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Substituent Effects in the Benzofuran System. III.[1] Cationic Polymerization

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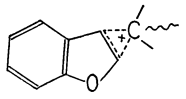
Cationic copolymerizations of various pairs of benzofuran derivatives have been carried out in CH_2Cl_2 using $SnCl_4$–CCl_3CO_2H (2: 1) as catalyst at 0 °C. Effects of 2- and 3-methyl substitutions on the monomer reactivity ratio suggested that the polymeric cation adds at the 2-carbon of benzofuran. Analysis of the effects of 5- and 6-substituents on the reactivity revealed that the transmission efficiency of electronic effects through the two paths, the bonds 8–3 and 9–1–2, is comparable in magnitude. It was concluded that the transition state of the propagation step closely resembles a bridged carbonium ion intermediate.

The bromination of benzofuran (BF) was treated in the preceding paper[1] as a typical example of electrophilic addition reactions. Cationic polymerization includes chain reactions of addition of a polymeric carbonium ion and can be classified as an electrophilic addition reaction.

Cationic polymerizability of BF has long been known since Kraemer and Spilker[2] noted the resinification upon treating BF with sulfuric acid. More recently, BF has attracted the attention of polymer chemists because of its possible formation of optically active polymers.[3] However, the orientation of the reaction is not established, being considered as styrene(ST)-type[4] or vinyl ether(VE)-type.[3b]

On the other hand, we have concluded, by a series of investigations on the structure-reactivity relationship of α,β-unsaturated ethers,[5] that the transition state in the carbonium-ion attack (propagation step) in the cationic polymerization closely resembles a symmetric cyclic carbonium ion like I.



I

This possible symmetric nature of the transition state can be judged by the analysis of the cross-ring transmission of the electronic effects of 5- and 6-substituents on the polymerizability of BF.

Thus, the present investigation concerns with the orientation of polymerization and the substituent effects on the reactivity of BF.

Results

Cationic copolymerizations of various pairs of BF derivatives were carried out in methylene chloride at 0 °C with the use of stannic chloride–trichloroacetic acid (2: 1) as catalyst. The reaction proceeds easily under these conditions; *e.g.*, *ca.* 30% conversion in 1 hr for the 1: 1 pair of BF and the 5-methyl derivative.

The monomer reactivity ratios calculated with the aid of the integral form of the Mayo-Lewis copolymerization equation[6] are given in Table 1. The table includes values of r_1r_2 and $(r_2/r_1)^{1/2}$. The products r_1r_2 provide information about the nature of an attacking polymeric cation and the values $(r_2/r_1)^{1/2}$ are considered to be the best estimation of relative polymerizability of M_2 and M_1.[6,7]

The 6-methoxy and 5-chloro derivatives showed reactivities greatly different from those of other derivatives, and accurate evaluation of the monomer reactivity ratios for the systems involving these derivatives has hardly been achieved. Hence, the reactivities of these derivatives have been estimated by the log-log method, which was conveniently used for the styryl ether system.[7] The relative polymerizability, r, of M_2 and M_1 is expressed as

TABLE 2. THE RELATIVE POLYMERIZABILITY, R, OF BENZOFURAN DERIVATIVES

Substituent	R[a]
H	(1.00)[b]
5-CH_3	4.81 ± 0.70
6-CH_3	6.03 ± 0.21
5-CH_3O	12.9 ± 0.9
6-CH_3O	241 ±24
5-Cl	0.017± 0.002

a) Shown with standard deviation.
b) Reference value.

TABLE 1. MONOMER REACTIVITY RATIOS[a] FOR THE CATIONIC COPOLYMERIZATION OF BENZOFURAN DERIVATIVES

Substituent M_1	Substituent M_2	r_1	r_2	r_1r_2	$(r_2/r_1)^{1/2}$
H	2-CH_3	0.25±0.06	0.74±0.01	0.19	1.72±0.24
H	3-CH_3	0.12±0.18	0.50±0.08	0.06	2.04±1.54
H	5-CH_3	0.21±0.06	4.86±0.24	1.02	4.81±0.70
H	5-CH_3O	0.16±0.01	5.83±0.17	0.93	6.03±0.21
5-CH_3O	6-CH_3	0.63±0.05	2.89±0.27	1.82	2.14±0.13
6-CH_3	6-CH_3O				18.7 ±1.3[b]
5-Cl	H				60.5 ±7.3[b]

a) Shown with standard deviation. b) Estimated by the log-log treatment.

