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Effects of Substituents on the Chain-transfer Reactivities of Nuclear-substituted Benzaldehydes to Polymer Radicals

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In order to study the effect of substituents on the chain-transfer reactivities of nuclear-substituted benzaldehydes toward polymethyl methacrylate (poly-MMA) and polystyryl (poly-St) radicals, the chain transfer constants (C) of six kinds of benzaldehydes in radical polymerizations of these monomers were determined at 60°C. The C values of all the substituted benzaldehydes toward the poly-MMA radical were larger than that of unsubstituted benzaldehyde, regardless of the electron-repelling or electron-attracting nature of the substituents, while those toward the poly-St radical increased with an increase in the electron-attracting nature of the substituents. The relative reactivities toward the poly-MMA radical could not be correlated with the ordinary Hammett equation, but they could be with this modified equation: $\log(k/k_0)=\rho\sigma+\gamma E_R$, with $\rho=+0.2$ and $\gamma=0.7$. On the other hand, the relative reactivities toward the poly-St radical also fit a modified Hammett equation with $\rho=+1.4$ and $\gamma=0.65$.

One of the most interesting problems in vinyl polymerization is to clarify the relationship between the structure and the reactivity toward the attack of a polymer radical. In connection with this problem, we have investigated the effects of substituents on the chain-transfer reactions of the nuclear-substituted cumenes[1] and toluenes[2] toward various polymer radicals. From the results of these investigations, we have found that their chain-transfer reactivities are correlated not with the ordinary Hammett equation, but with a modified Hammett equation[3] including the resonance term:

$$\log (k/k_0) = \rho\sigma + \gamma E_R \tag{1}$$

where σ is the polar substituent constant; E_R, the resonance one, and ρ and γ, reaction constants giving, respectively, the degree of the polar and resonance contributions by the substituents. Clearly these results suggest that neither the resonance effect nor the polar effect of the substituents on these chain-transfer reactions should be disregarded.

The present investigation was undertaken in order to ascertain further the effect of substituents on the chain-transfer reactivities of another substrate toward a polymer radical. As substrates, six kinds of nuclear-substituted benzaldehydes were chosen. It was known that the abstraction of a hydrogen atom on the carbonyl group of benzaldehyde is easier than that on the side-chain atom of hydrocarbons.[4] Since the benzaldehyde has an oxygen atom of the carbonyl group which lies beside the reacting side-chain hydrogen atom, its substituent effect may be expected to be different from those observed in the reactions of cumenes and toluenes.[1,2]

This paper will describe the effect of substituents on the chain-transfer reactivities of nuclear-substituted benzaldehydes toward poly-MMA and poly-St radicals, as evaluated from the results of the polymerizations of methyl methacrylate and styrene in the presence of the benzaldehydes, using α,α'-azobisisobutyronitrile (AIBN) as the initiator.

Experimental

Materials. The nuclear-substituted benzaldehydes used in this study had the following substituents: *p*-methoxy, *p*-chloro, H, *p*-bromo, *m*-chloro, and *p*-cyano. The *m*-chlorobenzaldehyde and *p*-cyanobenazldehyde were synthesized as follows. The *m*-chlorobenzaldehyde was prepared from *m*-aminobenzaldehyde through a Sandmeyer reaction; bp 84—86°C/8 mmHg (lit.,[5]

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[1] a) T. Yamamoto, This Bulletin, **40**, 642 (1967). b) T. Yamamoto and T. Otsu, *J. Polymer Sci.*, **A-6**, 49 (1968). c) T. Yamamoto and T. Otsu, *ibid.*, **B-4**, 1039 (1966); This Bulletin, **40**, 2449 (1967); *Kogyo Kagaku Zasshi* (*J. Chem. Soc. Japan, Ind. Chem. Sect.*), **70**, 2403 (1967).

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84—86°C/8 mmHg). The *p*-cyanobenzaldehyde was prepared from *p*-cyanobenzyl bromide according to the procedure of Hass and Bender;[6] mp 95°C (lit.,[6] 95—96°C). The other substituted benzaldehydes were commercial materials used after purification.

All these substituted benzaldehydes except for the *p*-cyano-derivative, methyl methacrylate (MMA), and styrene were redistilled in a stream of nitrogen under reduced pressure before use.

Polymerization Procedure. The polymerizations of MMA and styrene in substituted benzaldehydes were carried out at 60°C in the presence of AIBN (3.32×10^{-3} mol/*l*) as the initiator. After a given reaction time, the resulting polymer was isolated by pouring the polymerizing mixture into an excess of methanol. Polymerization was controlled below 10% conversion.

