BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3553—3556 (1970)

Structure and Reactivity of α,β-Unsaturated Ethers. XII. Cationic Copolymerization of Ring-Substituted Styryl Ethyl Ethers

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(Received June 1, 1970)

Several ring-substituted derivatives of *cis*- and *trans*-styryl ethyl ethers were copolymerized with the unsubstituted *trans* ether in methylene chloride at $-70°C$ with the use of boron trifluoride etherate as a catalyst. The ring substituents investigated include p-CH_3O, p-CH_3, m-CH_3, p-Cl, and m-Cl. It was found that the effects of substituents on the polymerizability obey the Hammett $\rho\sigma$ relationship with reaction constants $\rho=-2.4$ and -2.0 for *cis* and *trans* isomers, respectively. The structure of the transition state of the cationic polymeization was discussed.

There are many reports concerning the effects of ring substituents on various types of side-chain reactions of benzene derivatives.[1,2] In polymer chemistry, styrene and its derivatives are a typical class of compound which can be subjected to investigation. Thus, the effects of ring substituents on the polymerizability of styrene have been studied under various polymerization conditions.[3-6] Studies have recently been extended to the cationic copolymerization of phenyl vinyl ethers.[7]

We reported the cationic polymerization of styryl ethyl ether (SEE) with particular attention to the relative reactivities of its geometrical isomers.[8] Cationic polymerization of SEE takes place through the addition of a polymer chain-end on the carbon *alpha*[9] to the phenyl group.

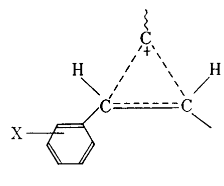
$$C_6H_5CH{=}CHOC_2H_5 \xrightarrow{\sim\sim C^+} \sim\sim\overset{C_6H_5}{\underset{H}{C}}-\overset{+}{C}\begin{smallmatrix}H\\ OC_2H_5\end{smallmatrix} \qquad (1)$$

This presents a striking contrast to the cationic polymerization of styrene, in which a chain-end addition occurs on the *beta*-carbon.[9]

$$C_6H_5CH{=}CH_2 \xrightarrow{\sim\sim C^+} \sim\sim CH_2-\overset{+}{C}\begin{smallmatrix}H\\ C_6H_5\end{smallmatrix} \qquad (2)$$

Thus, it seems interesting to compare the effects of ring substituents on the cationic polymerizability of SEE with those of styrene.

In the present investigation, *trans*-SEE has been copolymerized with several of its own ring-substituted derivatives as well as various *cis*-SEE derivatives in methylene chloride at $-70°C$, using $BF_3 \cdot OEt_2$ as a catalyst. The results have been examined in comparison with those of related reactions. From the magnitude of the reaction constants, it has been suggested that the cationic polymerization of SEE as well as that of styrene takes place through a cyclic intermediate.



Experimental

Materials. SEE and its ring-substituted derivatives were obtained as described previously[10] and distilled from calcium hydride under nitrogen atmosphere immediately before use.

Methylene chloride, tetralin and boron trifluoride etherate ($BF_3 \cdot OEt_2$) were purified as before.[7,11]

Procedure. Polymerization technique was the same as that described previously.[11] The relative reactivities were evaluated by the method of log-log plots.[8]

1) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y. (1940), Chapter 7.
2) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).
3) C. Walling, E. R. Briggs, K. B. Wolfstirn and F. R. Mayo, *J. Amer. Chem. Soc.*, **70**, 1537 (1948).
4) J. P. Kennedy, "Copolymerization," ed. by G. E. Ham, Interscience, New York, N. Y. (1964), p. 308.
5) M. Shima, D. N. Bhattacharyya and M. Szwarc, *J. Amer. Chem. Soc.*, **85**, 1306 (1963).
6) G. Natta, F. Dannuso and D. Sianesi, *Makromol. Chem.*, **30**, 238 (1959).
7) T. Fueno, T. Okuyama, I. Matsumura and J. Furukawa, *J. Polym. Sci.*, *A-1*, **7**, 1447 (1969).
8) T. Okuyama, N. Asami and T. Fueno, This Bulletin, **43**, 3549 (1970).
9) We use the words *alpha* and *beta* in reference to the olefinic carbon atoms located in the α- and β-positions, respectively, with respect to the phenyl ring. For this convention, see Ref. 10, Footnote 15.
10) T. Okuyama, T. Fueno and J. Furukawa, This Bulletin, **43**, 3256 (1970).
11) T. Okuyama, T. Fueno and J. Furukawa, *J. Polym. Sci.*, *A-1*, **6**, 993 (1968).