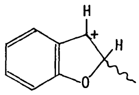
$$r=\frac{\log [M_2]/[M_2]_0}{\log [M_1]/[M_1]_0} \tag{2}$$

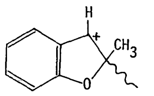
The results are included in Table 1.

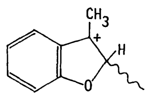
From $(r_2/r_1)^{1/2}$ and r values given in Table 1, the polymerizabilities, R, relative to the unsubstituted BF were calculated and summarized in Table 2. All the methyl and methoxy derivatives are more reactive than the parent BF. The 6-methoxy substitution greatly enhances the reactivity of BF. The 5-chloro derivative is *ca.* 1/60 as reactive as BF.

Discussion

Effect of the 2- and 3-Methyl Groups. As is seen in Table 1, the product r_1r_2 is much less than unity for the system comprising BF (M_1) and the 2- or 3-methyl derivative (M_2), implying the difference in the nature of attacking cations, M_1^+ and M_2^+. The methyl substitution at either of the 2- and 3-positions enhances the reactivity of BF toward $M_1^+ (r_1<1)$, whereas the methyl substitution reduces the reactivity of BF toward $M_2^+ (r_2<1)$. The reduction in the reactivity must be attributed to the steric effect of the methyl group close to the reaction center. This steric effect is greater for the 3-methyl than for the 2-methyl group, suggesting the formation of 3-cation. That is, the orientation of the ST-type in polymerization is very probable, in accord with the results of bromination.[1]





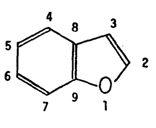


The enhancement in reactivity toward M_1^+ by either 2- or 3-methyl substitution (4 or 8 times) may be reasonably explained by assuming a cyclic onium-type transition state.[8]

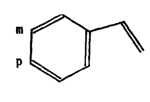
Cross-ring Substituent Effects. The effects of 5- and 6-substituents on the polymerizability of BF given in Table 2 can be analyzed by the Jaffé equation;[9]

$$\log R=\rho_1\sigma_1+\rho_2\sigma_2 \tag{3}$$

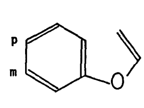
where suffixes 1 and 2 refer to the values concerning the transmitting routes 8–3 (ST-type) and 9–1–2 (PVE-type), respectively.



BF



ST



PVE

The least-squares treatment of R according to Eq. (3) gave $\rho_1=-3.39\pm0.19$ and $\rho_2=-2.79\pm0.34$. Brown-Okamoto's σ^+ values were used for σ_1. Linearity of the calculated and the observed values of $\log R$ is illustrated in Fig. 1.

The contribution of the PVE-type transmission to the observed substituent effects is nearly as great as that of the ST-type in spite of the orientation of addition of the ST-type. This situation is similar to that of bromination.[1] These observations can be considered to be characteristic of symmetric transition state resembling a cyclic onium ion like I and seem to be explainable only by this assumption. Thus, the course of polymerization is represented by

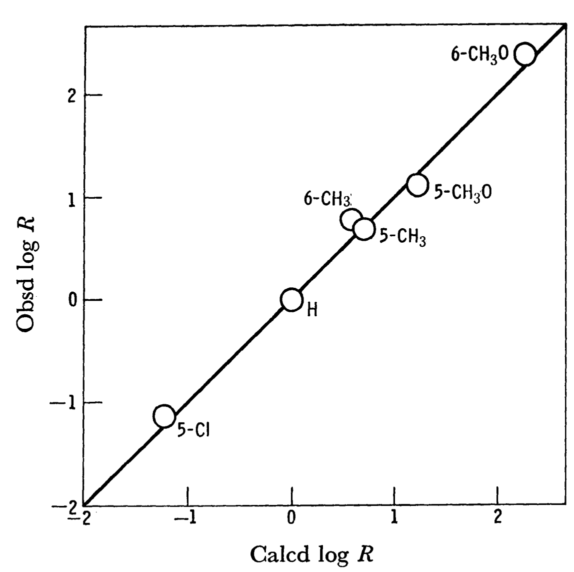
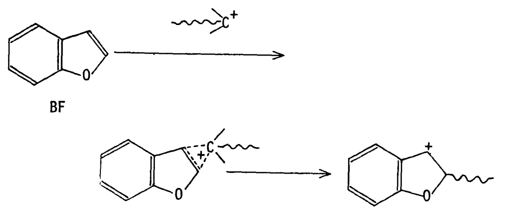


