Kinetic Study on the Group Transfer Polymerization of 1-Butadienyloxytrimethylsilane

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ABSTRACT: Kinetics for homogeneous aldol condensation-type of group transfer polymerization (aldol-GTP) of 1-butadienyloxytrimethylsilane (BdTMS) were investigated at $-78°C$ in toluene, employing benzaldehyde as an initiator and a solution of $ZnBr_2$ in diethyl ether (Et_2O) as a catalyst. The polymerization rate (R_p) was the first order function of concentration of the catalyst as well as initiator. The kinetic order with respect to the concentration of BdTMS depended on the molar ratio of Et_2O and $ZnBr_2$. The influence of Et_2O on R_p could be explained in terms of interaction between Et_2O and the carbocationic propagating center produced by coordination of a formyl group with $ZnBr_2$. The equilibrium constant for complexation between the formyl groups and $ZnBr_2$ was determined by ^{13}C NMR. The concentration of the activated formyl groups is considerably low compared with the total concentration of the formyl groups. On the assumption that the concentration of the activated formyl group is very low and constant, the rate equation for the homogeneous aldol-GTP was derived and the most probable kinetic scheme was formulated based on the experimental results.
 KEY WORDS Group Transfer Polymerization / Aldol Condensation / 1-Butadienyloxytrimethylsilane / Kinetics / Equilibrium Constant /

Aldol condensation-type of group transfer polymerization (aldol-GTP) of organosilyl vinyl ethers was disclosed by Webster et al. in 1986.[1] The aldol-GTP can be usually initiated by aromatic aldehyde with Lewis acid and its propagation process is accompanied by the migration of the organosilyl group from a monomer onto formyl oxygen in a polymer end and the building up of a new formyl group in the new polymer end. Although the aldol-GTP has a living nature, well-controlled molecular weight has not been attained yet in comparison with other living polymerization processes.

We have been interested in aldol-GTP of 1-Butadienyloxytrimethylsilane (BdTMS)[2-4] shown in Scheme 1. Various aldehydes[3] and catalysts[2,4] were examined with a view to improving the uniformity of the molecular weight of the polymer. It was confirmed that the aldol-GTP proceeded via cationization of formyl carbon at the propagating end. In our previous paper,[4] kinetics were discussed on the assumption that the aldol-GTP of BdTMS would proceed according to an ideal living process under given conditions. The discussion
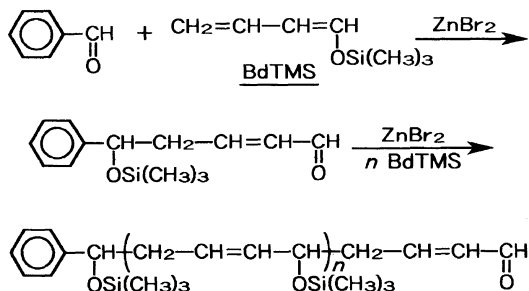
Scheme 1.

was useful enough to estimate roughly the ability of the catalysts. However, the above assumption is not always applicable, such as a case in which solid zinc halide catalyst is used at 35°C. Also the rather low ratio of [BdTMS]$_0$/[initiator]$_0$ (≈ 20) may cause variation in [BdTMS] even at the initial stage of polymerization. Our recent investigation[5] suggested that undesirable side reactions, *e.g.*, Diels–Alder cyclization etc., happen under the above conditions. Fortunately, such side reactions could be repressed when aldol-GTP was carried out in a homogeneous system including a small amount of diethyl ether (Et$_2$O) at -78°C. It became possible to obtain the polymer having high molecular weight and smaller distribution index.

It is now required to formulate a kinetic scheme for the homogeneous aldol-GTP. This paper deals with the kinetics of aldol-GTP of BdTMS in a homogeneous system at a low temperature.

EXPERIMENTAL

Materials

1-Butadienyloxytrimethylsilane (BdTMS) was prepared according to Danishefsky's procedure,[6] of which details were given also in our previous papers.[2-4] *E*-configurational BdTMS, free from *Z*-isomer, could be isolated by fractional distillation and freshly redistilled on calcium hydride under reduced pressure before use. ZnBr$_2$ was sublimed *in vacuo* at appropriate temperature and used as solution in Et$_2$O distilled over sodium. Benzaldehyde (BAld) was fractionally distilled immediately before use. Toluene was purified by the conventional method and dried over sodium, distilled just prior to each polymerization. Toluene-d_8 and methanol-d were commercially available in 99.9% and 99% isotopic purity, respectively.

Procedures of Aldol-GTP

In a dry glass tube equipped with a three-way stopcock, BdTMS, BAld, and toluene were mixed under nitrogen atmosphere. The mixture was cooled down to -78°C. Polymerization was initiated by adding a solution of ZnBr$_2$ in Et$_2$O and toluene *via* a syringe. After an adequate period, a mixture of methanol and triethylamine was added. The reaction mixture was washed with 5% aqueous sodium hydrogencarbonate solution and with water. The organic layer was dried over magnesium sulfate and evaporated *in vacuo* to give a product polymer. Conversion of BdTMS was determined by gravimetry of the product polymer.

