Group Transfer Polymerization of 1-Butadienyloxytrimethylsilane: Effects of Aldehydes on the Initiation Reaction

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ABSTRACT: The group transfer polymerization of 1-butadienyloxytrimethylsilane (BdTMS) was examined in the presence of various aldehyde and zinc chloride in benzene. The distribution of molecular weight of the resulting polymers, was estimated by a GPC method, depended on aldehydes used: $M_w/M_n = 1.28$, 1.40, 1.51, and 1.86, with *p*-anisaldehyde, *p*-tolualdehyde, benzaldehyde, and *p*-nitrobenzaldehyde, respectively. In ^{1}H NMR monitoring of the initial stage of polymerization, a certain induction period (T) was observed prior to consumption of BdTMS. The initial polymerization rate was almost constant regardless of a variety of aldehydes, indicating that propagation proceeds through a common mechanism. The shorter the induction period was, the narrower was the distribution of molecular weight of the obtained polymer. A plot of T_H/T_X ($X = OCH_3$, CH_3, NO_2) *vs.* Brown–Okamoto's substituent constants (σ^+) showed a linear relationship ($\rho = -0.75$). Therefore a more electron-donating substituent on the *para* position of benzaldehyde was advantage to start an initiation reaction ($=$ aldol addition) rapidly, resulting in a narrower distribution of the molecular weight of the polymer.

KEY WORDS   Group Transfer Polymerization / 1-Butadienyloxytrimethyl-
silane / Aldol Addition / Aldehyde / Zinc Chloride / Brown–Okamoto's
Substituent Constants (σ^+) / M_w/M_n /

Well-designed copolymers with respect to both sequence order and molecular weight are very interesting in researching the relationship between their structure and physical properties. Generally speaking, it must be difficult to synthesize directly such copolymers from the corresponding two monomers. However, it will be possible to prepare a certain polymer with monodisperse distribution of molecular weight and then, *via* suitable polymer reactions, remake the original polymer into a new "periodic copolymer" which has a regular sequence order as well as controlled molecular weight. In fact, nearly monodisperse polymers could be obtained by the group transfer polymerization method[1,2] and anionically initiated living polymerization of monomers containing masked functional groups[3] under rather mild conditions and by easier handling.

A diene compound including silyl enol ether structure, 1-butadienyloxytrimethylsilane [BdTMS, I in eq 1], seems suitable to examine above conception because the subsequent reactions, group transfer polymerization (aldol additon type) → hydrogenation → desilylation (hydrolysis) will give an alternating ethylene–vinyl alcohol copolymer with the controlled molecular weight.

Thus, we studied the polymerization of BdTMS in the presence of catalytic amount of zinc chloride ($ZnCl_2$) and benzaldehyde (BAld) in benzene at ambient temperature in a previous paper.[4] The polymers [II in eq 1] obtained has rather narrow distributions of molecular weight in terms of M_w/M_n (~ 1.5),

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clearly differing from *ca.* 3 in the case of $ZnCl_2$ alone. It was found that one end of the polymer was composed of $-CH=CH-CH=O$ group

and capable of living propagation on increment of monomer. The proposed mechanism for this polymerization is as follows.
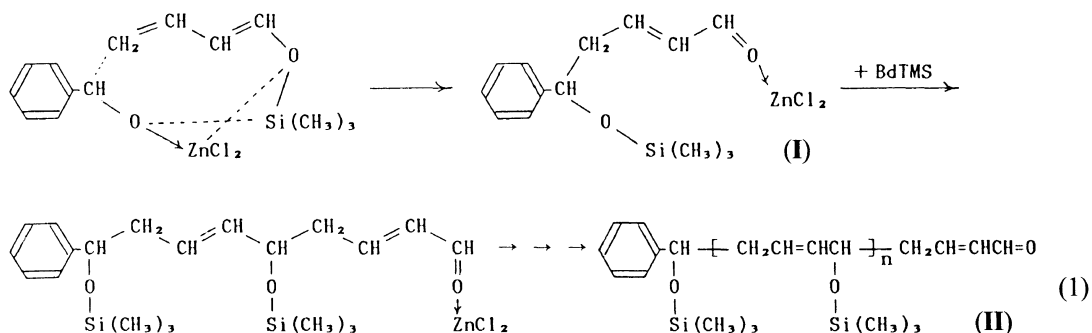
However, such M_w/M_n values do not satisfy the requirements for precise control of molecular weight. Observation on NMR suggested that this disadvantage was caused from rather slow initiation which must be in competition with propagation reaction.