Results

Polymerization was carried out in methylene chloride at the dry ice-methanol temperature (*ca.* $-70°C$) with the use of $BF_3 \cdot OEt_2$ as a catalyst. *trans*-SEE was used as a reference monomer for all runs of copolymerization.

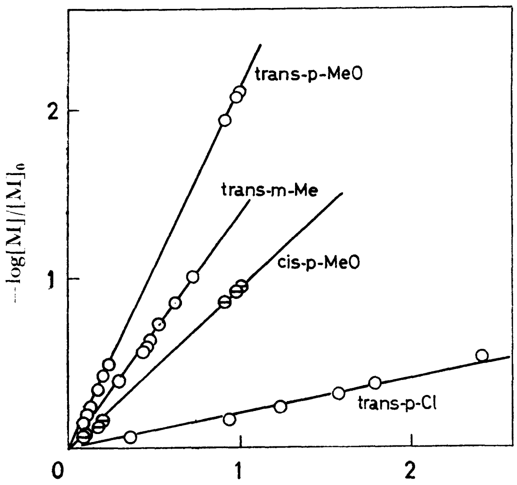


Fig. 1. Variations of monomer concentrations in the copolymerization of various ring-substituted SEE's with *trans*-SEE at $-70°C$: Solvent, methylene chloride; Catalyst, $BF_3 \cdot OEt_2$.

Examples of the courses of copolymerization between substituted SEE's and *trans*-SEE are shown in Fig. 1. Slopes of the linear relationships provide the relative reactivities[8] of the relevant SEE derivatives. The reactivity data thus obtained are summarized in Table 1.

TABLE 1. RELATIVE POLYMERIZABILITIES OF RING-SUBSTITUTED STYRYL ETHYL ETHERS AT $-70°C$

Substituent	Relative polymerizability	
	cis	*trans*
p-CH_3O	0.92	2.11
p-CH_3	0.65	1.98
m-CH_3	—	1.41
H	0.57	1.00
p-Cl	0.17	0.22
m-Cl	0.06	0.09

The reactivity of *trans*-m-CH_3-SEE (M_2) relative to *trans*-SEE (M_1) was also evaluated by the usual copolymerization experiments, in which variations of the comonomer composition were analyzed by the aid of the Mayo-Lewis copolymerization equation in an integral form. The *m-b* plot[7,8] pertinent to this analysis is shown in Fig. 2. The monomer reactivity ratios obtained were $r_1=0.62\pm0.01$ and

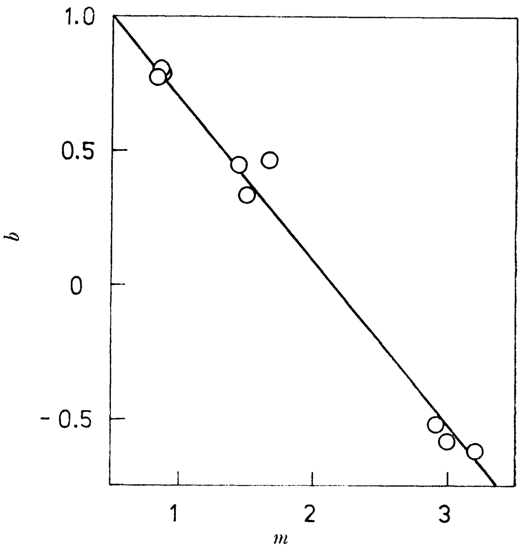


Fig. 2. The m–b plots for the copolymerization of *trans*-SEE (M_1) and *trans*-m-CH_3-SEE (M_2) at $-70°C$: Solvent, methylene chloride; Initial monomer concentration=8 vol%; Catalyst, $BF_3 \cdot OEt_2$ (0.024M).

