Cationic Polymerization of 1, 2-Dialkoxyethylenes*

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ABSTRACT: 1, 2-Dimethoxyethylene (DME) and 1, 2-diethoxyethylene (DEE) were polymerized by cationic catalysts in order to clarify the effect of an electron-donating group, an alkoxy group, at an olefinic β -carbon on the reactivity of vinyl ethers in cationic polymerization. Both DME and DEE were found to be very reactive and homopolymers were easily produced at high yield, in spite of the presence of a bulky β -alkoxy group. A partially crystalline polymer was formed in the polymerization of *cis*-DME catalyzed by the $\text{Al}_2(\text{SO}_4)_3\text{--H}_2\text{SO}_4$ complex catalyst. The relative reactivities of 1, 2-dialkoxyethylenes were measured on the basis of the results of copolymerization with vinyl ethers and alkenyl ethers. $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ and toluene were used as catalyst and solvent, respectively. The reactivity of these monomers increases as follows

methyl vinyl ether $\leq$ *trans*-DME < *trans*-methyl propenyl ether (MPE) < *cis*-MPE < *cis*-DME
and

ethyl vinyl ether $\approx$ *trans*-DEE < *cis*-DEE.

This order can be explained in terms of a model of the propagation step in which an attacking carbonium ion interacts with the π -electron on the olefinic double bond and the ether oxygen of vinyl ethers.

KEY WORDS 1, 2-Dimethoxyethylene / 1, 2-Diethoxyethylene /
Methyl Propenyl Ether / Methyl Butenyl Ether / Methyl Vinyl
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It was found that the alkenyl ethers having an alkyl group on the olefinic β -carbon were easily polymerized by cationic catalysts. Moreover, propenyl and butenyl ethers were more reactive than corresponding vinyl ethers in spite of the presence of a bulky β -alkyl group.^{1–5} On the basis of the observation that

an alkyl substituent at the β -position of vinyl ethers does not increase electron density on the β -carbon,⁶ some models have been proposed for the transition state of the propagation step to explain the high reactivity of the alkenyl ethers.^{7,8}

It is important, for the elucidation of a propagation reaction mechanism, to know how the reactivity of vinyl ethers is affected by the introduction of an electron-donating alkoxy group on the olefinic β -carbon. In radical copolymerization, the reactivity of 1, 2-dimethoxyethylene (DME) has been studied in detail.^{9,10} However, apart a recent paper by Okuyama, *et al.*,¹¹ no investigation has yet been made which would allow one to evaluate the

* This is the 13th in a series of papers concerned with cationic polymerization of α, β -disubstituted olefins. For the 12th paper, see T. Higashimura, *et al.*, *J. Polym. Sci., Part A-1*, **7**, 3129 (1969).

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reactivities of 1,2-dialkoxyethylenes in cationic polymerization.

This paper deals with the question of whether or not DME and 1,2-diethoxyethylene (DEE) will produce homopolymers by a cationic mechanism. As poly(1,2-dialkoxyethylene)s were found to be obtainable at high yield, the effect of a β -alkoxyl substituent on the reactivities of vinyl ethers was studied. The high reactivity of 1,2-dialkoxyethylenes is discussed in terms of the electronic stabilization energy based on delocalization between a monomer and an attacking carbonium ion, as reported in a previous paper.⁷ Properties of poly(1,2-dimethoxyethylene) and poly(1,2-diethoxyethylene) are also described briefly.

EXPERIMENTAL

Materials

DME and DEE were synthesized from vinyl acetate by the McElvain method as shown in eq 1.^{10,12} Alumina used for alcohol elimination was formed by heating it at 600°C after hydrolysis of aluminum isopropoxide. The main product of reaction scheme 1 was the *cis*-isomer.

The mixture of geometric isomers was separated into its components by distillation. The *trans*- and *cis*-isomers were identified by means of their IR and NMR spectra, and the relative proportions of the geometric isomers were determined by gas-chromatography.