In this paper, an important role of aldehyde (=initiator) in initiation was investigated in detail to achieve the lower M_w/M_n value of the resulting polymer.

EXPERIMENTAL

1-Butadienyloxytrimethylsilane (BdTMS)

According to Danishevsky procedure,[5] treatment of trimethylchlorosilane, crotonaldehyde, and triethylamine with a catalytic amount of $ZnCl_2$ at 60°C in benzene gave BdTMS, bp 59—60°C/45 mmHg, in 70% yield. Purity, 99.5% by gas chromatography. Spectroscopic data indicated the most stable geometry of BdTMS to be the *s-trans-Z-* form.

Aldehydes, Zinc Chloride (ZnCl₂), Solvent

Commercially available benzaldehyde, *p*-anisaldehyde, *p*-tolualdehyde, *p*-nitrobenzaldehyde, cinnamaldehyde, and pivalaldehyde were purified by fractional distillation or recrystallization according to literature.[6] $ZnCl_2$ was recrystallized[6] from a boiling dioxane solution under nitrogen and dried *in vacuo.*

Benzene was purified by the conventional method[6] and dried over sodium, distilled just prior to polymerization.

Polymerization

In a dry box under a nitrogen atmosphere, $ZnCl_2$, solvent, and aldehyde were magnetically stirred in a dry Schlenk tube with a stopcock and a septum cap for 30 min, and then BdTMS was injected through the septum at a breath. The tube was immersed in a thermostated bath. After the monomer was used up, the tube was again brought into the dry box, connected with a set of glass filters (No. 4 mesh) instead of a stopcock. The solution was separated from $ZnCl_2$ by filtration under nitrogen pressure, and then allowed to evaporated *in vacuo.* The polymer was obtained as a highly viscous liquid in 80—95% yield. Polymerization was also run in an NMR tube at probe temperature. In this case, precise amounts of benzene-d_6, aldehyde (liq), BdTMS were fed by microsyringe provided with a glass-made needle.

Analyses

Measurement of ^1H and ^{13}C NMR spectra was carried out on a Varian XL-200 or Hitachi R-24A instrument in benzene-d_6 or deuterochloroform solution. IR was taken on a JASCO IR-R100 spectrometer. Gel permeation chro-

matography (GPC) in tetrahydrofuran (THF) was recorded on a Toso HLG-803-D equipped with GMX-, G1000-, G2000-, and G4000-HXL columns in series at 37°C, by monitoring differential refractometrically. The molecular weights of the polymers were calibrated by standard polystyrene samples.

