Substituent Effects on the Addition Reaction Rate of Thiophenols to Ethynylbenzenes as a Model of Polyaddition. Study on the Relative Reactivity and Reaction Mechanism on the Basis of Hammett Correlation

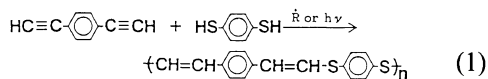Takatsugu Obata, Eiichi Kobayashi,* Sadahito Aoshima, and Junji Furukawa

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ABSTRACT: The addition reactions of thiophenols to ethynylbenzenes having *p*-methoxy, *p*-methyl, and *p*-chloro substituent groups occurred readily without appreciable side reactions. Adducts of the anti-Markownikoff's structure were obtained in 95—99% yields. The relative reactivities of the addition reactions of benzenethiyl radical to substituted ethynylbenzenes, the rate-determining step, were found to be quite opposite to those of substituted benzenethiyl radicals to ethynylbenzene. For example, *p*-methoxyethynylbenzene has the highest reactivity in the ethynylbenzenes. The *p*-methoxybenzenethiyl radical exhibits the lowest reactivity. The relative rates of the chain transfer reaction among β-phenylthiostyrylene radical ($\phi\dot{C}=CHS\phi$) and thiophenols were also determined. That is, the electron-donating *p*-substituent group on the thiophenols increased the chain transfer reaction rate. These relative reactivities were correlated by three Hammett's equations. Better correlation was found with the Brown–Okamoto's equation and Yamamoto's equation considering a resonance effect. The results are discussed in relation to the transition state of the addition reaction of thiophenols to ethynylbenzenes. The substituent effects on the addition reactions between thiophenols and styrenes or thiophenols and ethynylbenzenes are comparatively discussed based on the energy levels of HOMO, SOMO, and LUMO calculated by MINDO/3. Polyaddition reactivity of 1,4-benzenedithiol to 1,4-diethynylbenzene was also estimated to be four times higher than the addition of thiophenol to ethynylbenzene.
    KEY WORDS   Kinetics / Polyaddition / Addition Reaction / Reaction Mechanism / Substituent Effect / Hammett Correlation / Molecular Orbital Calculation / Thiophenol Derivatives / Ethynylbenzene Derivatives / Styrene /

A polymer having many interesting properties was obtained by a polyaddition of 1,4-benzenedithiol (BDT) to 1,4-diethynylbenzene (DEB) as shown in eq 1.[1]

$$HC\equiv C\text{-}\underset{}{\bigcirc}\text{-}C\equiv CH \ + \ HS\text{-}\underset{}{\bigcirc}\text{-}SH \xrightarrow{\dot{R} \text{ or } h\nu}$$

$$\leftarrow CH=CH\text{-}\underset{}{\bigcirc}\text{-}CH=CH\text{-}S\text{-}\underset{}{\bigcirc}\text{-}S\rightarrow_n \qquad (1)$$

However, the detailed polyaddition mechanism is still unclear. The polymer has a relative low molecular weight and is insoluble in conventional organic solvents.

In the previous study,[2] as a model of the polyaddition the addition reaction of thiophenol to ethynylbenzene was investigated (eq 2).

$$\underset{}{\bigcirc}\text{-}C\equiv CH \ + \ \underset{}{\bigcirc}\text{-}SH \xrightarrow[\text{in benzene}]{AIBN} \underset{}{\bigcirc}\text{-}CH=CHS\text{-}\underset{}{\bigcirc} \qquad (2)$$

Side reactions such as homopolymerization of ethynylbenzene and coupling reaction of benzenethiyl radicals occurred scarcely and the adduct of the anti-Markownikoff's structure

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was prepared preferentially. The reaction proceeded a radical chain mechanism and the reaction order was as follows[2] (eq 3).

$$\text{Rate} = k[\phi C \equiv CH][\text{AIBN}]^{0.5} \qquad (3)$$

A rate-determining step of the reaction was estimated as the addition reaction of benzenethiyl radical to ethynylbenzene.[2]