Calculation of Number-average Degree of Polymerization ($\bar{P}_n$) and Chain-transfer Constant (*C*). The resulting polymer was purified by reprecipitating it from a benzene solution into a large amount of methanol. The intrinsic viscosty $[\eta]$ of the polymers was determined by the viscosity measurement of its benzene solution at 30°C using an Ubbelohde viscometer. The $\bar{P}_n$ was calculated from the intrinsic viscosity obtained according to the following equations, (2) and (3):

$$\text{Poly-MMA:}^{7)}\ \log(\bar{P}_n) = 3.420 + 1.13\log[\eta] \qquad (2)$$

$$\text{Poly-St:}^{8)}\ \log(\bar{P}_n) = 3.205 + 1.37\log[\eta] \qquad (3)$$

The chain-transfer constants ($C=k_{tr}/k_p$) to benzaldehydes were determined by the Mayo equation (4):

$$1/\bar{P}_n = \text{Constant} + C[\text{S}]/[\text{M}] \qquad (4)$$

where [S] and [M] are the initial concentrations of benzaldehydes and the monomer respectively.

Results and Discussion

The plots of the $1/\bar{P}_n$ of the polymers obtained against [S]/[M] are shown in Figs. 1 and 2. According to Eq. (4), from the slopes of the straight lines the chain-transfer constants were calculated to be as tabulated in Table 1. This table also shows the σ and E_R constants for the substituents used.

Chain-transfer Reactivities of Benzaldehydes with the Poly-MMA Radical. In Table 1 the resulting *C* values of substituted benzaldehydes may be seen to be larger than that of unsubstituted benzaldehyde, regardless of the electron-attracting or electron-repelling character of the substituents. The plot of the logarithms of the relative chain-transfer reactivities ($C/C_0=k/k_0$) toward the attack of the poly-MMA radical on the Hammett σ constants of the corresponding substituents is shown

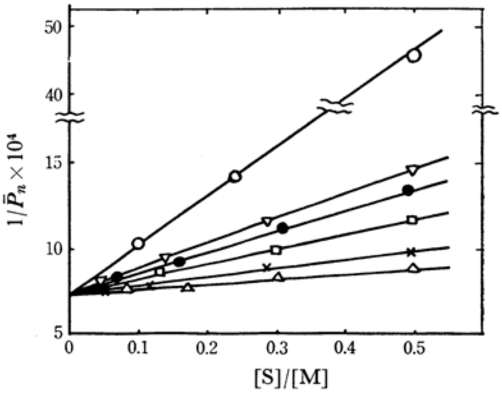

Fig. 1. The plots by Eq. (4) for the polymerization of styrene in the presence of substituted benzaldehydes at 60°C: ○ *p*-CN, ▽ *m*-Cl, ● *p*-Cl, □ H, × *p*-OCH$_3$, △ *p*-Br benzaldehydes.

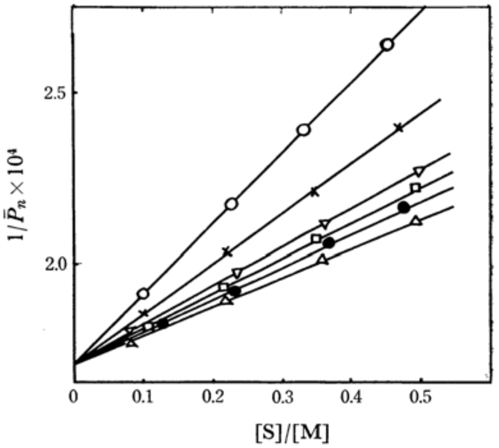

Fig. 2. The plots by Eq. (4) for the polymerization of MMA in the presence of substituted benzaldehydes at 60°C: ○ *p*-CN, × *p*-Br, ▽ *p*-OCH$_3$, □ *p*-Cl, ● *m*-Cl, △ H benzaldehydes.

TABLE 1. CHAIN-TRANSFER CONSTANTS (*C*) OF SUBSTITUTED BENZALDEHYDES IN THE RADICAL POLYMERIZATION OF MMA AND STYRENE AT 60°C

Substituent in benzaldehyde	$\sigma^{9)}$	$E_R{}^{3)}$	$C\times10^4$ MMA	$C\times10^4$ Styrene
p-CH$_3$O	−0.268	0.11	1.11	2.86
H	0.00	0.00	0.86	4.54
p-Cl	0.227	0.10	1.03	8.63
p-Br	0.232	0.12	1.43	12.2
m-Cl	0.373	0.08	0.96	13.7
p-CN	0.660	0.24	2.06	76.7

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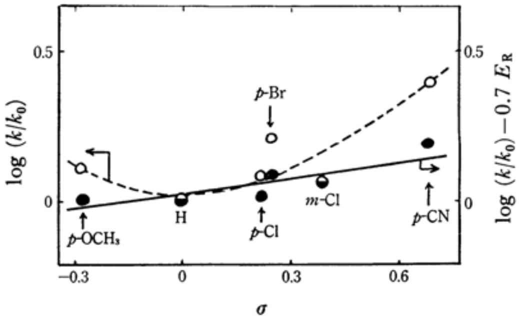

Fig. 3. The plots by the Hammett equation and Eq. (1) for the relative reactivities of benzaldehydes toward poly-MMA at 60°C.

in Fig. 3.