Propenyl methyl ether and butenyl methyl ether were synthesized by the elimination of alcohol from acetals as described previously.^{1,3} The monomers synthesized, commercial vinyl ethers, catalysts, and solvents were purified using the same methods as described in a previous paper.¹

Procedures

Copolymerizations were carried out in a reaction vessel equipped with a stirrer and

thermometer, and fitted with a stopcock at the bottom. Details of the procedure were described in a previous paper.² After a specified time, the amounts of residual monomer were determined by gas-chromatography, and the rate of polymerization was calculated from a first-order plot of residual monomer concentrations. Column packings in gas-chromatography were PEG 4000 (1 m)+DNP (1 m), PEG 6000 AgNO₃, and PEG 400 (1 m)+DNP (2 m) for copolymerizations involving DME, DEE, and alkenyl ethers, respectively. Homopolymers of DME and DEE were obtained by polymerizing the individual monomer under dry N₂.

Intrinsic viscosities were measured in toluene solution at 30°C. NMR spectra of polymers were measured in *p*-dichlorobenzene solution (10% w/v) at 140°C with a Varian A-60.

RESULTS

Reactivity of 1,2-Dialkoxyethylenes

1,2-Dialkoxyethylenes were polymerized in toluene at -75—-78°C by BF₃OEt₂. In the procedure described above, the reaction system contained a small amount of water (1—3 mmol/l). Water was not excluded more rigorously, since the relative reactivity of a monomer will not be affected by a small amount of water. Polymerization proceeded smoothly without an induction period. As will be described later, the product was a solid polymer formed by vinyl polymerization and no side reaction was found in the course of this experiment. Therefore, the rate of monomer consumption can be regarded as the rate of vinyl polymerization.

Effect of a β -Alkoxyl Group on the Reactivity.

To clarify the effect of a β -alkoxyl group on the reactivity of vinyl ethers, a mixture of DME isomers was copolymerized with methyl vinyl ether (MVE), since it can be assumed that the structure of the propagating carbonium ion produced from DME will be similar to that from MVE.¹³ Figure 1 shows the time-conversion curve first-order plots in the terpolymerization of *cis*- and *trans*-DME with MVE. As the first-order plot in this monomer-pair was not linear, the relative reactivities were estimated from the ratios of the initial slopes in the first-

Figure 1. Copolymerization of *cis*- and *trans*-DME with MVE: ●, *cis*-DME; ◐, *trans*-DME; ○, MVE; $[M]_0$, 5.0 vol %; DME/MVE, 2.0/1.0, v/v; *cis*-DME/*trans*-DME, 0.82/1.0; $[C]$, 20.0 mmol/l.

Figure 2. Copolymerization of *cis*-DEE with EVE: ●, *cis*-DEE; ○, EVE; $[M]_0$, 10 vol %; *cis*-DEE/EVE, 1.0/1.0, v/v; $[C]$, 9.0 mmol/l.

Figure 3. Copolymerization of *trans*-DEE with EVE: ●, *trans*-DEE; ○, EVE; $[M]_0$, 10 vol %; *trans*-DEE/EVE, 1.86/1.0, v/v; $[C]$, 36 mmol/l.

order plot. The relative reactivity of these monomers decreased as follows

cis-DME was 6–7 times more reactive than MVE or *trans*-DME.

From an experiment in which pure *cis*-DME was copolymerized with MVE, *cis*-DME was found to be 15 times more reactive than MVE. Thus, although the numerical value of the relative reactivities of a monomer pair varies with the components of the reactive mixture, the order of reactivities remains constant.

