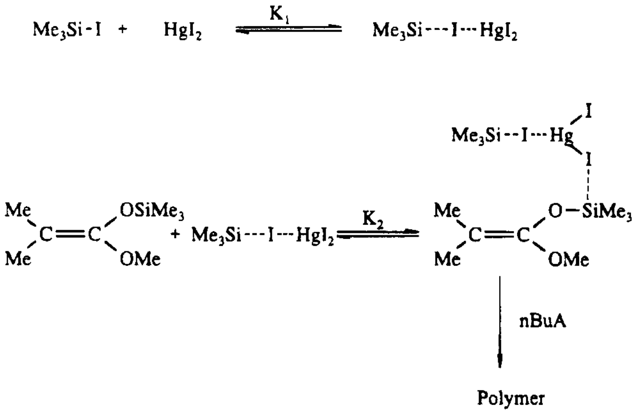
Scheme 6. Metal Exchange Reaction between MTS and HgI$_2$



Scheme 7. Reaction between MTS and Iodine



Scheme 8. Activation through HgI$_2$/TMSI Complex



have good molecular weight control, compared to the reaction mixture from MTS and HgI$_2$ as initiator. However, we obtained only a few oligomers from such experiments. This indicates that the mercuric enolate or α-mercuro ester is not the active species for the polymerization.

On the other hand, when a solution of iodine in toluene (3.0×10^{-4} mol/L) was added to an MTS/toluene solution (5.0×10^{-2} mol/L), the color of iodine disappeared immediately. The mixture was stirred with monomer (1.3 mol/L) overnight, and no monomer conversion was detected. One hour after adding HgI$_2$ (2.0×10^{-3} mol/L) monomer conversion reached 85%, much faster than without addition of iodine. The reason for this effect may be the formation of TMSI from MTS and iodine (cf. Scheme 7). Thus, we assume that TMSI forms a complex with HgI$_2$, which in turn activates MTS to form an active center capable of initiating the polymerization (Scheme 8).

It is noteworthy that TMSI is formed as a byproduct of the reaction in Scheme 5. Thus, the essence of the induction periods is the formation of TMSI. In the second part of this series[26] it will be shown that TMSI indeed plays a very important role in the polymerization process.

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References and Notes

(1) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.
(2) Sogah, D. Y.; Hertler, W. R.; Webster, O. W.; Cohen, G. M. *Macromolecules* **1987**, *20*, 1473.
(3) Sogah, D. Y.; Farnham, W. B. In *Organosilicon and Bioorganosilicon Chemistry*; Sakurai, H., Ed.; Wiley: New York, 1986; p 219.
(4) Farnham, W. B.; Sogah, D. Y. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1986**, *27* (1), 167.
(5) Müller, A. H. E. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 87.
(6) Quirk, R. P.; Bidinger, G. P. *Polym. Bull. (Berlin)* **1989**, *22*, 63.
(7) Quirk, R. P.; Ren, J.; Bidinger, G. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 351.
(8) Quirk, R. P.; Ren, J. *Macromolecules* **1992**, *25*, 6612–6620.
(9) Schubert, W.; Bandermann, F. *Makromol. Chem.* **1989**, *190*, 2161.
(10) Schubert, W.; Sitz, H.-D.; Bandermann, F. *Makromol. Chem.* **1989**, *190*, 2193.
(11) Schmalbrock, U.; Bandermann, F. *Makromol. Chem.* **1993**, *194*, 2543–2551.
(12) Hertler, W. R.; Sogah, D. Y.; Webster, O. W.; Trost, B. M. *Macromolecules* **1984**, *17*, 1415.
(13) Reetz, M. T.; Ostarek, R.; Piejko, K. E.; Arlt, D.; Bömer, B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1108.
(14) Hirai, H.; Komiyama, M. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2701.
(15) Liaw, D.-J.; Chung, K.-C. *Makromol. Chem.* **1983**, *184*, 29–40.
(16) Liaw, D.-J.; Chung, K.-C. *J. Chin. Inst. Eng.* **1982**, *5*, 75.
(17) Bamford, C. H.: *Molecular Behaviour and the Development of Polymeric Materials*; Chapman & Hall: London, 1975.
(18) Dicker, I. B. U.S. Pat. 4,732,955, 1988 (to E. I. Du Pont de Nemours & Co.); *Chem. Abstr.* **1988**, *109*, 038426a.
(19) Dicker, I. B. U.S. 4943648, 1990 (to E. I. du Pont de Nemours and Co.); *Chem. Abstr.* **1990**, *113*, 212834b.
(20) Dicker, I. B. WO 8909236, 1989 (to E. I. du Pont de Nemours and Co.); *Chem. Abstr.* **1989**, *112*, 140016r.
(21) Dicker, I. B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (2), 114.
(22) Brittain, W. J.; Aquino, E. C.; Dicker, I. B.; Brunelle, D. J. *Makromol. Chem.* **1993**, *194*, 1249.
(23) Brittain, W. J.; Dicker, I. B. *Polym. Int.* **1993**, *30*, 101.

(24) Litvinova, O. V.; Baukov, Y. I.; Lutsenko, I. F. *Dokl. Akad. Nauk SSSR* **1967**, *173*, 578.
(25) Baukov, Y. I.; Burlachenko, G. S.; Lutsenko, I. F. *Dokl. Akad. Nauk SSSR* **1964**, *157*, 119.
(26) Zhuang, R.; Müller, A. H. E. *Macromolecules* **1995**, *28*, 8043.
(27) Janata, M.; Lochmann, L.; Müller, A. H. E. *Makromol. Chem.* **1990**, *191*, 2253.
(28) Brittain, W. J.; Dicker, I. B. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 373.
(29) Brittain, W. J.; Dicker, I. B. *Macromolecules* **1989**, *22*, 1054.
(30) Gold, L. J. *Chem. Phys.* **1958**, *28*, 91.
(31) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62*, 1561.
(32) Müller, A. H. E.; Zhuang, R.; Yan, D. Y.; Litvinenko, G. *Macromolecules* **1995**, *28*, 4326.
(33) Mai, P. M.; Gores, F. G.; Müller, A. H. E. *Makromol. Chem.*, manuscript in preparation.
(34) Doherty, M. A.; Gores, F.; Mai, P. M.; Müller, A. H. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1988**, *29* (2), 73.
(35) Meyer, R.; Maroni, L. G. *J. Organomet. Chem.* **1977**, *129*, c7.
(36) Meyer, R.; Maroni, L. G. *J. Organomet. Chem.* **1980**, *188*, 11.
(37) House, H. O.; Auerbach, R. A.; Gall, M.; Peet, N. P. *J. Org. Chem.* **1973**, *38*, 514.

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