$r_2=1.32\pm0.01$, which lead to the relative reactivity $(r_2/r_1)^{1/2}=1.45$, in essential agreement with the value, 1.41, listed in Table 1.

At the present polymerization temperature, the *trans* isomers are more reactive than the corresponding *cis* isomers. The polymerizability of SEE derivatives is clearly enhanced with the increase in the electron-releasing character of the ring substituents.

Discussion

Effects of Substituents. Figure 3 shows the Hammett plots of the observed polymerizabilities.

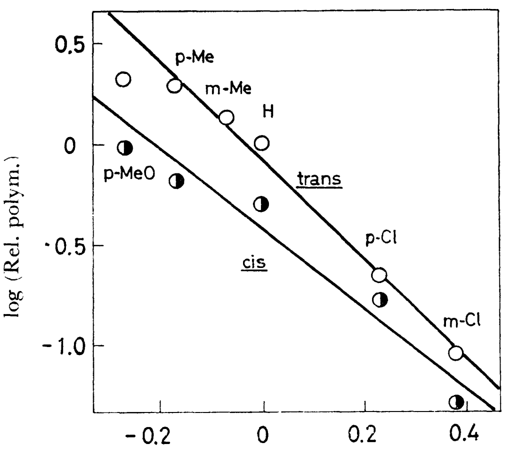


Fig. 3. The Hammett plots of cationic polymerizability of SEE derivatives.

TABLE 2. REACTION CONSTANTS FOR VARIOUS ELECTROPHILIC REACTIONS OF STYRYL COMPOUNDS, XC_6H_4–CH=CH–Y

No.	Compound	Y	Reaction	ρ	Intermediate[a]	Product orientation[b]	Ref.
1	*cis*-Cinnamic acid	COOH	Isomerization	−4.3	I	—	12
2[c]	Styrene	H	Bromination	−4.3	I	*beta*	13
3	Cinnamic acid	COOH	Chlorination	−4.01	I	*beta*	14
4	Styrene	H	Hydration	−3.43	I	*beta*	15
5	*cis*-Stilbene	C_6H_5	Isomerization	−3.30	I	—	16
6	Styrene	H	ArSCl addition	−2.41—−2.29	III	*beta*	17
7[d]	Styrene	H	Bromination	−2.24—−1.93	III	*beta*	18
8	Styrene	H	Cationic polymn	−2.03	?	*beta*	4
9	SEE	OC_2H_5	Cationic polymn	−2.4, −2.0	?	*alpha*	Present work
10	SEE	OC_2H_5	Hydrolysis	−1.1, −0.7	II	*alpha*	10
11	*cis*-Stilbene	C_6H_5	Isomerization	−0.96	II	—	16

a) See text.
b) Position of the addition of an electrophile in the product.
c) Substituents studied include p-CH_3O, p-CH_3, m-CH_3, and p-F.
d) Substituents studied include m-F, m-Cl, m-Br, m-NO_2, p-NO_2, and p, m-dichloro.

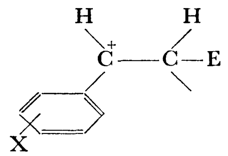
Although the substituents adopted for the plots are few in number, they still suffice to show a general trend. It appears that linear relationships hold for both *cis* and *trans* isomers. The reaction constants, ρ, are roughly −2.0 and −2.6 for *cis* and *trans* isomers, respectively.

These ρ values are comparable in magnitude with the value (−2.03) for the cationic polymerization of styrenes,[4] even though the reaction sites of SEE and styrene are different; the former polymerizes through the addition of polymer chain end on the carbon *alpha* to the phenyl group while the latter polymerizes through the addition on the *beta*-carbon. Therefore, it seems interesting to further examine the magnitudes of substituent effects in these reactions.

Magnitude of the ρ Values. The reaction constants of the Hammett $\rho\sigma$ relations for various electrophilic reactions of styryl compounds related to the present reaction range from −4.3 to −0.7, depending on the type of reaction. Examples in the literature are compared in Table 2.

The reactions listed in Table 2 can be classified by the magnitude of the ρ values into three groups; $\rho = -3.8 \pm 0.5$ (Nos. 1—5), *ca.* −2 (Nos. 6—9) and *ca.* −1 (Nos. 10 and 11).

