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Structure and Reactivity of α,β-Unsaturated Ethers. XI. Cationic Copolymerization and Acetal Addition of *cis*- and *trans*-Styryl Ethyl Ethers

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The cationic copolymerization between *cis*- and *trans*-styryl ethyl ethers in methylene chloride was investigated in the temperature range from −70 to 0°C with boron trifluoride etherate as catalyst. It was found that at lower temperatures the *trans* ether is more reactive than its *cis* isomer, although the relative reactivities are reversed at 0°C. Addition reactions of various acetals to *cis*- and *trans*-styryl ethyl ethers were carried out at 0°C with the same Lewis acid as catalyst. The relative *cis-trans* reactivities are largely dependent on the bulkiness of an attacking oxycarbonium ion. It was concluded that the *cis* isomer, which is electronically more reactive toward cations, is liable to suffer adverse steric effect, especially when the attacking carbonium ion is bulky.

β-Substituted vinyl ethers are known to be easily polymerized by cationic mechanism. Previous investigations dealt mostly with alkenyl[1-4] and β-chlorovinyl[5] alkyl ethers. In all these cases, *cis* isomers were found to be more reactive than the corresponding *trans* isomers. In the case of β-methylstyrene, however, the *trans* isomer proved to be more reactive.[6,7] The relative *cis-trans* reactivities of α,β-disubstituted olefins in cationic polymerization are apparently not simple and the origin remains to be clarified.

In terms of chemical constitution, styryl alkyl ethers may be regarded as derivatives of either vinyl ether or styrene. Mizote *et al.* reported that the *cis* ether can readily be polymerized by cationic agents.[8] Our interest in the relative reactivities of geometrical isomer pairs of α,β-unsaturated ethers led us to compare the cationic polymerizabilities of *cis*- and *trans*-styryl ethyl ethers.

In the present study, we first investigated the mutual copolymerization between *cis*- and *trans*-styryl ethyl ethers (SEE) at various temperatures. Next, addition reactions of various acetals[4,9]

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[1] T. Okuyama, T. Fueno and J. Furukawa, *J. Polym. Sci. A*-1, **6**, 993 (1968).

[2] T. Okuyama, T. Fueno, J. Furukawa and K. Uyeo, *ibid.*, **6**, 1001 (1968); and references cited therein.

[3] T. Higashimura, S. Kusudo and S. Okamura, *Kobunshi Kagaku*, **25**, 698 (1968); and their previous papers.

[4] T. Okuyama, T. Fueno and J. Furukawa, *J. Polym. Sic. A*-1, **7**, 3045 (1969).

[5] T. Okuyama, T. Fueno and J. Furukawa, *ibid.*, **7**, 2433 (1969); and references cited therein.

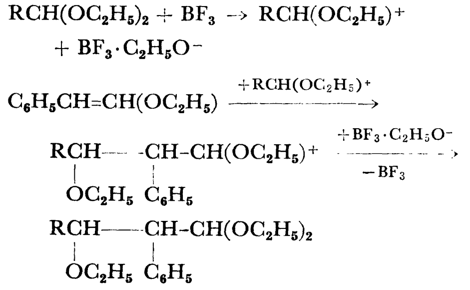
[6] C. G. Overberger, D. Tanner and E. M. Pearce, *J. Amer. Chem. Soc.*, **80**, 4566 (1958).

[7] A. Mizote, T. Higashimura and S. Okamura, *J. Polym. Sci. A*-1, **6**, 1825 (1968).

[8] A. Mizote, T. Higashimura and S. Okamura, *J. Macromol. Sci. (Chem.)*, **A2**, 717 (1968).