Equilibrium Constant (K) for Complex Formation of Aldehyde with ZnBr$_2$

The equilibrium constant for complex formation of aldehyde with ZnBr$_2$ was determined by ^{13}C NMR. ^{13}C NMR spectra were recorded with a Varian XL-200 spectrometer. An NMR tube was charged with aldehyde, ZnBr$_2$ (as a solution in Et$_2$O), and toluene-d_8 under nitrogen atmosphere, and frozen, sealed, and subjected to NMR measurement at -78°C.

Determination of Basicity of BdTMS and Aldehydes

The basicity (pK_b) of BdTMS and aldehydes was measured by IR according to Gordy's method.[7] A 0.1 mol l^{-1} solution of methanol-d in BdTMS or aldehydes was prepared under nitrogen atmosphere at room temperature. IR spectra were recorded with a JASCO DS-701G.

RESULTS AND DISCUSSION

A possible kinetic scheme for the aldol-GTP of BdTMS is shown in Scheme 2. Complexation of an initiator with ZnBr$_2$ occurs first, followed by cationization of formyl carbon. Nucleophilic addition of BdTMS to the cationic site should be accompanied by smooth transferring of a trimethylsilyl group from the monomer to formyl oxygen. Thus a new formyl group can

Table I. GTP of BdTMS with *p*-anisaldehyde (AAld) and $ZnBr_2$

| Run	$[BdTMS]_0$ mol l^{-1}	$\dfrac{[BdTMS]_0}{[AAld]_0}$	$\dfrac{[ZnBr_2]_0}{[AAld]_0}$	Solvent	Temp °C	Time h	Conv. %	M_n Calcd[a]	M_n Obsd[b]	M_w/M_n
Heterogeneous (solid $ZnBr_2$)
1	3.70	300	3	Benzene	30	23	88	37700	9850	3.10
Homogeneous ($[Et_2O]_0/[ZnBr_2]_0 = 7$)
2	1.04	300	3	Toluene	30	1	75	32100	5830	1.86
3	1.08	300	3	Toluene	−78	12	90	38500	31500	1.24

[a] $[BdTMS]_0/[AAld]_0 \times$ Conv./100 $\times$ (mol wt of BdTMS) + (mol wt of AAld).
[b] Determined by GPC using the extended chain length model (Q factor).

Initiation:
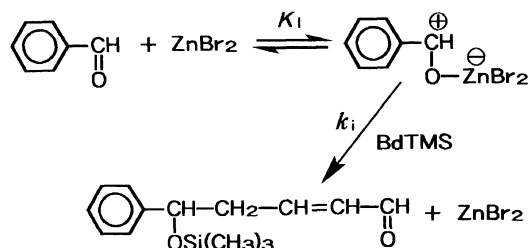
Propagation:
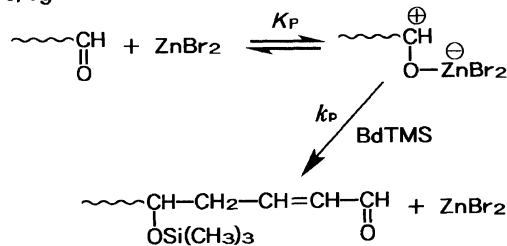
Scheme 2.

be generated in an adduct and a polymer is built up by repeating the same process.

The aldol-GTP of BdTMS at a high temperature was often accompanied by some side reactions leading to termination or at least retardation.[5] Especially, when most of the monomer was consumed, some undesirable reactions of the formyl group took place at the polymer end. However, these side reactions could be repressed when aldol-GTP was carried out in a homogeneous system including a small amount of Et_2O at −78°C.[5] Table I shows the results of heterogeneous and homogeneous aldol-GTP of BdTMS. Well-controlled molecular weight was achieved by homogeneous aldol-GTP at −78°C. The present kinetic study of the aldol-GTP of BdTMS was carried out under such preferable conditions.