RESULTS AND DISCUSSION

Effects of Aldehydes upon Distribution of Molecular Weights of Polymers

The Polymerization of BdTMS by equimolar mixtures of $ZnCl_2$ (=catalyst) and various aldehydes (=initiator) is summarized in Table I. All catalytic systems successfully gave polymers similar to **II** except for each polymer end. The structures were identified by NMR
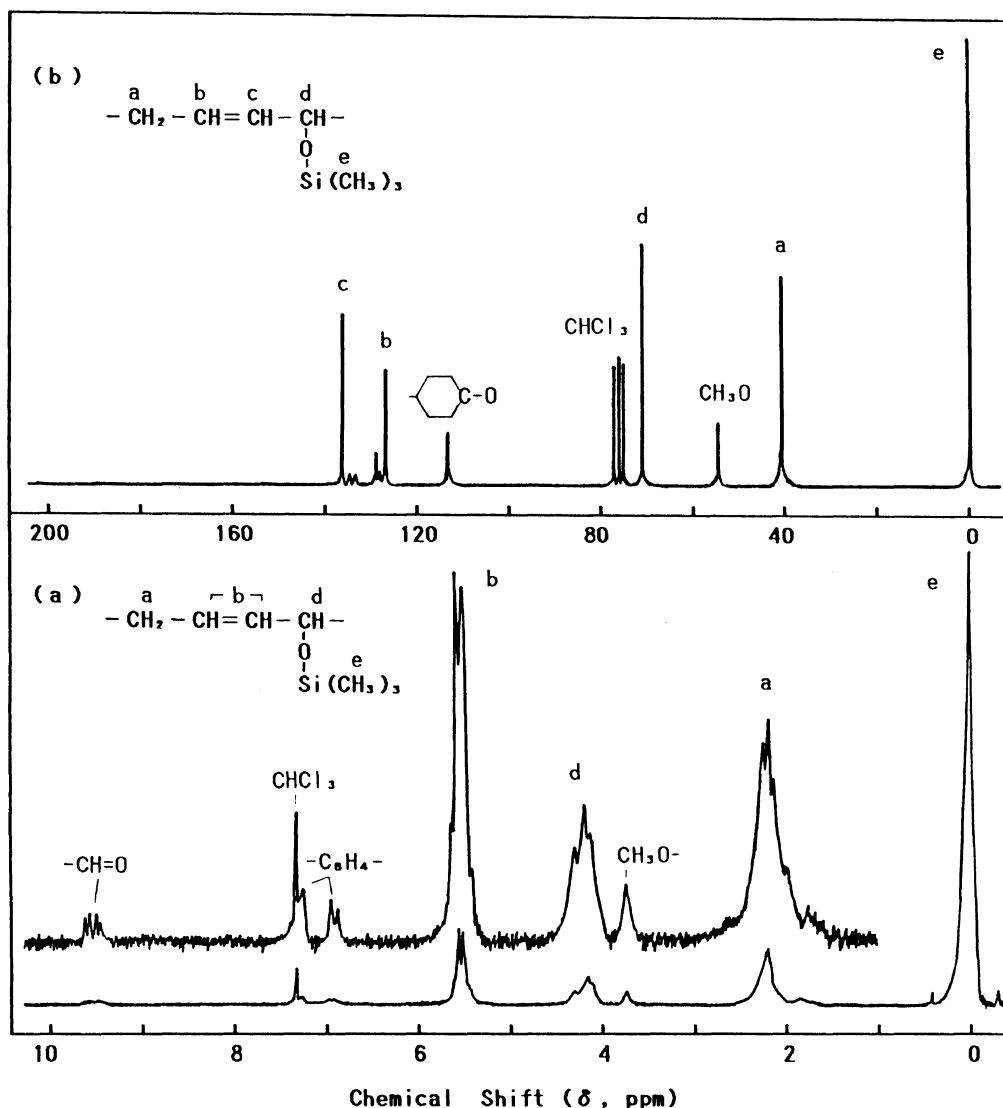

Figure 1. ^1H (a) and ^{13}C NMR (b) spectra of poly(BdTMS) initiated by the *p*-Anisaldehyde–$ZnCl_2$ system; $[BdTMS]_0/[p$-Anisaldehyde$]_0 = 20$.