[9] R. I. Hoaglin and D. H. Hirsh, *J. Amer. Chem. Soc.*, **71**, 3468 (1949).

toward *cis*- and *trans*-SEE's were studied kinetically in order to obtain information on the steric effect of attacking carbonium ions on the reactivities of SEE.



$$RCH(OC_2H_5)_2 + BF_3 \rightarrow RCH(OC_2H_5)^+ + BF_3\cdot C_2H_5O^-$$

$$C_6H_5CH{=}CH(OC_2H_5) \xrightarrow{+RCH(OC_2H_5)^+} \underset{OC_2H_5}{RCH}-\underset{C_6H_5}{CH}-CH(OC_2H_5)^+ \xrightarrow[-BF_3]{+BF_3\cdot C_2H_5O^-} \underset{OC_2H_5}{RCH}-\underset{C_6H_5}{CH}-CH(OC_2H_5)_2$$

From the results obtained, the factors influencing the *cis*-*trans* reactivities have been discussed.

Experimental

Materials. SEE was obtained as described previously[10] and distilled from calcium hydride under dry nitrogen immediately before use.

1,1-Diethoxyethane and 1,1-diethoxypropane were prepared by the method described previously.[4] 1,1-Diethoxybutane and 1,1-diethoxy-2-methylpropane were prepared from appropriate aldehydes and ethanol.[4,11] The boiling points were 144—146°C and 136—137°C, respectively. All the acetals were purified by distillation from metallic sodium.

Methylene chloride, tetralin, *o*-dichlorobenzene and boron trifluoride etherate ($BF_3\cdot OEt_2$) were purified as described previously.[1,12]

Cationic Polymerization. Polymerization technique was essentially the same as that described previously.[1]

Polymerization temperature (−70 to −20°C) was controlled to within ±0.5°C with a bath filled with dry ice-cold methanol. Monomer concentrations were determined by means of a Shimadzu gas chromatograph Model 4APT. A 3-m column packed with Apiezon Grease L was operated at *ca.* 130°C with hydrogen as a carrier gas. The internal standard method with half-height width evaluation of peak areas was applied for determining the monomer concentrations. Tetralin or dichlorobenzene was used as internal standard.

For experiments conducted at −70°C, the monomer reactivity ratios were evaluated with the aid of the integral form of the Mayo-Lewis copolymerization equation.[1] In all other cases, the monomer reactivities were evaluated from the slopes of the linear plots of the logarithms of instantaneous concentrations of *cis*-SEE *vs.* those of the *trans*-SEE isomer.

Acetal Addition. The method of the reaction was the same as that described previously.[4] The reaction was allowed to take place in excess acetal at 0°C with $BF_3\cdot OEt_2$ as catalyst. The residual ethers were determined by gas chromatography as in cationic polymerization.

Results

Cationic Copolymerization. A nearly equimolar mixture of *cis*- and *trans*-SEE's was copolymerized in methylene chloride at temperatures between 0 and −70°C. Concentration of each comonomer decreased with the progress of reaction in such a way that a linear relationship held between log[*cis*-SEE] and log[*trans*-SEE] down to at least 80% conversion of the *trans* isomer. The linear relationships at various temperatures are shown in Fig. 1. These results evidently indicate that no geometrical isomerization accompanies the polymerization reaction in the temperature range we studied. The slopes of these linear relationships may then be taken as indicating the relative reactivity *r* of *cis*- to *trans*-SEE at the given temperatures:

$$r = \frac{\log [cis\text{-SEE}]/[cis\text{-SEE}]_0}{\log [trans\text{-SEE}]/[trans\text{-SEE}]_0} \qquad (1)$$

where the subscript 0 indicates initial concentrations.

