Effects of Substituents on Chain Transfer Reactivities of Substituted Cumenes toward the Poly-*p*-chlorostyryl Radical*[1]

Tadahiro Yamamoto*[2] and Takayuki Otsu

Department of Applied Chemistry, Faculty of Engineering, Osaka City University,
Sugimotocho, Sumiyoshi-ku, Osaka

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It has been reported that the reactivities of a series of compounds toward a radical can be correlated with the modified Hammett equation (1) including the resonance term[1]:

$$\log (k/k_0) = \rho \sigma + \gamma E_R \qquad (1)$$

where E_R and σ are resonance and polar substituent constants (see Table 1), and where γ and ρ are reaction constants giving, respectively, the susceptibilities of resonance and polar effects caused by the substituents. In a reaction in which the resonance effect by the substituents is not important, *i. e.* when $\gamma=0$, Eq. (1) comes to be equal to the ordinary Hammett equation.

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*[1] Vinyl Polymerization. 183.

*[2] Present address: Himeji Institute of Technology, Himeji.

[1] T. Otsu and T. Yamamoto, *Yuki Gosei Kagaku Kyokaishi (J. Soc. Org. Synth. Chem., Japan)*, **23**, 643 (1965); *Chem. and Ind.*, **19**, 787 (1967).

In previous papers[2-4] it was found that the chain-transfer reactivities of nuclear-substituted cumenes toward some polymer radicals are expressed by Eq. (1) rather than by the ordinary Hammett equation. In order to clarify further the effect of the substituents in the attacking radical, the present paper will describe our findings on the chain-transfer reactivities of substituted cumenes in the radical polymerization of *p*-chlorostyrene.

Experimental

Nuclear-substituted cumenes were prepared by the method described in a previous paper.[2] *p*-Chlorostyrene was obtained according to the procedure of Brooks.[5]

Polymerizations of *p*-chlorostyrene in the presence of cumenes were carried out in a sealed tube using α, α'-azobisisobutyronitrile (4.66×10^{-3} mol/*l*) at 60°C. After the polymerization to *ca.* 5% conversion, the resulting polymer was isolated by the addition of a large amount of methanol.

The number-average degrees of the polymerization ($\bar{P}_n$) of the polymers were calculated from their intrinsic viscosities ($[\eta]$) determined in benzene, according to the following equation[6]:

$$\log \bar{P}_n = 3.419 + 1.29[\eta]$$

The chain-transfer constants (C) of cumenes were determined by means of the Mayo plots[7] between $1/\bar{P}_n$ and the concentration of the cumenes.

Results and Discussion

The chain-transfer constants of cumenes are summarized in Table 1.

TABLE 1. CHAIN-TRANSFER CONSTANTS OF CUMENES IN THE POLYMERIZATION OF *p*-CHLOROSTYRENE AT 60°C

p-Sustituents in cumenes			$C\times10^4$
Kind	σ	E_R	
OCH_3	-0.268	0.11	3.86
t-C_4H_9	-0.197	0.03	3.52
i-C_3H_7	-0.15	0.03	7.24 (3.62)*
H	0.00	0.00	3.44
Cl	0.227	0.10	4.97
Br	0.232	0.12	5.71
CN	0.660	0.24	8.84

* This value indicates the C value per isopropyl group.

In Table 1 it can be seen that the C values of *p*-substituted cumenes are greater than that (C_0) of unsubstituted cumene, regardless of whether the substituents are electron-attracting or electron-repelling. Figure 1 shows the plots by the ordinary Hammett equation and Eq. (1).

As the dotted line in Fig. 1 shows, the Hammett plots did not give a straight-line relationship. By assuming that $\gamma=1.0$ in Eq. (1), however, the plots between $\log(C/C_0)-E_R$ and σ constants were found to give a good straight line, with $\rho=+0.2$. Therefore, it was obvious that the resonance effect of the substituents on the chain-transfer reactivities of cumenes was as important as their polar effects.

TABLE 2. REACTION CONSTANTS IN EQ. (1)

Attacking radical	ρ	γ	Ref.
Poly-*p*-methylstyryl	0.8	1.1	3
Polystyryl	0.7	1.0	2
Poly-*p*-chlorostyryl	0.2	1.0	This work
Polymethyl methacrylate	0.03	0.9	4

Similar observations were obtained regarding the chain-transfer reactivities of cumenes toward attacks of polystyryl,[2] poly-*p*-methylstyryl,[3] and polymethyl methacrylate radicals.[4] The reaction constants obtained from the plots of Eq. (1) are summarized in Table 2.

As can be seen from Table 2, the ρ values regularly changed with the polar nature of the substituents in the attacking radical; *i. e.*, the introduction of the electron-attracting substituent decreased the ρ value. However, the γ values obtained were observed to be almost unchanged by the substituents in the attacking radical.

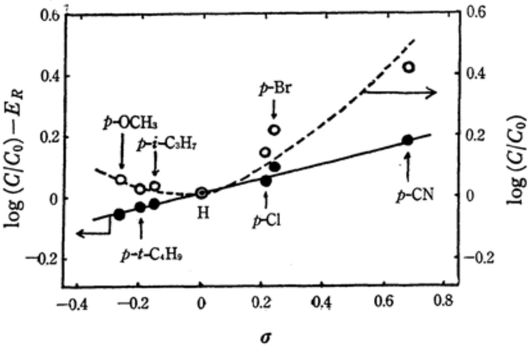

Fig. 1. Plots by the ordinary Hammet equation and by Eq. (1).

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[5] L. A. Brooks, *J. Am. Chem. Soc.*, **66**, 1295 (1944).
[6] N. Fuhrman and R. R. Mesrobian, *ibid.*, **76**, 3281 (1954).
[7] F. R. Mayo, *ibid.*, **65**, 2324 (1943).