Next, the effect of an ethoxyl group, which is bulkier than a methoxyl group was studied. Figures 2 and 3 show the results of the copolymerization of ethyl vinyl ether (EVE) with *cis*- and *trans*-DEE, respectively. As seen from Figure 2, *cis*-DEE is about 8.0 times more reactive than EVE in spite of the bulkiness of the β -ethoxyl group. On the other hand, the reactivity of *trans*-DEE appeared to be almost the same as that of EVE, and the rate of copolymerization of *trans*-DEE with EVE was much smaller than that of *cis*-DEE with EVE. Also, as shown in Figure 4, *cis*-DEE was slightly more reactive than *cis*-DME in the

Figure 4. Copolymerization of *cis*-DEE with *cis*-DME: ○, *cis*-DEE; ●, *cis*-DME; $[M]_0$, 10 vol %; *cis*-DEE/*cis*-DME, 1.0/1.0, v/v; $[C]$, 9.0 mmol/l.

Table I. Effect of monomer composition and catalyst concentration on the relative reactivities of *cis*-DEE against EVE^a

Monomer composition, <i>cis</i> -DEE/EVE, v/v	BF ₃ OEt ₂ , mmol/l	Relative reactivity
1.0/1.0	9.0	9.5
1.0/2.33	9.0	7.2
2.33/1.0	9.0	8.4
1.0/1.0	5.4	8.0

^a $[M]_0$, 10 vol%; solvent, toluene, -78°C .

copolymerization of *cis*-DEE with *cis*-DME.

To test the validity of the relative reactivity, *cis*-DEE was copolymerized with EVE under various conditions. The relative reactivity was found to be independent of the monomer feed composition and catalyst concentration as shown in Table I.

Comparison of the Reactivities of 1,2-Dialkoxyethylenes with Alkenyl Ethers. The results described above indicate that the introduction of a *cis*- β -alkoxyl group increases the reactivity of vinyl ethers, while the introduction of a *trans*- β -alkoxyl group has no effect on reactivity.

Similarly, β -alkyl groups increase the reactivity of vinyl ethers in cationic polymerization.¹⁻⁵ As described in the preceding section, the value of the relative reactivity of one monomer with another depends on whether or not it is determined by direct copolymerization. Therefore, 1,2-dialkoxyethylenes have to be copolymerized directly with alkenyl ethers in order to obtain accurate information on the relative reactivity of 1,2-dialkoxyethylene against propenyl ether. *cis*-DME was copolymerized with *cis*- and *trans*-methyl propenyl ethers (MPE). As shown in Figure 5, the first-order plots were linear for both monomers, and the reactivity of the monomers decreased as follows.

cis-DME was 8 times more reactive than *cis*-MPE. In the copolymerization of MVE with *cis*- and *trans*-MPE under the same condition, *cis*-MPE was 3.8 times and *trans*-MPE 1.2 times more reactive than MVE.

cis-DME was also copolymerized with *cis*-butenyl methyl ether (BME) where the bulkiness of β -substituent seems to be almost the same as in *cis*-DME. Figure 6 shows that *cis*-DME was

Figure 5. Copolymerization of *cis*-DME with *cis*- and *trans*-MPE: ●, *cis*-DME; ○, *cis*-MPE; ●, *trans*-MPE; $[M]_0$, 5.0 vol %; *cis*-DME/MPE, 1.0/1.7, v/v; *cis*-MPE/*trans*-MPE, 1.0/1.1, v/v; $[C]$, 18 mmol/l.

Figure 6. Copolymerization of *cis*-DME with *cis*-BME: ●, *cis*-DME; ○, *cis*-BME; $[M]_0$, 10 vol %, *cis*-DME/*cis*-BME, 1.0/1.0, v/v; $[C]$, 18 mmol/l.

about 13 times more reactive than *cis*-BME.

It is concluded that *cis*-DME is more reactive than *cis*-MPE and *cis*-BME, and that *trans*-DME is less reactive than *trans*-MPE, that is, an electron-donating substituent at the *cis*- β -position of vinyl ethers increases the relative reactivity of the monomer.

Reactivity of Geometric Isomers. The results described above suggest that the *cis*-isomers of DME and DEE are highly reactive. To confirm this, *cis*-DME was copolymerized with *trans*-DME. As shown in Figure 7, the first-order plots were linear, and *cis*-DME was 4.9 times more reactive than *trans*-DME. This behavior is the same as that of other β -substituted vinyl ethers.