Table I. Results of polymerization of BdTMS with various aldehydes–ZnCl$_2$ systems

Exptl. No.	Aldehyde	Yield[a]	Molecular weight $\times 10^{-3}$			M_w/M_n
		%	M_n[b]	[calcd][c]	M_w[b]	
1	p-CH$_3$O–C$_6$H$_4$–CH=O	95	2.95	[3.01]	3.78	1.28
2	p-CH$_3$–C$_6$H$_4$–CH=O	89	3.00	[2.86]	4.20	1.40
3	C$_6$H$_5$–CH=O	86	3.00	[2.98]	4.52	1.51
4	p-NO$_2$–C$_6$H$_4$–CH=O	78	3.53	[3.02]	6.57	1.86
5	C$_6$H$_5$–CH=CH–CH=O	93	2.96	[3.00]	3.98	1.34
6	(CH$_3$)$_3$C–CH=O	84	3.12	[2.93]	4.95	1.59

[a] Yield after 18 h polymerization at room temp. (No. 4: 24 h).
[b] Determined by GPC, calibrated by standard polystyrene samples.
[c] Calculated from [BdTMS]$_0$/[Aldehyde]$_0 \sim 20$.
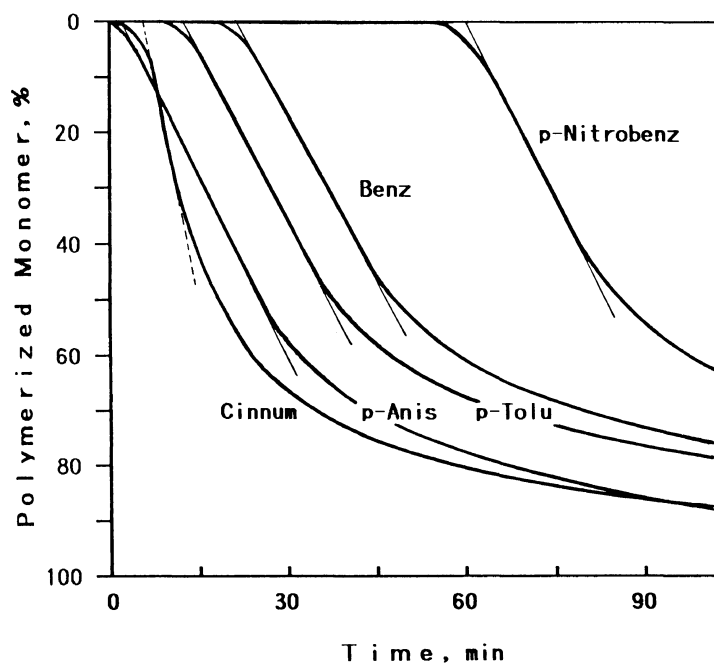
Figure 2. Polymerization of BdTMS with various aldehydes and ZnCl$_2$ in benzene-d_6 at 37°C (NMR-probe temperature). [BdTMS]$_0$/[–CH=O]$_0$ = 20.0; [–CH=O]$_0$/[ZnCl$_2$]$_0$ = 1.0; ZnCl$_2$, 5.0×10^{-5} M; C$_6$D$_6$, 0.5 cm^3.

and IR spectra, as explained in the previous paper.[4] In this paper, as one example, ^{1}H and ^{13}C NMR spectra of the polymer prepared with p-CH$_3$O–C$_6$H$_4$–CH=O/ZnCl$_2$ are illustrated in Figure 1(a) and (b), respectively. Molecular weight, as estimated from an intensity ratio of the signals due to the aromatic protons of the

polymer end and those due to the olefinic protons in the polymer chain, was in agreement with that by the GPC method.

The distribution of molecular weights of the polymers was evaluated in terms of M_w/M_n, which was calculated from each GPC curve. The M_w/M_n values were obviously dependent

upon the aldehydes used. Making a comparison among *para*-substituted derivatives of benzaldehyde, electron-donating substituents($-OCH_3$, $-CH_3$) caused M_w/M_n to be smaller, while electron-accepting one ($-NO_2$) resulted clearly in large M_w/M_n value. Cinnamaldehyde was also favorable for making the M_w/M_n value of the polymer smaller. Pivalaldehyde was comparable to benzaldehyde. The steric influence of $(CH_3)_3C-$ group surely complicates the situation in spite of its electron-donating character.