Dependence of Polymerization Rate (R_p) on Catalyst Concentration

The following kinetic experiments were done to determine the dependence of R_p on catalyst concentration. While keeping the initial concentrations of the monomer ($[BdTMS]_0$) and initiator ($[BAld]_0$) constant, the initial concentration of the catalyst ($[ZnBr_2]_0$) was varied from 0.40×10^{-2} to 6.48×10^{-2} mol l^{-1}. Figure 1 shows time-conversion curves in various $[ZnBr_2]_0$. $[Et_2O]_0/[ZnBr_2]_0$ ratios are 5, 7, and 10 in Figures 1a, 1b, and 1c, respectively. The $[Et_2O]_0/[ZnBr_2]_0$ ratio of 5 was close to the lower limit to hold the polymerization solution homogeneous. R_p could be calculated from the initial slopes of the curves. These results are summarized in Table II. As the $[Et_2O]_0/[ZnBr_2]_0$ ratio became larger, R_p decreased at the same $[ZnBr_2]_0$. Figure 2 shows a bilogarithmic plot of R_p vs. $[ZnBr_2]_0$. When the $[Et_2O]_0/[ZnBr_2]_0$ ratio was 5, the plot gave a linear relationship. From the slope of the plot, R_p is the first order with respect to $[ZnBr_2]_0$. However, when the $[Et_2O]_0/[ZnBr_2]_0$ ratio was 7 or 10, the plot gave curved lines. R_p is likely of the first order with respect to $[ZnBr_2]_0$ in the region of lower
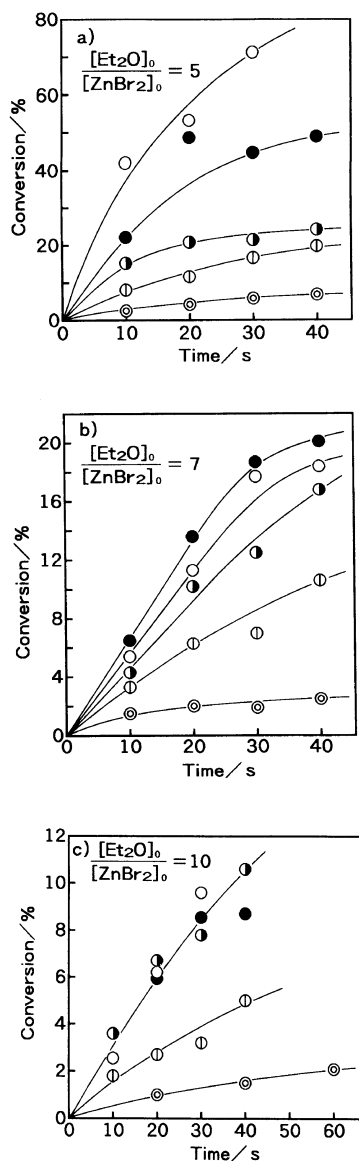
Figure 1. Effects of $[ZnBr_2]_0$ on aldol-GTP of BdTMS in toluene at $-78°C$: $[BdTMS]_0$, $1.140\,mol\,l^{-1}$; $[BAld]_0$, $0.81 \times 10^{-2}\,mol\,l^{-1}$; $[ZnBr_2]_0$, ○, $6.48 \times 10^{-2}\,mol\,l^{-1}$; ●, $3.24 \times 10^{-2}\,mol\,l^{-1}$; ◐, $1.62 \times 10^{-2}\,mol\,l^{-1}$; ◍, $0.81 \times 10^{-2}\,mol\,l^{-1}$; ◎, $0.40 \times 10^{-2}\,mol\,l^{-1}$.

Table II. GTP of BdTMS at various $[ZnBr_2]_0$ and $[Et_2O]_0$ in toluene at $-78°C$[a]

Run	$\dfrac{[Et_2O]_0}{[ZnBr_2]_0}$	$[ZnBr_2]_0$ $mol\,l^{-1}$	R_p $mol\,l^{-1}\,s^{-1}$
1	5	0.40×10^{-2}	0.26×10^{-2}
2		0.81×10^{-2}	0.85×10^{-2}
3		1.62×10^{-2}	1.87×10^{-2}
4		3.24×10^{-2}	2.51×10^{-2}
5		6.48×10^{-2}	4.79×10^{-2}
6	7	0.40×10^{-2}	1.68×10^{-3}
7		0.81×10^{-2}	3.69×10^{-3}
8		1.62×10^{-2}	5.51×10^{-3}
9		3.24×10^{-2}	7.60×10^{-3}
10		6.48×10^{-2}	6.73×10^{-3}
11	10	0.40×10^{-2}	0.57×10^{-3}
12		0.81×10^{-2}	1.39×10^{-3}
13		1.62×10^{-2}	3.55×10^{-3}
14		3.24×10^{-2}	3.29×10^{-3}
15		6.48×10^{-2}	3.55×10^{-3}

[a] $[BdTNS]_0$, $1.140\,mol\,l^{-1}$; $[BAld]_0$, $0.81 \times 10^{-2}\,mol\,l^{-1}$.
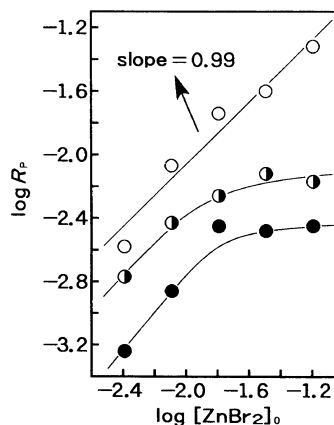
Figure 2. Bilogarithmic plot of R_p vs. $[ZnBr_2]_0$: $[Et_2O]_0/[ZnBr_2]_0$; ○, 5; ◐, 7; ●, 10.

$[ZnBr_2]_0$. At higher $[ZnBr_2]_0$, increments of R_p became smaller with increasing $[ZnBr_2]_0$.

Here, it is necessary for us to pay attention to the fact that $ZnBr_2$ was supplied as solution in Et_2O. Increase of $[ZnBr_2]_0$ means that

$[Et_2O]_0$ increased in the polymerization mixture. The cationic site induced through the complexation of formyl group with $ZnBr_2$ may be solvated by excess Et_2O, resulting in restriction of the nucleophilic addition of BdTMS. This depression effect can be demonstrated by Figure 2. In additional experiments, R_p increased remarkably as $[ZnBr_2]_0$ increased at constant $[Et_2O]_0$, and no polymerization oc-

Scheme 3.