Polymer Structure

Properties of poly(dialkoxyethylene)s have not yet been reported. In this paper, the properties of the polymers from the *cis*-isomers are described briefly, since it was difficult to obtain large amounts of polymer from the *trans*-isomer.

White solid polymer was obtained in the polymerization of *cis*-DME catalyzed by $BF_3 \cdot OEt_2$

Figure 7. Copolymerization of *cis*-DME with *trans*-DME: ●, *cis*-DME; ○, *trans*-DME; $[M]_0$, 5.0 vol %, *cis*-DME/*trans*-DME, 1.0/1.2, v/v, $[C]$, 36 mmol/l.

in toluene at -78°C . The polymer was amorphous and its softening temperature was about 60°C . The molecular weight of the polymer was not large; $[\eta]$ was about 0.3. The solubility of the polymer was similar to that of poly(methyl vinyl ether); it was soluble in most common organic solvents and cold water, but insoluble in petroleum ether and hot water. The NMR spectrum of the polymer showed two proton signals at 6.1τ and $6.4\text{--}6.6\tau$. The former may be due to methine protons, and the latter to methoxy protons. The ratio of the intensities of these two signals was in the range of 1.0:2.9–3.0 in all poly-DME samples, and it was concluded that the product was a vinyl polymer formed *via* a reaction of the olefinic double bond. Similar results were obtained when methylene chloride was used as solvent.

Also, a white amorphous polymer was produced from *cis*-DEE under similar conditions to those used in polymerizing *cis*-DME. $[\eta]$ of the polymers were about 0.25 and the product was identified as a vinyl polymer on the basis of NMR data.

Thus, *cis*-DME and *cis*-DEE formed amorphous polymers when the homogeneous catalysts,

(BF_3OEt_2 and SnCl_4), were used irrespective of the polarity of the solvent. On the other hand, when an $\text{Al}_2(\text{SO}_4)_3\text{-H}_2\text{SO}_4$ complex was used as a heterogeneous catalyst below 0°C , *cis*-DME produced a partially crystalline polymer on the surface of the catalyst particles. This is similar to the results obtained with *cis*-propenyl ethers.¹⁴ IR and NMR spectra of the partially crystalline polymer showed some differences from those of the amorphous polymer.

DISCUSSION

Formation of Polymer. It has been found that 1,2-dialkoxyethylenes readily produce homopolymers by cationic catalysis in spite of the presence of a bulky alkoxy group on the β -carbon of an olefinic double bond and the polymer is formed by the reaction of an olefinic double bond. Although 1,2-dialkoxyethylenes were very reactive, the molecular weight of the polymer was not high. The formation of a partially crystalline polymer formed by the heterogeneous catalyst suggests the possibility of the formation of a stereoregular polymer although the reaction mechanism is not yet clear.

Relative Reactivities of 1,2-Dialkoxyethylenes. From the copolymerization of DME or DEE with the corresponding vinyl ether, a β -alkoxy group at the *cis*-position was found to increase the reactivity of vinyl ethers. When BF_3OEt_2 was used as catalyst and toluene as solvent, the order in the relative reactivity of the monomers was found to be as follows

On the other hand, in the polymerization of EVE derivatives catalyzed by BF_3OEt_2 in methylene chloride, the following order was reported;¹¹

cis-Ethyl propenyl ether (EPE) was reported to be more reactive than *cis*-DEE and the β -methyl group increased the reactivity of vinyl ethers

more strongly than did the β -alkoxy group. We cannot confirm conclusively the order in the relative reactivity of ethyl vinyl ether derivatives from the present experimental results, since *cis*-DEE was not directly copolymerized with *cis*-EPE. In our experiment in toluene solution, *cis*-DEE was 9.5 times more reactive than EVE and *cis*-EPE was 4 times more reactive than EVE. Therefore, *cis*-DEE seems to be more reactive than *cis*-EPE, and this is not in agreement with the order in eq 4.