Thus, electron density on carbonyl group in aldehyde may play an important role in determining the dispersities of molecular weight of the resulting polymers. In other words, the rate of initiation proposed in eq 1 must be enhanced by introducing electron-donating substituent. To prove the above hypothesis, features of the initiation reaction were investigated in detail by ^1H NMR-monitoring.

Features of Polymerization by ^1H NMR-Monitroring Method

Polymerization of BdTMS initiated by various aldehydes–$ZnCl_2$ was also carried out in NMR-tube at its probe temperature (37°C). Because the signals at 6.55—7.0 ppm of BdTMS did not overlap with the signals of the formed polymer, the progress of polymerization could be pursued visually. The amounts of reacted monomer are plotted against polymerization time in Figure 2, where some induction periods are observed prior to consumption of BdTMS. Various induction periods (T_X, X=OCH_3, CH_3, H, NO_2) depended upon the aldehydes used. *p*-Nitrobenzaldehyde, which has a more electron-accepting substituent on the *para* position of
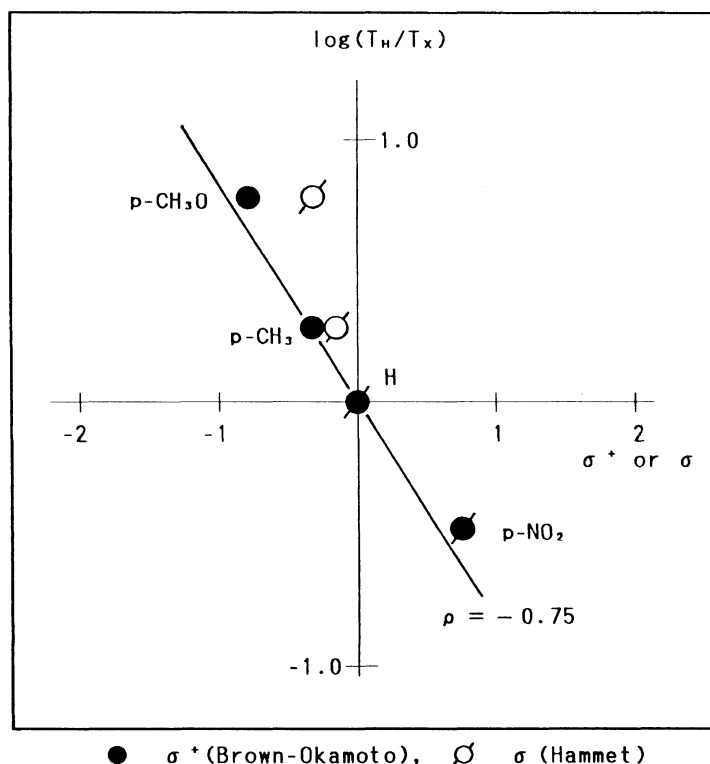

Figure 3. Plots of $\log[T_H/T_X]$ *vs.* Brown–Okamoto's (●) and Hammet's (○) substituent constants. Induction periods (T) were determined as intercepts at zero conversion of curves in Figure 2.

benzaldehyde, exhibited a longer induction period, but this was hardly discerned for *p*-anisaldehyde with an electron-donating substituent. However, each curve in Figure 2 shows almost the same slope at the first stage of propagation, suggesting that propagation rates (Rpr) must be the same regardless of the type of aldehydes employed. According to the mechanism proposed as eq 1, the initiation reaction must be directly influenced by the aldehydes used, while all propagation reactions (*i.e.*, successive aldol addition of monomer to adducts having a –CH=CH–CH=O moiety at their end) should be the same irrespective of the aldehydes. The facts coincide very well with the porposed mechanism.