In this paper, the substituent effects on the addition reaction of various thiophenols to ethynylbenzenes were investigated in order to make clear the transition state of the reaction. Such substituent effect has been reported scarcely except for the case of the addition reactions of benzenethiyl radicals to ethynylbenzenes by flash photolysis method, and the properties of benzenethiyl and β-phenylthiostyrylene radicals ($\phi\dot{C}=CHS\phi$) were discussed.[3] The rate-determining step of the reaction was different from that of the addition reaction of thiophenol to styrene, where the rate-determining step is the chain transfer reaction.[4] This difference is discussed based on the energy levels of HOMO, SOMO, and LUMO.

EXPERIMENTAL

Reagents

Thiophenol and *p*-chlorothiophenol were provided by Sumitomo Seika Chem. Co. *p*-Chloroethynylbenzene was prepared from *p*-chlorostyrene provided by Hokko Chem. Co. by bromination and then elimination of hydrogen bromide.[5] *p*-Methyl and *p*-methoxyethynylbenzenes were synthesized according to the literature.[6] Ethynylbenzene (Wako Pure Chem. Co.), *p*-methyl, and *p*-methoxythiophenols (Aldrich Chem. Co.) were obtained commercially. The reagents were purified more than two times by vacuum distillation under a nitrogen atmosphere before use. Benzene (Wako Pure Chem. Co.) as a reaction solvent was distilled over CaH_2 and then deairing to exclude oxygen by vacuum for 20 min before use. 2,2′-Azobisisobutyronitrile (AIBN, Wako

Pure Chem. Co.) was used as received. Nitrogen gas was purified as shown in the previous paper.[2]

Addition Reaction

The addition reactions of thiophenols to ethynylbenzenes were carried out similarly as in the previous paper.[2] The course of the reaction was monitored every *ca.* 10 min by measurements of the concentrations of adducts or both monomeric reagents by GC using benzophenone (column temp, 250°C) or decane (column temp, 140°C) as internal references, respectively.

Measurements

Gas chromatograms were measured on a Shimadzu GC-4BMPF equipped with a flame ionization detector (FID) and a silicon GE SE-30 column (2m) under a nitrogen carrier gas. ^{1}H NMR spectra were obtained with a JEOL JNM-FX90Q in $CDCl_3$ with tetramethylsilane as an internal standard. IR spectra were recorded on a Hitachi 260-50 spectrophotometer by the KBr method. EI mass spectra were obtained on a JEOL JMS-G3000. Sulfur content of the adducts was determined by the modified Schoeniger's method.[7] The energy levels of frontier orbitals of all substrates in the addition reaction of thiophenol to styrene and to ethynylbenzene were calculated by the MINDO/3 method in the DEC-VAX8350 system.

RESULTS AND DISCUSSION

Addition Reactions of Thiophenols to Ethynylbenzenes

Thiophenol adds preferentially to ethynylbenzene together with few side reactions to give an adduct of the anti-Markownikoff's structure in a high yield.[2]

The addition reactions of thiophenols to ethynylbenzenes were carried out at 60°C in benzene under a nitrogen atmosphere. As the derivatives, *p*-chloro, *p*-methyl, and *p*-methoxy

Table I. Synthesis of adducts of thiophenols with ethynylbenzenes at 60°C for 2 h under a nitrogen atmosphere