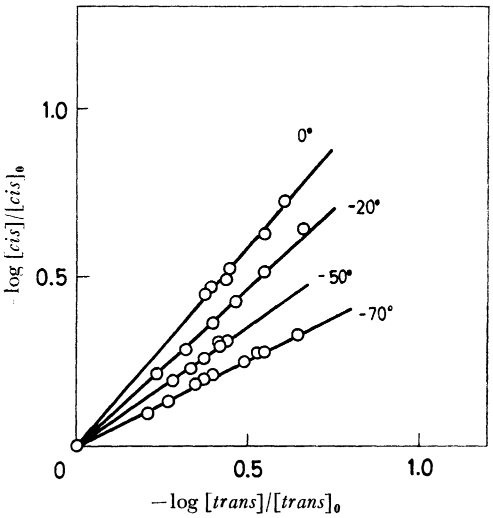


Fig. 1. Variations of monomer concentrations in the mutual copolymerization between *cis*- and *trans*-styryl ethyl ethers at various temperatures. Solvent, methylene chloride. Initial monomer concentration, 7 vol%, in which $[cis\text{-SEE}]_0/[trans\text{-SEE}]_0 = 1.08—1.34$. Catalyst, $BF_3\cdot OEt_2$.

In principle, the above treatment is based on the assumption that the monomer selection in the chain growth is governed by the statistics of the Bernoullian type:

$$r_{cis} r_{trans} = 1 \qquad (2)$$

Strictly, it is only when Eq. (2) is satisfied that the

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[10] T. Okuyama, T. Fueno and J. Furukawa, This Bulletin, **43**, 3256 (1970). Part X of this series.

[11] H. Adkins and B. H. Nissen, "Organic Syntheses," Coll. Vol. 1, p. 1 (1932).

[12] T. Fueno, T. Okuyama, I. Matsumura and J. Furukawa, *J. Polym. Sci. A*-1, **7**, 1447 (1969).

customary equation for binary copolymerization can be replaced by an expression of the type of Eq. (1).

In order to examine whether the relative reactivity as determined from Eq. (1) really makes sense, we have undertaken the usual copolymerization experiments between *cis*- and *trans*-SEE's of varying isomeric ratios at −70°C. The least-squares treatment[12] (Fig. 2) of the data with the aid of the integral form of the Mayo-Lewis copolymerization equation gave $r_{cis}=0.46\pm0.08$ and $r_{trans}=1.42\pm0.25$. The monomer reactivity ratios thus obtained lead to the $r_{cis}r_{trans}$ product value amounting only to 0.65 ± 0.26, which clearly violates the requirement (2). In such a case, the relative reactivity may best be estimated[1,2] from the value of $(r_{cis}/r_{trans})^{1/2}$. The relative reactivity thus evaluated turned out to be 0.57, which is in perfect agreement with the value 0.58 obtained from Eq. (1) at the same temperature. Thus, the convenient log—log method for evaluating the relative reactivity seems to be useful for copolymerization systems including the cases where the condition (1) is not rigorously satisfied.

The relative reactivity data evaluated from the plots in Fig. 1 are listed in Table 1. At lower temperatures, *cis*-SEE is less reactive than *trans*-SEE. However, the relative reactivity of the former isomer tends to increase with the rise in temperature and exceeds that of the latter at 0°C.

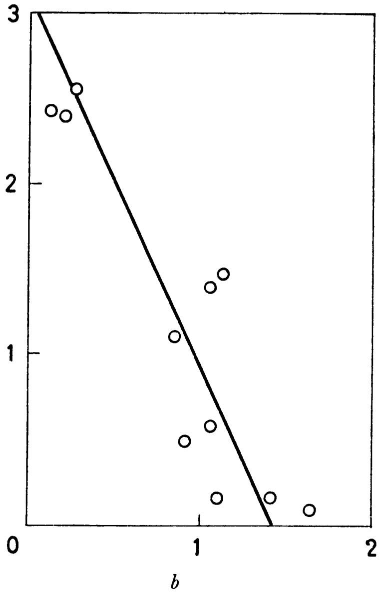


Fig. 2. An *m*-*b* plot for copolymerization between *cis*- and *trans*-styryl ethyl ethers at −70°C.

Quantities *m* and *b* were determined experimentally with the aid of the integral form of the Lewis-Mayo copolymerization equation and are related with the monomer reactivity ratios by $b=-r_{cis}m+r_{trans}$.[12]

Solvent, methylene chloride. Initial monomer concentration, 7 vol%. Catalyst, $BF_3\cdot OEt_2$ (0.024 M).