These induction periods surely reflect how easily each initiation reaction occurs. Figure 3 shows plots of $\log(T_H/T_X)$ [X=*p*-OCH$_3$, *p*-CH$_3$, *p*-NO$_2$] *vs.* Brown–Okamoto's[7] as well as Hammet's[8] substituent constants, σ^+ and σ, respectively. The former plots showed a good linear relation ($\rho = -0.75$) but not the latter, implying that a rate-determining stage of the initiation reaction is conversion of a formyl group into carbonium cation. In other words, when the cation could be stabilized by the electron-donating substituents, it should be attributable to a more rapid initiation (=aldol addition by a terminal carbon of conjugated system in BdTMS). Higher electron density on an oxygen atom of a formyl group have a merit, too, for stronger interaction of the formyl group with not only ZnCl$_2$ also –Si(CH$_3$)$_3$ group in BdTMS monomer. The above explanation is schematically shown as followes.
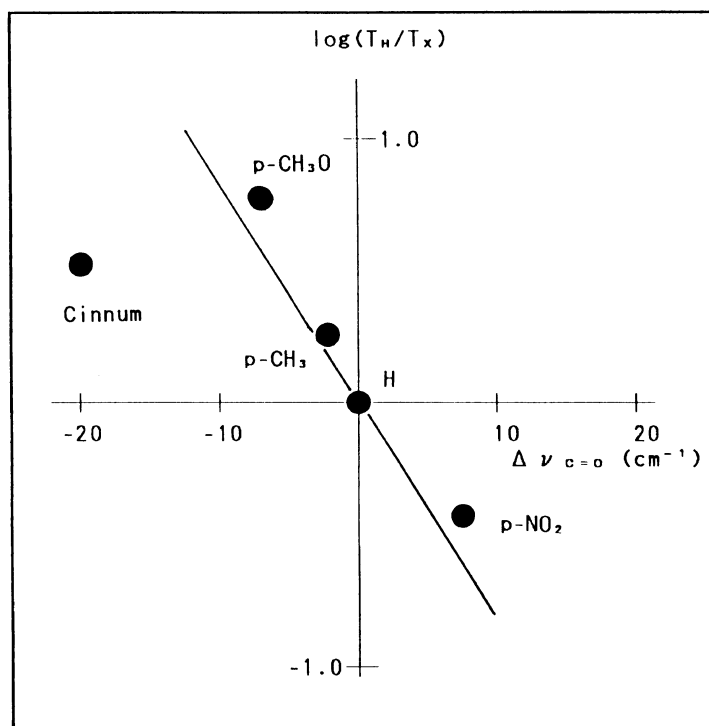