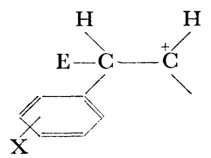
The first group undoubtedly consists of reactions involving an *alpha*-carbonium ion intermediate (I), which is produced by the electrophilic attack of reagents on the *beta*-carbon (with respect to the phenyl group).



I. *alpha*-Carbonium ion

The ρ values around −4 for the reactions involving the rate-determining formation of the *alpha*-carbonium ions (I) are also known for the solvolyses (S_N1) of benzyl-type compounds, $C_6H_5C(CH_3)_2Cl$ and $C_6H_5CH(CH_3)Cl$.[19] In this type of intermediate, charge delocalization into the phenyl group is very important and the effect of substituents on the charge delocalization should be great.

The last group of reactions with $\rho \simeq -1$ include those taking place with the attack of an electrophile on the carbon attached by the phenyl group, thus forming a *beta*-carbonium ion intermediate like II.



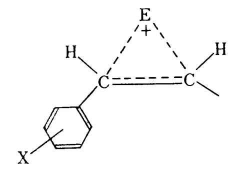
II. *beta*-Carbonium ion

This type of reaction has hitherto been known only in a very limited number; there are only two examples reported so far.[10,16] The smaller effects

12) D. S. Noyce, and H. S. Avarbock *J. Amer. Chem. Soc.*, **84**, 1644 (1968).
13) J. E. Dubois and A. Schwarcz, *Tetrahedron Lett.*, **1964**, 2167.
14) H. P. Rothbaum, I. Ting and P. W. Robertson, *J. Chem. Soc.*, **1948**, 980.
15) W. H. Schubert, B. Lamm and J. R. Keefe, *J. Amer. Chem. Soc.*, **86**, 4272 (1964).
16) D. S. Noyce, D. R. Hatter and F. B. Miles, *ibid.*, **90**, 4633 (1968).
17) W. L. Orr and N. Kharasch, *ibid.*, **78**, 1201 (1956).
18) K. Yates and W. V. Wright, *Can. J. Chem.*, **45**, 167 (1967).
19) *E. g.*, H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **79**, 1913 (1957).

of substituents are easily understandable since the carbonium-ion center is insulated from the ring by an intervening methylene group.

The second group, which have ρ values intermediate in magnitude (*ca.* -2), include the reactions of some intermediate character. In these reactions, addition of sulfenyl chlorides to olefins (No. 6) is well established to take place through cyclic episulfonium ions.[17,20] Bromination of styrenes (No. 7) carrying an electron-attracting substituent has been confirmed to occur with the formation of cyclic bromonium ions like III.[21]



III. α,β-Intermediate

Thus, the reactions seem to take place with simultaneous attack of an electrophile on both the α- and β-carbons forming an intermediate like III. Cationic polymerization of both styrenes and SEE's apparently belongs to this category and should involve the cyclic α,β-intermediate III.[22]

Styrene and SEE differ from each other in product orientation. The identical magnitudes of the ρ values for these two reactions may be reconciled if we assume a common mechanism involving the formation of a cyclic α,β-intermediate of type III. The cationic polymerization of vinyl ethers proceeds through the cyclic α,β-intermediate, which agrees with our previous conclusion obtained from the results of calculations of the transition state stability.[23] An experimental investigation[7] of the ring-substituent effects on the phenyl vinyl ether polymerizability also supports the low carbonium-ion character of the transition state. Our recent results on the cationic polymerizations of benzofuran derivatives lend further support to the validity of the α,β-intermediate mechanism.[24]

20) W. H. Mueller and P. E. Butler, *ibid.*, **90**, 2075 (1968); and references cited therein.

21) The conclusion was based on a comparison of the ρ-values of the first and second groups of reactions.[18]

22) This intermediate does not necessarily mean a symmetrical one with respect to the strength of the bonds which an electrophile formed with the α- and the β-carbons. Rather, some asymmetry must be present in view of the definite product orientation.

23) T. Fueno, T. Okuyama and J. Furukawa, *J. Polym. Sci., A-1*, **7**, 3219 (1969).

24) T. Okuyama, K. Kunugiza and T. Fueno, to be published.