Table 1. Relative cationic polymerizabilities of *cis*- to *trans*-styryl ethyl ether

Temp., °C	Rel. polym. *cis*/*trans*
−70	0.58
−50	0.71
−20	0.94
0	1.16

Acetal Additions. Additions of various acetals to SEE have been carried out at 0°C with the use of $BF_3\cdot OEt_2$ as catalyst in excess of acetals themselves. An example of the kinetic courses is shown in Fig. 3. From such kinetic courses which are first-order in SEE (for *cis* and *trans* separately), relative reactivities of geometrical isomers have been evaluated and given in Table 2. The relative reactivities are largely dependent on the attacking acetals. For acetals of normal aldehydes, the *cis* isomer is more reactive, while, for the acetals of

Table 2. Relative reactivities of *cis*- to *trans*-styryl ethyl ether toward various alkoxycarbonium ions, $RCH(OC_2H_5)^+$

R	E_s	Rel. react. *cis*/*trans*
CH_3	0	4.26
C_2H_5	−0.07	2.26
n-C_3H_7	−0.36	1.47
i-C_3H_7	−0.47	0.61

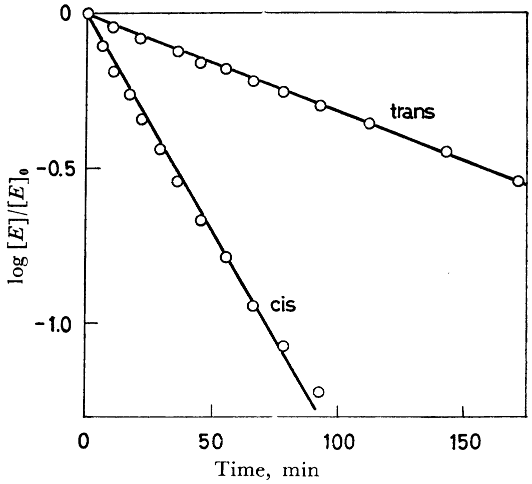


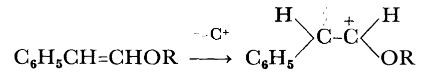
Fig. 3. First-order plots for the reaction of 1,1-diethoxyethane with *cis*- and *trans*-styryl ethyl ethers at 0°C.

Initial concentration, 9 vol%, in which $[cis\text{-SEE}]_0/[trans\text{-SEE}]_0=1.10$. Catalyst, $BF_3\cdot OEt_2$ (8×10^{-3} M).

branched aldehydes, the *trans* isomer is more reactive.

Discussion

Orientation in Polymerization. The head-to-tail orientation of SEE in cationic polymerization might not be intuitively obvious. Mizote *et al.*[8] concluded from the studies on polymerization kinetics that styryl alkyl ethers polymerize through the β-addition of a polymer chain end.



$$C_6H_5CH{=}CHOR \xrightarrow{\sim C^+} \overset{H}{\underset{C_6H_5}{>}}C\text{-}\overset{+}{C}\overset{H}{\underset{OR}{<}} \qquad (3)$$

The conclusion seems to be reasonable from the stability of an intermediate carbonium ion. An alkoxycarbonium ion is recognized to be more stable than benzyl-type cations.[13] The previous investigation[10] on the acid-catalyzed hydrolysis ascertained that the protonation of SEE takes place at the β-carbon atom:

$$C_6H_5CH{=}CHOC_2H_5 \xrightarrow{+H^+} C_6H_5CH_2\overset{+}{C}HOC_2H_5$$
$$\xrightarrow{+H_2O} C_6H_5CH_2CHO + C_2H_5OH \qquad (4)$$

a fact which lends support to the reaction mode as represented by (3).