p-X Ethynyl-benzenes	p-Y Thio-phenols	Isolated yield %	bp °C/mmHg	m/z (calcd)	S wt% (calcd)	^{1}H NMR spectra[a] ppm	IR spectra[b] cm^{-1}
H	H	97	122—3/0.07	212 (212)	15.2 (15.1)	6.20—6.80 (m, 2H, CH=CH) 6.80—7.40 (m, 10H, benzene rings)	940, 1350 (–CH=CH–) 3000–3050 (=CH–)
CH$_3$	H	96	124—5/0.18	226 (226)	14.4 (14.2)	2.30 (S, 3H, CH$_3$), 6.45—6.90 (m, 2H, CH=CH) 7.05—7.45 (m, 9H, benzene rings)	960, 1360 (–CH=CH–), 2930 (–CH$_3$) 3000—3050 (=CH–)
Cl	H	98	136—7/0.11	246 (246)	13.1 (13.0)	6.25—6.70 (m, 2H, CH=CH) 7.25—7.40 (m, 9H, benzene rings)	960, 1360 (–CH=CH–), 1095 (C–Cl) 3020—3070 (=CH–)
CH$_3$O	H	96	128—9/0.12	242 (242)	13.4 (13.2)	3.80 (S, 3H, CH$_3$) 6.40—7.45 (m, 11H, CH=CH and benzene rings)	950, 1350 (–CH=CH–), 2840 (–OCH$_3$) 1250 ($\rangle$C–O–C), 3000—3050 (=CH–)
H	CH$_3$	97	114—5/0.10	226 (226)	14.3 (14.2)	2.35 (S, 3H, CH$_3$), 6.40—6.95 (m, 2H, CH=CH) 7.10—7.40 (m, 9H, benzene rings)	950, 1350 (–CH=CH–), 2920 (–CH$_3$) 3010—3050 (=CH–)
H	Cl	99	129/0.10	246 (246)	13.3 (13.0)	6.30—6.75 (m, 2H, CH=CH) 7.20—7.45 (m, 9H, benzene rings)	950, 1350 (–CH=CH–), 1095 (C–Cl) 3020—3070 (=CH–)
H	CH$_3$O	95	135—6/0.10	242 (242)	13.4 (13.2)	3.75 (S, 3H, CH$_3$) 6.35—7.45 (m, 11H, CH=CH and benzene rings)	940, 1350 (–CH=CH–), 2830 (–OCH$_3$) 1240 ($\rangle$C–O–C), 3000—3050 (=CH–)

$[X-\phi C \equiv CH]_0 = [Y-\phi SH]_0 \simeq 1 \, mol\, l^{-1}$; $[AlBN]_0 \simeq 1 \times 10^{-2} \, mol\, l^{-1}$ in benzene.

[a] Solv., CDCl$_3$; ref, TMS.

[b] KBr method.

ethynylbenzenes and thiophenols were used. In the combination of monomers, the addition reactions proceeded without an induction period and were completed within 2 h. Adducts were isolated by vacuum distillation in 95—99% yields as shown in Table I. All adducts isolated were pale yellow solids. Melting points of the adducts were not clear, since the adducts were mixture of *cis* and *trans* isomers. The adducts had the anti-Markownikoff's type structures by ^{1}H NMR and IR analyses similar as the adduct of thiophenol and ethynylbenzene. For example, the ^{1}H NMR spectrum of the adduct of *p*-methylthiophenol and ethynylbenzene shows absorptions at δ 2.4 ppm due to methyl protons, at δ
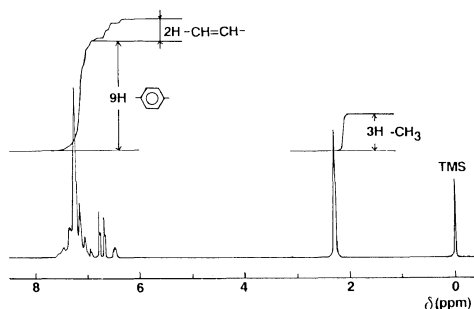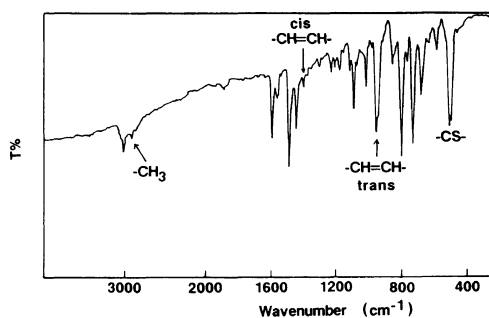

Figure 1. ^{1}H NMR spectrum of the adduct of *p*-methylthiophenol with ethynylbenzene obtained at 60°C for 2 h under a nitrogen atmosphere. $[CH_3 - \phi SH]_0 = [\phi C \equiv CH]_0 \simeq 1\,mol\,l^{-1}$; $[AIBN]_0 \simeq 1 \times 10^{-2}\,mol\,l^{-1}$ in benzene.