Also, the *cis*-isomer was more reactive than the *trans*-isomer in all cases, and this behavior is the same as in the other β -substituted vinyl ethers. As the relationship between the polymerizability and the stability of the geometric isomer has been studied in detail,^{11,15,16} the relative reactivities of geometric isomers is not discussed in the present paper.

Interpretation of the Effect of a β -Alkoxy Group on the Reactivity of Vinyl Ethers. In a previous paper,⁷ some models for a transition state were proposed to explain the effect of β -substituents on the reactivities of vinyl ethers. The π -electronic stabilization energies (ΔE), or the delocalization energy from the occupied orbital of the monomer to the vacant orbital of the propagating carbonium ion, were calculated in terms of eq 5, where ϵ_j is the energy of i th molecular orbital obtained by the extended Hückel method, and C_r^j is the coefficient of the r th $p\pi$ -atomic orbital in the j th π -molecular orbital.

$$\Delta E = 2 \sum_j^{\text{occ}} \{ (C_r^j + C_s^j + \dots)^2 / -\epsilon_j \} \quad (5)^*$$

As shown in the previous paper,⁷ the stabilization energy for model I increased in the order

The agreement of this order with experimental results (eq 3) suggests that the transition state

* The denominator of eq 5 may be written exactly as the difference between the energy level of the occupied orbital of the monomer and that of the vacant orbital of the propagating carbonium ion, as given by eq 5'. In eq 5, the energy level of the vacant level in the propagating carbonium ion was taken as a constant ($\epsilon^+ = 0$) for simplicity.

for the propagation reaction is model I, where model I' is proposed for *cis*-DME since two methoxyl groups are on the same side of an olefinic double bond.

A strong electron-donating group on a β -olefinic carbon decreases electron density on the β -carbon.⁷ Therefore, it is assumed that the reactivities of *trans*-DME and *trans*-DEE do not differ greatly from those of corresponding vinyl ethers, since the transition state for the *trans*-isomer may be model I. This assumption is borne out by the experimental results. The high reactivities of *cis*-DME and *cis*-DEE compared with corresponding propenyl ethers can be explained only by assuming an interaction of the propagating carbonium ion not only with the olefinic carbon, but also with the etheric oxygen.

On the other hand, Okuyama, *et al.*,⁸ proposed model II for the transition state, in which the propagating carbonium ion interacts with the olefinic α - and β -carbons of the monomer. They calculated the delocalization energy which

was derived in terms of the second-order perturbation method and which was calculated from eq 7 by considering the lowest vacant level (ϵ^+) of the propagating carbonium ion.

$$\Delta E_{\alpha\beta} = 2 \sum_j^{\text{occ}} \frac{(C_{\alpha}^j + C_{\beta}^j)^2}{\epsilon^+ - \epsilon_j} (-\gamma^2) \quad (7)$$

The calculation showed that the delocalization energy increased as follows¹¹

$$\text{MVE} < \text{cis- and trans-DME} < \text{cis- and trans-MPE} \quad (8)$$

and that the delocalization energy of the *cis*-isomer was almost equal to that of the *trans*-isomer. They concluded that model II was sufficient to explain the reactivity of vinyl ether

derivatives, because of the agreement between the relative reactivity calculated (eq 8) and the experimental results given in eq 4.

It will depend entirely upon the relative reactivities of *cis*-1, 2-dialkoxyethylenes to *cis*-propenyl ethers as to whether model I or model II is a suitable explanation for their reactivities. Therefore, at the present time, the most important thing is to identify the causes of the disagreement between the results. The following remarks summarize the causes of the disagreement.

(i) In this paper, DME was used to compare the reactivities of 1, 2-dialkoxyethylenes with propenyl ethers, because the steric hindrance of a β -methoxyl group is smallest among 1, 2-dialkoxyethylenes. As an ethoxyl group is bulkier than a methoxyl group, the reactivity of DEE may be lower than expected.