Figure 3. Effects of $[BAld]_0$ on aldol-GTP of BdTMS in toluene at $-78°C$: $[BdTMS]_0$, $1.140 \, mol \, l^{-1}$; $[ZnBr_2]_0$, $3.26 \times 10^{-2} \, mol \, l^{-1}$; $[Et_2O]_0/[ZnBr_2]_0$, 10; $[BAld]_0$, $\bigcirc$, $3.25 \times 10^{-2} \, mol \, l^{-1}$; $\bullet$, $1.62 \times 10^{-2} \, mol \, l^{-1}$; $\oplus$, $0.81 \times 10^{-2} \, mol \, l^{-1}$; $\ominus$, $0.40 \times 10^{-2} \, mol \, l^{-1}$.

Scheme 4.

curred in Et_2O. These results suggest that excess Et_2O beyond that required for solvation of $ZnBr_2$ may interfere with the reactivity of formyl cations on the propagating polymer end, as shown in Scheme 3.

Consequently, the results of Figure 2 could be explained as follows: Retardation of R_p in the higher $[ZnBr_2]_0$ must be caused by excess Et_2O beyond that required for solvation of $ZnBr_2$. In the lower $[ZnBr_2]_0$ region, such effect of Et_2O must be negligible and the order of polymerization with respect to $[ZnBr_2]_0$ could be noted as the first order.

Dependence of R_p on Initiator Concentration

To determine the kinetic order of the initiator in homogeneous aldol-GTP, $[BAld]_0$ was varied from 0.40×10^{-2} to $3.25 \times 10^{-2} \, mol \, l^{-1}$ under constant $[BdTMS]_0$ and $[ZnBr_2]_0$. Figure 3 shows time-conversion curves at various $[BAld]_0$. All curves were so close with each other that R_p was apparently independent of $[BAld]_0$. However, increase of R_p must be expected by increasing $[BAld]_0$ according to the mechanism in Scheme 2, because $[BAld]_0$ was assumed to be equal to the total concentration of the formyl group. Such discrepancy might be explained by considering the basicity of the formyl group. Although the concentration of the activated formyl group increased with increasing $[BAld]_0$, the concentration of free formyl group also increased. It is worth while remembering that the only formyl group complexed with $ZnBr_2$ should contribute to propagation. According to calculation based on an equilibrium constant, the absolute amount of activated formyl group is rather
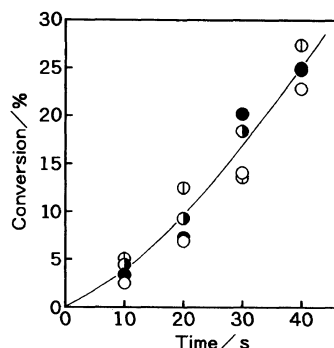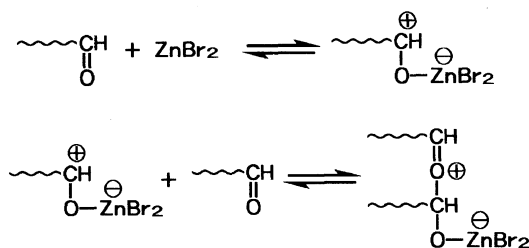
less than that of inactivated one under given conditions. Coordination between the free formyl group and the active cationic site must lead to depression of polymerization. This is depicted in Scheme 4.

An alternative experiment was done to confirm the above idea. $[BAld]_0$ was varied at constant $[BAld]_0/[ZnBr_2]_0$ ($=1/2$). The results are shown in Figure 4 and summarized in Table III. Figure 5 shows a bilogarithmic plot of R_p *vs.* $[BAld]_0$. The slope was 1.19. In this experiment, R_p may depend not only on $[BAld]_0$ but $[ZnBr_2]_0$, because both $[BAld]_0$ and $[ZnBr_2]_0$ were changed. Judging from the results in Figure 1c ($[Et_2O]_0/[ZnBr_2]_0 = 10$), however, R_p was not so susceptible to $[ZnBr_2]_0$ in the corresponding region. Thus, increased R_p in Figure 5 would be attributed mainly to increased $[BAld]_0$, and the kinetic order may be concluded to be unity with respect to
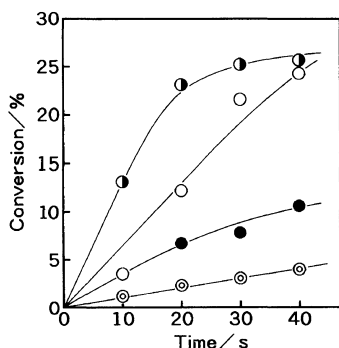
Figure 4. Aldol-GTP of BdTMS in toluene at $-78°C$: $[BdTMS]_0$, $1.140\,mol\,l^{-1}$; $[BAld]_0/[ZnBr_2]_0 = 1/2$; $[Et_2O]_0/[ZnBr_2]_0$, 10; $[BAld]_0$, ◐, $3.24 \times 10^{-2}\,mol\,l^{-1}$; ○, $1.62 \times 10^{-2}\,mol\,l^{-1}$; ●, $0.81 \times 10^{-2}\,mol\,l^{-1}$; ◉, $0.40 \times 10^{-2}\,mol\,l^{-1}$.