Figure 2. IR spectrum of the adduct of *p*-methylthiophenol with ethynylbenzene obtained at 60°C for 2 h under a nitrogen atmosphere. $[CH_3 - \phi SH]_0 = [\phi C \equiv CH]_0 \simeq 1\,mol\,l^{-1}$; $[AIBN]_0 \simeq 1 \times 10^{-2}\,mol\,l^{-1}$ in benzene.

6.4—7.0 ppm due to vinylene protons, and at δ 7.1—7.4 ppm due to benzene ring protons as shown in Figure 1. In the IR spectrum of the adduct, the CH_3 absorption at 2920 cm^{-1} and $CH = CH$ absorption at 950 cm^{-1} were observed as shown in Figure 2. Table I summarizes m/z, S wt%, ^{1}H NMR, and IR spectral data of the adducts.

It was found that thiophenols added quantitatively to ethynylbenzenes according to the anti-Markownikoff's rule, and side reactions scarcely occurred.

Substituent Effects on the Addition Step

Substituent effects on the addition step of *para*-substituted (*p*-Y) benzenethiyl radicals to *para*-substituted (*p*-X) ethynylbenzenes, the rate-determining step,[2] were evaluated to elucidate the transition state of the addition reactions of thiophenols to ethynylbenzenes.

At first, the relative rates of the addition reaction of the benzenethiyl radical to ethynylbenzene and *p*-X ethynylbenzene were determined by competitive reactions. The rate equation of the adduct formation is

$$R^H = d[A^H]/dt = k_a^H[\phi C \equiv CH][\phi \dot{S}] \quad (4)$$

where R^H and $d[A^H]/dt$ mean the rates of the adduct formation of thiophenol and ethynylbenzene, and k_a^H means the addition rate constant of benzenethiyl radical to ethynylbenzene. Accordingly, the relative rate of the adduct formation of ethynylbenzenes is expressed as eq 5,

$$\frac{d[A^X]/dt}{d[A^H]/dt} = \frac{d[A^X]}{d[A^H]} = \frac{k_a^X[X - \phi C \equiv CH]}{k_a^H[\phi C \equiv CH]} \quad (5)$$

where $[A^X]$ means the concentrations of the adducts of thiophenol and *p*-X ethynylbenzene, and k_a^X is the addition rate constant of benzenethiyl radical to *p*-X ethynylbenzene. Eq 5 is integrated to eq 6.

$$\frac{k_a^X}{k_a^H} = \frac{[A^X][\phi C \equiv CH]_0}{[A^H][X - \phi C \equiv CH]_0} \quad (6)$$

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Consequently, k_a^X/k_a^H is calculated readily by determination of the concentrations of both adducts.

In the case of the addition step between ethynylbenzene and p-Y benzenethiyl radicals containing p-methoxy, p-methyl, H, or p-chloro substituents, the reaction rates were determined individually by first order plots on the adduct formation of p-Y thiophenols to ethynylbenzene. The reaction rates can be expressed as eq 7,[2]

$$R^H = \left(\frac{k_d[AIBN]}{k_4^H}\right)^{0.5} k_a^H [\phi C \equiv CH] \quad (7)$$

where k_d means the dissociation rate constant of AIBN, and k_4^H means the coupling reaction rate constant between benzenethiyl radicals. The relative rates are represented as,

$$\frac{R^Y}{R^H} = \left(\frac{k_d[AIBN]}{k_4^Y}\right)^{0.5} k_a^Y \bigg/ \left(\frac{k_d[AIBN]}{k_4^H}\right)^{0.5} k_a^H$$