Fig. 1. Linearity of the observed and the calculated log R values (Eq. (3)).



(4)

I

The possibility of symmetric transition state like I has already been suggested by us for the cationic polymerization of vinyl monomers on the basis of various sources of evidence.[5] The present results provide additional confirmative evidence to support our earlier suggestion.[5]

The values ρ_1 and ρ_2 are compared with those for the cationic polymerization of ST and PVE; $\rho_{ST}^+=-2.03$[10] and $\rho_{PVE}=-1.76$.[11] Both ρ_1 and ρ_2 are appreciably greater in magnitude than ρ_{ST} and ρ_{PVE}, respectively. However, relative magnitude, $\rho_2/\rho_1=0.82$, is close to $\rho_{PVE}/\rho_{ST}=0.87$. The transmission efficiency through oxygen atom in cyclic compound, BF, is close to that in acyclic system, PVE.

All the observations in the BF polymerization conforms to the symmetric cyclic transition state which structurally resembles I.

Experimental

Materials. Benzofuran (BF) and its derivatives were obtained as described previously.[12] Methylene chloride was dried and distilled from calcium hydride. Tetralin and stannic chloride were purchased and distilled. Trichloroacetic acid was of the best grade commercially available.

Polymerization. Cationic copolymerization was carried out in methylene chloride under a nitrogen atmosphere at 0 °C by using stannic chloride–trichloroacetic acid (2: 1) as catalyst. Monomer and catalyst concentrations were usually

7 vol% and 0.03 M, respectively. The detailed procedure was the same as described before.⁶⁾ Monomer reactivity ratios were calculated with the aid of the integral form of the Mayo-Lewis copolymerization equation by the least-squares method based on the VPC analysis as described previously.⁶⁾ The relative polymerizability of a great magnitude was estimated by the relative monomer consumption method (the log-log treatment).⁷⁾

Roferences

1) Part II. T. Okuyama, K. Kunugiza, and T. Fueno, This Bulletin, the preceding paper.

2) G. Kraemer and A. Spilker, *Ber.*, **23**, 78 (1890).

3) (a) G. Natta, M. Farina, M. Peraldo, and G. Bressan, *Makromol. Chem.*, **43**, 68 (1961); (b) Y. Takeda, Y. Hayakawa, T. Fueno, and J. Furukawa, *ibid.*, **83**, 234 (1965); (c) Y. Hayakawa, T. Fueno, and J. Furukawa, *J. Polym. Sci. A-1*, **5**, 2099 (1967).

4) A. Mizote, T. Tanaka, T. Higashimura, and S. Okamura, *J. Polym. Sci. A-1*, **4**, 869 (1966).

5) See for a review, T. Okuyama and T. Fueno, *Kobunshi Kagaku*, **28**, 369 (1971).

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

7) T. Okuyama, N. Asami, and T. Fueno, This Bulletin, **43**, 3549 (1970).

8) G. M. Beverly and D. R. Hogg, *J. Chem. Soc. B*, **1971**, 175; R. C. Fahey and H. J. Schneider, *J. Amer. Chem. Soc.*, **90**, 4429 (1968).

9) H. H. Jaffé, *ibid.*, **76**, 4261 (1954).

10) J. P. Kennedy, in "Copolymerization," G. E. Ham, Ed., Interscience, New York, N. Y., 1964, p. 308.

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

12) T. Okuyama and T. Fueno, This Bulletin, **47**, 1263 (1974).