Table III. GTP of BdTMS at various $[BAld]_0$ in toluene at $-78°C^a$

Run	$[BAld]_0$ $mol\,l^{-1}$	$[ZnBr_2]_0$ $mol\,l^{-1}$	R_p $mol\,l^{-1}\,s^{-1}$
1	0.40×10^{-2}	0.81×10^{-2}	1.18×10^{-3}
2	0.81×10^{-2}	1.62×10^{-2}	3.55×10^{-3}
3	1.62×10^{-2}	3.26×10^{-2}	7.98×10^{-3}
4	3.24×10^{-2}	6.51×10^{-2}	14.3×10^{-3}

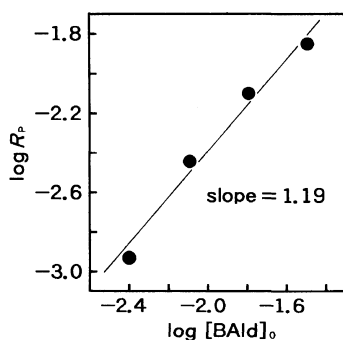^{a} $[BdTMS]_0$, $1.140\,mol\,l^{-1}$; $[BAld]_0/[ZnBr_2]_0 = 1/2$; $[Et_2O]_0/[ZnBr_2]_0 = 10$.

Figure 5. Bilogarithmic plot of R_p vs. $[BAld]_0$ at $[BAld]_0/[ZnBr_2]_0 = 1/2$.

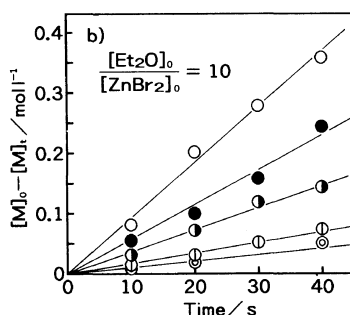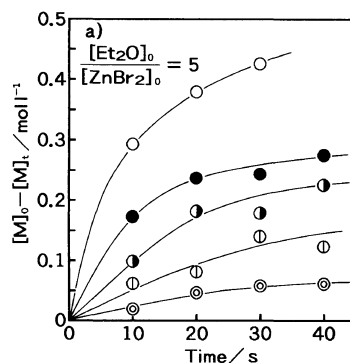$[BAld]_0$ (strictly speaking, with respect to the concentration of the true activated formyl group).

Figure 6. Effects of $[BdTMS]_0$ on aldol-GTP of BdTMS in toluene at $-78°C$: $[BAld]_0$, $0.81 \times 10^{-2}\,mol\,l^{-1}$; $[ZnBr_2]_0$, $1.62 \times 10^{-2}\,mol\,l^{-1}$; $[BdTMS]_0$, ○, $1.629\,mol\,l^{-1}$; ●, $1.140\,mol\,l^{-1}$; ◐, $0.814\,mol\,l^{-1}$; ◑, $0.570\,mol\,l^{-1}$; ◉, $0.407\,mol\,l^{-1}$.

Dependence of R_p on Monomer Concentration

With both $[BAld]_0$ and $[ZnBr_2]_0$ constant, $[BdTMS]_0$ was varied from 0.407 to 1.629 mol l^{-1}. Figure 6 shows time-conversion curves under two conditions. $[Et_2O]_0/[ZnBr_2]_0$ ratios are 5 and 10 in Figures 6a and 6b, respectively. The results are summarized in Table IV. Figure 7 shows a bilogarithmic plot of R_p vs. $[BdTMS]_0$. The slopes were calculated as 2.09 ($[Et_2O]_0/[ZnBr_2]_0 = 5$) and 1.57 ($[Et_2O]_0/[ZnBr_2]_0 = 10$). The kinetic order with respect to $[BdTMS]_0$ depended on the molar ratio of $[Et_2O]_0/[ZnBr_2]_0$.

Basicity of BdTMS and Formyl Group

From the above experimental results, it seems that the cationic site is coordinated with excess Et_2O or the free formyl group. Here, it

Table IV. GTP of BdTMS at various $[BdTMS]_0$ in toluene at $-78°C^a$

Run	$\dfrac{[Et_2O]_0}{[ZnBr_2]_0}$	$\dfrac{[BdTMS]_0}{mol\,l^{-1}}$	$\dfrac{R_p}{mol\,l^{-1}\,s^{-1}}$
1	5	0.407	0.25×10^{-2}
2		0.570	0.52×10^{-2}
3		0.814	1.12×10^{-2}
4		1.140	1.87×10^{-2}
5		1.629	4.82×10^{-2}
6	10	0.407	1.08×10^{-3}
7		0.570	1.76×10^{-3}
8		0.814	3.70×10^{-3}
9		1.140	5.84×10^{-3}
10		1.629	9.14×10^{-3}

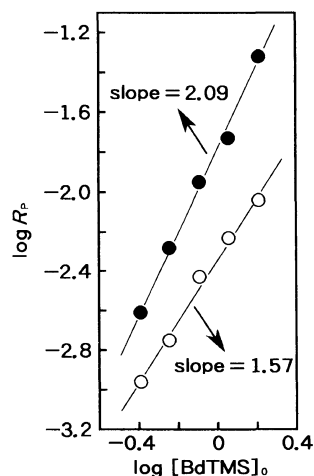^{a} $[ZnBr_2]_0$, $1.62 \times 10^{-2}\,mol\,l^{-1}$; $[BAld]_0$, 0.81×10^{-2} $mol\,l^{-1}$.