Figure 4. Plots of $\log[T_H/T_X]$ *vs.* $\Delta v_{C=O}$ defined as the difference in formyl carbonyl absorption ($\sim 1700\,\mathrm{cm}^{-1}$) of various aldehydes and benzaldehyde on their IR spectra.
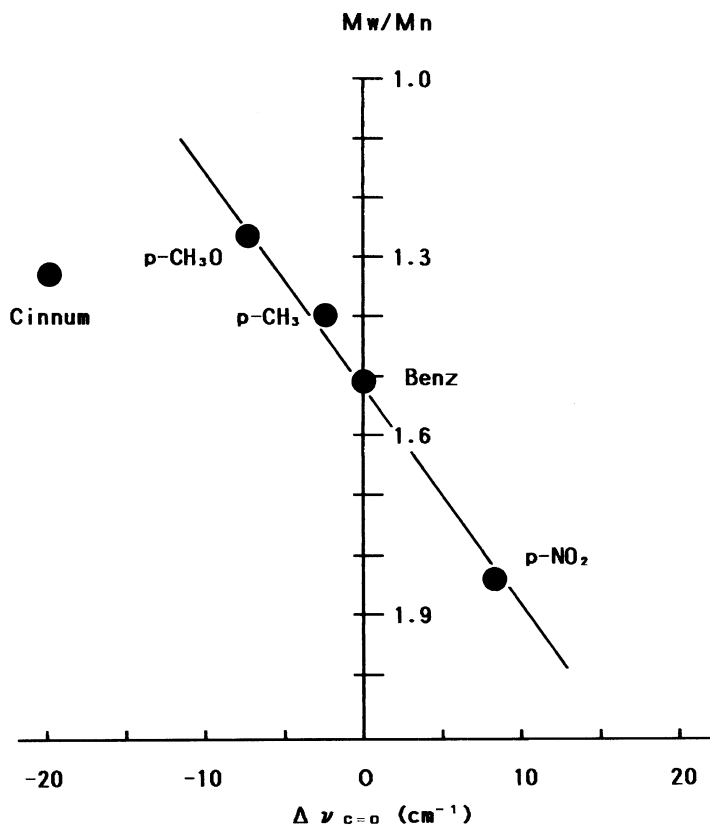
$$X-\bigotimes-CH=O \quad + \quad ZnCl_2 \quad \longleftrightarrow \quad X^+=\bigotimes=CH-O^-\cdots\rightarrow ZnCl_2 \quad etc. \tag{2}$$
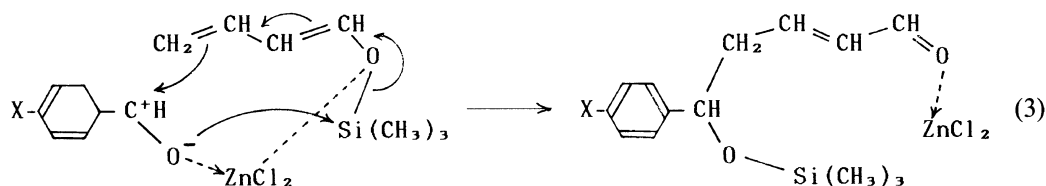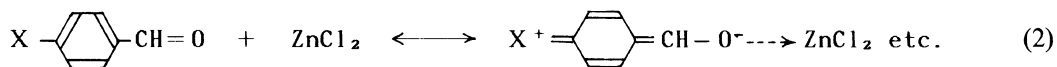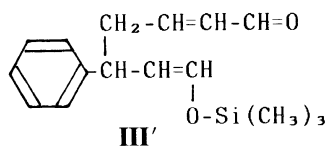
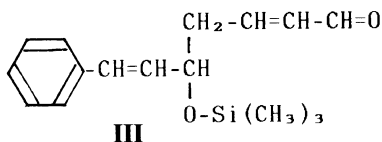

Figure 5. Correlations between molecular weight distribution (M_w/M_n) of poly(BdTMS)s obtained from various aldehydes–ZnCl$_2$ systems and $\Delta v_{C=O}$.

Cinnumaldehyde was similar to p-anisaldehyde concerning the induction period and distribution of molecular weight for a resulting polymer. However, it should be noted that the slope of the time–conversion diagram in Figure 2 was curved in somewhat a different manner from those with benzaldehyde derivatives. The polarizability of a carbon–oxygen double bond in cinnumaldehyde can be probably revealed[9] by comparing IR absorption at near 1700 cm^{-1} with those of other aldehydes. Thus, Figure 4 shows a relationship between differences from

benzaldehyde in the wavenumber of carbonyl streching, ($\Delta\nu_{C=O}$, cm^{-1}), and $\log(T_H/T_X)$ described above, and Figure 5 gives a relationship between $\Delta\nu_{C=O}$ and M_w/M_n values of the polymers obtained from corresponding aldehydes. In both Figures, a series of benzaldehyde derivatives was again aligned on a line like as Figure 3, while cinnamaldehyde was located in a spot with smaller $\log(T_H/T_X)$ or larger M_w/M_n than values predicted from

$\Delta\nu_{C=O}$. Cinnumaldehyde was examined in the hope that it might induced a narrower distribution of the molecular weight of the resulting polymer than p-anisaldehyde. However, such expectation was not realized. Although this can not explained yet, behaviour of cinnumaldehyde may be caused by jumbling up the initial adduct, Formula **III**, and another one, Formula **III'**, in this polymerization system.

CH₂-CH=CH-CH=O / CH=CH-CH / O-Si(CH₃)₃

III

CH₂-CH=CH-CH=O / CH-CH=CH / O-Si(CH₃)₃

III'

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