(ii) In this paper, toluene was used as solvent. Other workers determined the order of the reactivities in eq 4 in methylene chloride solution.¹¹ The low reactivity of *cis*-DEE in methylene chloride may be ascribed to a decrease in the interaction between the propagating carbonium ion and the oxygen atom of the alkoxy group in a polar solvent.

Finally, we would like to compare eq 7 with our treatment. Okuyama, *et al.*,¹¹ criticized our

Table II. The highest occupied level of monomers and the lowest vacant level of their carbonium ion^a

Monomer	Highest occupied level of monomer, eV	Lowest vacant level of carbonium ion, eV
$\text{CH}_2=\text{CHOCH}_3$	-12.82578	-9.99196
<i>cis</i> - $\text{CH}_3\text{CH}=\text{CHOCH}_3$	-12.40632	-9.98222 ^b
<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHOCH}_3$	-12.37510	-9.99582
<i>cis</i> - $\text{CH}_3\text{OCH}=\text{CHOCH}_3$	-12.45580	—
<i>trans</i> - $\text{CH}_3\text{OCH}=\text{CHOCH}_3$	-12.45125	—
$\text{CH}_2=\text{CHOC}_2\text{H}_5$	-12.81880	-10.00205

^a The structure with a methyl group on the β -carbon was assumed to be that of the carbonium ion.

^b As the carbonium ion formed from the *cis*-isomer is more unstable than that from the *trans*-isomer, -9.99582 eV, may be more reasonable than -9.98222 eV for the *cis*-isomer.

Table III. Comparison of stabilization energies (ΔE)^a calculated from eq 5 and 5'.

Monomer	ΔE for model I		ΔE for model II	
	By eq 5	By eq 5' ^b	By eq 5	By eq 5' ^b
$\text{CH}_2=\text{CHOCH}_3$	0.16266	0.56093	0.12200	0.53707
<i>cis</i> - $\text{CH}_3\text{CH}=\text{CHOCH}_3$	0.16494	0.61016	0.12736	0.62419
<i>trans</i> - $\text{CH}_3\text{CH}=\text{CHOCH}_3$	0.16466	0.60178	0.12750	0.62887
<i>cis</i> - $\text{CH}_3\text{OCH}=\text{CHOCH}_3$	0.20826 ^c	0.63669 ^c	0.12529	0.60125
<i>trans</i> - $\text{CH}_3\text{OCH}=\text{CHOCH}_3$	0.16288	0.58887	0.12530	0.60177
$\text{CH}_2=\text{CHOC}_2\text{H}_5$	0.16368	0.56271	0.12201	0.53718

^a γ^2/eV unit.^b $\epsilon^+ = -10.0 \text{ eV}$.^c Calculated value for model I'.

results derived from eq 5, on the ground that the energy level of the propagating carbonium ion was not considered in eq 5. However, if the energy level does not greatly depend on the kind of monomer used, the values calculated in eq 5 should be useful as a first approximation. Table II shows the highest occupied level of the monomer and the lowest vacant level of the propagating carbonium ion. The structure having a methyl group on a β -carbon was assumed as that of the carbonium ion, as described in the previous paper.⁷ The lowest vacant level of the propagating carbonium ion was found to be about -10 eV , irrespective of the kind of β -substituent.

Now, eq 5 was modified to eq 5' to take account of the energy level of the propagating carbonium ion.

$$\Delta E = 2 \sum_j^{\text{occ}} \frac{(C_r^j + C_s^j + \dots)^2}{\epsilon^+ - \epsilon_j} \gamma^2 \quad (5')$$

The stabilization energy was calculated in terms of eq 5' at $\epsilon^+ = -10.0 \text{ eV}$. The results are summarized in Table III together with the values calculated by eq 5.⁷ As Table III shows, the order in values of the stabilization energy calculated by using eq 5' is completely consistent with that by eq 5. Thus, we cannot conclude from the results of our experiments (eq 2) that model II was more likely than model I or I'.

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