Figure 7. Bilogarithmic plot of R_p vs. $[BdTMS]_0$: $[Et_2O]_0/[ZnBr_2]_0$, ●, 5; ○, 10.

should be considered that BdTMS is an ether which may interact with the active cationic site. It is necessary to compare with the basicity of BdTMS, a formyl group, and Et_2O. The electron donating ability of BdTMS and a formyl group was measured by Gordy's method[7] in which frequency due to OD stretching vibration of metanol-d in each donor was measured by IR. Shifts of OD frequency in donors from that in benzene (reference) and pK_b are listed in Table V. Crotonaldehyde was used as the

Table V. OD vibrational frequency and pK_b

Comound	ν_{OD}		$\Delta\mu$	pK_b^a
	cm^{-1}	μ		
Benzene	2667	3.750	(Reference)	
Et_2O	2591	3.860	0.110	5.71
Crotonaldehyde	2601	3.838	0.088	7.20
Benzaldehyde	2622	3.819	0.069	8.83
BdTMS	2637	3.792	0.042	10.32

^{a} Calculated by Gordy's equation[7]: $\Delta\mu = 0.0147 \log K_b + 0.194$.

model of the propagating polymer end. pK_b of BdTMS was larger than that of Et_2O. Consequently, the effect of BdTMS as ethers on the polymerization is negligible. Although pK_b of BAld or crotonaldehyde was also larger than that of Et_2O, the basicity of the aldehyde was higher than that of BdTMS. As already described in Scheme 4, the free formyl group depresses the polymerization rate.

Complexation between Formyl Group and $ZnBr_2$

Equilibrium constant (K) of complexation between the formyl group in the polymer end or initiator and $ZnBr_2$ was determined by ^{13}C NMR. Hanna and Ashbaugh showed that NMR spectroscopy was useful for the estimation of equilibrium constants of some charge transfer complexes.[8] The equilibrium between aldehyde and $ZnBr_2$ is expressed as

$$\sim CHO + ZnBr_2 \xrightleftharpoons{K} \sim CHO \rightarrow ZnBr_2 \quad (1)$$
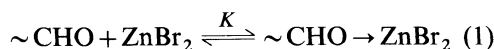
The chemical shift observed for the formyl group (δ_{obsd}) is a weighted average of the shift due to the free formyl group (δ_0) and that due to the complex (δ_{comp}). The relationship of K and the chemical shifts is expressed as

$$\frac{1}{K} = [ZnBr_2]_0 \left(\frac{\Delta_{comp}}{\Delta_{obsd}} - 1 \right)$$
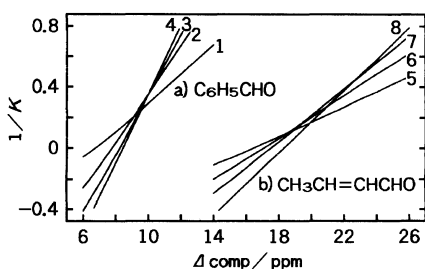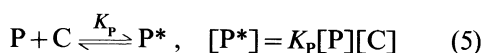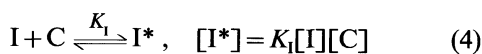$$- [\sim CHO]_0 \left(1 - \frac{\Delta_{obsd}}{\Delta_{comp}} \right) \quad (2)$$

Figure 8. Evaluation of K for the complex of aldehyde and $ZnBr_2$ in toluene-d_8 from eq 2: $[ZnBr_2]_0$, 9.8×10^{-2} mol l^{-1}, temperature, $-78°C$; (a) $[BAld]_0$, no. 1, 0.69 mol l^{-1}; no. 2, 1.28 mol l^{-1}; no. 3, 1.67 mol l^{-1}; no. 4, 1.97 mol l^{-1}; (b) $[crotonaldehyde]_0$, no. 5, 0.85 mol l^{-1}; no. 6, 1.22 mol l^{-1}; no. 7, 1.58 mol l^{-1}; no. 8, 1.95 mol l^{-1}.

$$\Delta_{obsd} = \delta_{obds} - \delta_0, \quad \Delta_{comp} = \delta_{comp} - \delta_0 \quad (3)$$

According to eq 2, the relationship between Δ_{comp} and K^{-1} was directly determined under several conditions. The formyl carbon of aldehyde with $ZnBr_2$ gave only one resonance peak, indicating that complexation of aldehyde with $ZnBr_2$ was in rapid equilibrium within an NMR time scale. Figure 8 shows the curves of K^{-1} vs. Δ_{comp} at each concentration of aldehyde. The intersection of the curves gives K and Δ_{comp}. Crotonaldehyde is the model of the polymer end. Thus K for the complexation of $ZnBr_2$ with the initiator and polymer end were ca. 3.8 and 5.0 l mol^{-1}, and Δ_{comp} were 9.4 and 20.0 ppm, respectively. It seems that these constants are considerably small in contrast to those of MMA with $ZnCl_2$.[9] Competitive solvation onto $ZnBr_2$ by Et_2O would make K smaller and therefore depress the amount of responsible species for aldol-GTP.