***cis-trans* Polymerizability.** At lower temperatures, *cis*-SEE is less reactive than *trans*-SEE. However, the relative reactivity is considerably dependent on temperature as is seen in Table 1. From the Arrhenius-type plots of the data, the differences in activation parameters have been evaluated to be $\delta\Delta H^{\neq}=1.4$ kcal/mol and $\delta\Delta S^{\neq}=5.6$ e.u. That is, the *trans* isomer is energetically more reactive by 1.4 kcal/mol. This is contradictory to the expectationfrom the ground-state stability[16] and seems to be ascribable to the structural difference between the geometrical isomers; *cis*-SEE is non-planar whereas *trans*-SEE is planar as has been concluded previously.[10,17]

One possible interpretation is that the twisted phenyl group in *cis*-SEE hinders an attacking carbonium ion from approaching the olefinic bond, thus rendering the transition state of polymerization far less stable for *cis*-SEE than for *trnas*-SEE. The looser activated complex for the *cis* isomer might be rationalized from its greater entropy of activation as compared with that for the *trans* isomer. The situation seems to be similar to that in the acid-catalyzed hydrolysis.[10]

A greater reactivity of *trans* isomer has been noted or the cationic polymerization of β-methylstyrene and a similar reasoning has been presented.[6,7] In the investigation of the cationic oligomerization of stilbene, Brackman and Plesch[18] estimated that the rate of reaction of a stilbene ion with *trans*-stilbene is at least one hundred times as great as that of its reaction with *cis*-stilbene. The large difference in reactivity was likewise ascribed to steric reasons.

Acetal Additions. The addition reaction of an acetal to α,β-unsaturated ethers is essentially an addition of the alkoxycarbonium ion formed from the acetal to the double bond of ethers.[4,9] Thus, the primary reaction is the same as that of the propagation step of the cationic polymerization of ethers.[4]

The data given in Table 2 indicate that the relative reactivities of *cis*- and *trans*-SEE's are largely dependent on the attacking carbonium ions, $RCH(OC_2H_5)^+$. The magnitude of reactivity seems to be influenced primarily by the bulkiness of carbonium ion. Reactivity of the *cis* isomer relative to the *trans* isomer tends to decrease with the increasing bulkiness (Taft's steric substituent constants E_s[19]) of group R.

The present observation is consistent with the conclusion that the greater reactivity of the *trans* isomer in the cationic polymerization of SEE is due to steric reasons. The steric hindrance in the reaction becomes greater as the attacking species becomes bulkier, and thus the *cis* isomer becomes less reactive with the increasing bulkiness of R in acetals.

In terms of the electronic factor, on the other hand, *cis*-SEE may be considered to be more reactive than *trans*-SEE, as has been observed with a simple acetal. This seems to be related with the observation[1,2,5] that all the β-substituted vinyl ethers studied so far are more reactive in the *cis* form in cationic polymerization, irrespective of the relative thermochemical stabilities of geometrical isomer pairs. The coincidence is reasonable, since from the viewpoint of reaction mode SEE can be considered as a vinyl ether derivative rather than a styrene derivative.

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[13] The appearance potential of $CH_3OCH_2^+$ is lower than that of $C_6H_5CH_2^+$,[14] and α-chloromethyl ethers are easily solvolyzed as compared with benzyl chloride.[15]

[14] R. W. Taft, R. H. Martin and F. W. Lampe, *J. Amer. Chem. Soc.*, **87**, 2490 (1956).

[15] H. Böhme, *Ber.*, **74**, 248 (1941).

[16] *trans*-SEE is thermochemically more stable than the *cis* isomer.[17]

[17] T. Okuyama, T. Fueno and J. Furukawa, *Tetrahedron*, **25**, 5409 (1969).

[18] D. S. Brackman and P. H. Plesch, *J. Chem. Soc.*, **1958**, 3563.

[19] R. W. Taft, Jr., "Steric Effects in Organic Chemistry," ed. by M. S. Newman, John Wiley & Sons, Inc., New York, N.Y. (1956), Chapter 13.