It may be seen that the plot of Fig. 3 gives not a straight line, but a concave curve. Such a parabola-type relation has always been observed in various chain-transfer reactions of cumenes and toluenes toward various polymer radicals[1,2] and in many radical reactions.[3a,10] Therefore, the effect of substituents on the reactivities of benzaldehydes toward the poly-MMA radical, as well as that on the other chain-transfer reactions, can not be explained by only a polar factor.

However, when Eq. (1) was applied to the present chain-transfer reaction, the straight-line relationship illustrated in Fig. 3 was obtained. From the slope of the straight line, the reaction constants, ρ and γ in Eq. (1), were found to be $+0.2$ and 0.7 respectively. The ρ and γ values indicated that the polar effect of substituens on the present chain-transfer reactivities was rather small, while the resonance effect was relatively important.

In previous papers, the chain-transfer reactivities of the nuclear-substituted cumenes,[1b] toluenes,[2] and acetophenones[11] toward the poly-MMA radical fit not the ordinary Hammett equation, but a modified Hammett equation (1). Tsuda and Otsu[12] reported that the chain-transfer reactivities of substituted dibenzoyl disulfides toward the poly-MMA radical were also correlated with Eq. (1).

For various chain-transfer reactions, it is interesting to compare the magnitude of the reaction constants, ρ and γ, obtained from the application of Eq. (1). Table 2 summarizes the ρ and γ values obtained for various substrates.

TABLE 2. THE ρ AND γ VALUES OF THE CHAIN-TRANSFER REACTIONS OF VARIOUS SUBSTRATES TOWARD THE POLY-MMA RADICAL

Substrate	ρ	γ	Ref.
Benzaldehyde	+0.2	0.7	This work
Cumene	+0.03	0.9	1a)
Toluene	+0.01	0.6	2)
Acetophenone	−0.01	2.0	11)
Diphenyl disulfide	+0.01	0.75	13)
Dibenzoyl disulfide	+0.07	0.75	12)
Phenylacetylene	0.0	1.7	14)

As can be seen in Table 2, all of the ρ values for these substrates toward the poly-MMA radical are close to zero, regardless of the substrate structure. In general, the sign and the magnitude of the ρ value are determined by both the polar character of the attacking radical and the electron density in the reaction center in the substrate. Accordingly, the fact that all of the ρ values in Table 2 are close to zero suggests that the poly-MMA radical has only a small polar character.

On the other hand, the γ values in Table 2 are relatively large and change with the substrate structure. Hence, it may be concluded that the polar factor of the substituents slightly affects the reactivities of these substrates toward the attack of a poly-MMA radical, while the resonance has a significant effect.

Chain-transfer Reactivities of Benzaldehydes with the Polystyryl Radical. The C values of substituted benzaldehydes toward the poly-St radical, shown in Table 1, increases gradually with an increase in the electron-attracting character of their nuclear substituents. The ordinary Hammett plots of these results, shown in Fig. 4, do not give a straight-line relationship.

However, when the σ^- canstant for the p-cyano substituent ($\sigma^- = 1.00$)[15] was used, a fairly good

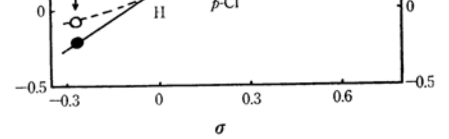

Fig. 4. The plots by the Hammett equation and Eq. (1) for the relative reactivities of benzaldehydes toward poly-St at 60°C.

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linear relationship was observed. This result is understandable if this reaction series is a nucleophilic reaction; the formation of the carbanion in the transition state thus becomes important.

On the other hand, when the plot was made by a modified Hammett equation (1), a much better linear relationship was obtained, as is shown in Fig. 4. From this plot, the ρ and γ values may be found to be $+1.4$ and 0.65 respectively. When we compare these ρ and γ values with those of the attack by the poly-MMA radical, it is noted that the γ values are almost the same, while the ρ values are quite different from each other.

As has been described in a previous paper,[3] the ρ values in Eq. (1) are mainly dependent on the polar natures of both the attacking radical and the substrate structure. Accordingly, the positively-large ρ value in the attack of poly-St, as compared with that of poly-MMA, is understandable, since the poly-MMA radical is less nucleophilic than the polystyryl radical because of its own α-carbomethoxy group.