The equilibrium between $ZnBr_2$ and the formyl group of BAld or propagating polymer end is expressed as

$$I + C \underset{K_I}{\rightleftharpoons} I^*, \quad [I^*] = K_I[I][C] \quad (4)$$

$$P + C \underset{K_P}{\rightleftharpoons} P^*, \quad [P^*] = K_P[P][C] \quad (5)$$

where I, C, and P mean an initiator, catalyst, and polymer, respectively. I* and P* are the

complexes responsible for the propagation. Since the experimental data allowed equilibrium constant K_I to be nearly to K_P, eq 6 was obtained.

$$[I^*] + [P^*] = K_P([I] + [P]) \quad (6)$$

Following mass balances hold concerning the initiator and catalyst:

$$[I]_0 = [I] + [I^*] + [P] + [P^*] \quad (7)$$

$$[C]_0 = [C] + [I^*] + [P^*] \quad (8)$$

From eq 6 and 7,

$$[I^*] + [P^*] = \frac{K_P[C][I]_0}{K_P[C] + 1} \quad (9)$$

and then eq 10 was derived from eq 8 and 9.

$$[C]_0 = [C] + \frac{K_P[C][I]_0}{K_P[C] + 1} \quad (10)$$

When $K_P[C]$ is much smaller than 1,

$$[C] = \frac{[C]_0}{K_P[I]_0 + 1} \quad (11)$$

[C] calculated from eq 11 as $K_P = 5.0$ was close to that calculated from eq 10. Substitution of eq 11 into eq 9 results in eq 12.

$$[I^*] + [P^*] = \frac{K_P[C]_0[I]_0}{K_P[C]_0 + K_P[I]_0 + 1} \quad (12)$$

Thus the total concentration of the activated formyl group can be evaluated by eq 12. At constant $[BAld]_0$ (0.81×10^{-2} mol l^{-1}), $([I^*] + [P^*])$ was 0.15×10^{-3} to 1.92×10^{-3} mol l^{-1} corresponding to variation of $[ZnBr_2]_0$ from 0.40×10^{-2} to 6.48×10^{-2} mol l^{-1}. At constant $[ZnBr_2]_0$ (3.26×10^{-2} mol l^{-1}), $([I^*] + [P^*])$ was from 0.55×10^{-3} to 4.00×10^{-3} mol l^{-1} corresponding to variation of $[BAld]_0$ from 0.40×10^{-2} to 3.25×10^{-2} mol l^{-1}. These calculated $([I^*] + [P^*])$ are the maximum concentrations of the activated formyl group in the polymerization solution.

Possible Kinetic Mechanism for Homogeneous Aldol-GTP of BdTMS

On the basis of stereochemical studies on aldol-GTP,[10] we propose a concerted mechanism for propagation. Two processes, (1) transfer of the trimethylsilyl group from monomer to the formyl oxygen on the polymer end and (2) nucleophilic addition resulting in a new carbon–carbon bond, should occur *via* the bicyclic transition in Scheme 5.

Taking account of the kinetics in this work and stereochemical data, the most possible kinetic scheme of homogeneous aldol-GTP of BdTMS is developed as follows.

i) Activation of initiator by $ZnBr_2$:

$$I + C \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I^* \qquad (13)$$

ii) Initiation:

$$I^* + M \xrightarrow{k_i} P^* \qquad (14)$$

iii) Activation of polymer end by $ZnBr_2$:

$$P + C \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} P^* \qquad (15)$$

iv) Propagation:

$$P^* + M \xrightarrow{k_P} P^* \qquad (16)$$
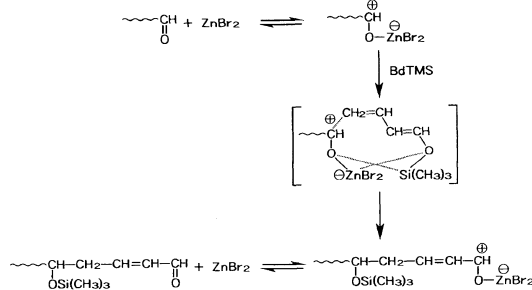
where M is a monomer. Each k represents a rate constant of each elemental reaction. Stereochemical requirements concerned only process iv.

In this kinetic experiment, R_P was observed

Scheme 5.

at the initial stage of the polymerization. The equilibrium for the complexation of formyl group with $ZnBr_2$ may not be reached in a short period of time from 0. In this case $[I^*]$ or $[P^*]$ is lower than $([I^*] + [P^*])$ estimated by eq 12. $[I^*]$ can be found by eq 18 derived on the assumption that $[I^*]$ is constant.

$$\frac{d[I^*]}{dt} = k_1[I][C] - k_{-1}[I^*]$$
$$- k_i[I^*][M] = 0 \qquad (17)$$

$$\therefore \quad [I^*] = \frac{k_1[I][C]}{k_{-1} + k_i[M]} \qquad (18)$$

Similarly, $[P^*]$ can be obtained by eq 20.

$$\frac{d[P^*]}{dt} = k_i[I^*][M] + k_2[P][C]$$
$$- k_{-2}[P^*] = 0 \qquad (19)$$

$$\therefore \quad [P^*] = \frac{1}{k_{-2}}(k_i[I^*][M] + k_2[P][C]) \qquad (20)$$

The mass balance of $[I]_0$ is again given in eq 7,

$$[I]_0 = [I] + [I^*] + [P] + [P^*] \qquad (7)$$

Considering $[I] \gg [I^*]$ and $[P] \gg [P^*]$,

$$[I]_0 = [I] + [P] \qquad (21)$$

Consequently, $[P^*]$ can be approximated as eq 22 by substituting eq 18 and 21 into 20.

$$[P^*] = \frac{1}{k_{-2}} \left(\frac{k_i k_1[I][C]}{k_{-1} + k_i[M]}[M] \right.$$
$$\left. + k_2([I]_0 - [I])[C] \right) \qquad (22)$$

The rate of monomer consumption is shown by eq 23.

$$-\frac{d[M]}{dt} = k_i[I^*][M] + k_P[P^*][M]$$

$$= \frac{k_i k_1[I][C]}{k_{-1} + k_i[M]}[M]$$

$$+ \frac{k_P}{k_{-2}} \left(\frac{k_i k_1[I][C]}{k_{-1} + k_i[M]} \right)[M]$$

$$+k_2([I]_0-[I])[C]\Big)[M] \quad (23)$$

Since the concentration of complexed $ZnBr_2$ was also very low, [C] could be replaced by $[C]_0$. In addition, at the initial stage of this polymerization condition, [I] and [M] may be replaced by $[I]_0$ and $[M]_0$, respectively. Therefore, eq 23 can be transformed to eq 24.

$$-\frac{d[M]}{dt}=\frac{k_i k_1 [I]_0 [C]_0}{k_{-1}+k_i[M]_0}[M]_0$$
$$+\frac{k_P k_i k_1 [I]_0 [C]_0}{k_{-2}(k_{-1}+k_i[M]_0)}[M]_0^2 \quad (24)$$

Based on eq 24, the rate of homogeneous aldol-GTP of BdTMS may be the first or second order function depending upon two sets of rate constants, k_i and k_{-1} as well as k_P and k_{-2}. Two limited cases are:

(Case A) When $k_{-1} \ll k_i[M]_0$, eq 24 is simplified to

$$-\frac{d[M]}{dt}=k_1[I]_0[C]_0\left(1+\frac{k_P}{k_{-2}}[M]_0\right) \quad (25)$$

In this case, if transition between the monomer and activated polymer end readily occurs while deactivation of polymer end is relatively slow, namely very large k_P/k_{-2}, R_P should be first order with respect to $[BAld]_0$, $[ZnBr_2]_0$, and also $[BdTMS]_0$. However, this does not seem to be the case for the experimental results in this study.

(Case B) On the contrary, $k_{-1} \gg k_i[M]_0$ leads to equation 26. This condition means that the initiation is not so rapid.

$$-\frac{d[M]}{dt}=\frac{k_i k_1}{k_{-1}}[I]_0[C]_0\left([M]_0+\frac{k_P}{k_{-2}}[M]_0^2\right) \quad (26)$$

In this case, R_P should still be first order with respect to $[BAld]_0$ and $[ZnBr_2]_0$ in accord with eq 26. So long as the ratio of k_P/k_{-2} is very large, R_P should be mainly controlled by the last term and approximated as the second order function with respect to $[BdTMS]_0$. When k_P

is relatively small, however, R_P is intermediate between first and second order with respect to $[BdTMS]_0$. The overall kinetic order of $[BdTMS]_0$ was 2.09 at $[Et_2O]_0/[ZnBr_2]_0=5$, and 1.57 at $[Et_2O]_0/[ZnBr_2]_0=10$, as shown in Figure 7.

Equation 27 is an alternative expression of eq 26.

$$\frac{R_P}{K_I[I]_0[C]_0[M]_0}=k_i+\frac{k_i k_P}{k_{-2}}[M]_0 \quad (27)$$

k_P/k_{-2} was roughly estimated by eq 27 as *ca.* 16 and 1.3 at $[Et_2O]_0/[ZnBr_2]_0=5$ and 10, respectively. It is an important finding that the ratio of two rate constants, propagation (k_P) and deactivation (k_{-2}) of the activated polymer end, remarkably decreased by increasing Et_2O.

Thus, Et_2O plays conflicting roles in homogeneous aldol-GTP of BdTMS. Rate depression was observed in the case of excess Et_2O. However, ether-free $ZnBr_2$ induces many side reactions undesirable for controlling the molecular weight of the polymer. It is essential to maintain a balance between Et_2O and other components in order to control the molecular weight of the polymer.

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