$$= \frac{k_a^Y}{k_a^H} \left(\frac{k_4^H}{k_4^Y}\right)^{0.5} \simeq \frac{k_a^Y}{k_a^H} \quad (8)$$

where R^Y means the rate of the adduct formation of p-Y thiophenols and ethynylbenzene, and k_a^Y means the addition reaction rate constant of p-Y benzenethiyl radicals to ethynylbenzene. To estimate relative rates of the addition step, k_a^Y/k_a^H was tentatively calculated assuming that the coupling reaction rate constant k_4^Y equals k_4^H.

The relative rates, k_a^X/k_a^H and k_a^Y/k_a^H, are shown in Table II. k_a^X/k_a^H are calculated based on the concentration of the both adducts as shown in eq 6, and k_a^Y/k_a^H are the experimental data, R^Y/R^H, itself as shown in eq 8.

In the case of ethynylbenzenes, k_a^X/k_a^H decreased in the order of MeO, Me, Cl, and H. On the other hand, k_a^Y/k_a^H of thiophenols increased in the order of MeO, Me, H, and Cl. For example, methoxyethynylbenzene has the highest reactivity in the ethynylbenzenes, and methoxythiophenol exhibits the lowest reactivity in the thiophenols. That is, the electron-donating p-X group on ethynylben-

Table II. Relative rates (k_a^X/k_a^H and k_a^Y/k_a^H) of the addition step and (k_{tr}^{HY}/k_{tr}^{HH}) of the chain transfer step in the reaction between thiophenols and ethynylbenzenes at 25°C in the dark under a nitrogen atmosphere

p-X Ethynylbenzenes or p-Y thiophenols	k_a^X/k_a^H [a]	k_a^Y/k_a^H [b]	k_{tr}^{HY}/k_{tr}^{HH} [c]
MeO	3.07	0.10	4.72
Me	1.41	0.55	1.55
H	1.00	1.00	1.00
Cl	1.28	1.69	1.55

[a] $[X - \phi C \equiv CH]_0 = [\phi C \equiv CH]_0 = 0.15 \, mol \, l^{-1}$; $[\phi SH]_0 = 0.3 \, mol \, l^{-1}$ in benzene; $[AIBN]_0/[\phi SH]_0 = 1/100$.
[b] $[\phi C \equiv CH]_0 = [Y - \phi SH]_0 = 0.3 \, mol \, l^{-1}$ in benzene; $[AIBN]_0/[\phi C \equiv CH]_0 = 1/100$.
[c] $[\phi C \equiv CH]_0 = 0.3 \, mol \, l^{-1}$; $[Y - \phi SH]_0 = [\phi SH]_0 = 0.15 \, mol \, l^{-1}$ in benzene; $[AIBN]_0/[\phi C \equiv CH]_0 = 1/100$; cf. see latter section: Substituent Effect on the Chain Transfer Step.

zenes increases the reaction rate, in contrast to the electron-donating p-Y group on thiophenols decreases the reaction rate. The substituent effect of ethynylbenzenes is found to be nearly opposite to that of thiophenols.

These kinetic data were plotted with Hammett's equations. The simple Hammett's eq 9, Brown–Okamoto's eq 10[8], and Yamamoto's eq 11[9] were studied:

$$\log(k/k_0) = \rho\sigma \quad (9)$$

$$\log(k/k_0) = \rho\sigma^+ \quad (10)$$

$$\log(k/k_0) = \rho\sigma + \gamma E_R \quad (11)$$

In eq 11, σ and E_R are polar and resonance substituent constants, ρ and γ are reaction constants giving the susceptibility of the polar and resonance effects caused by the substituent, respectively. That is, the $\rho\sigma$ shows a polar term and γE_R is a resonance term. Figures 3 a, b, and c show Hammett plots of the addition reactions of benzenethiyl radical to p-X ethynylbenzenes according to eq 9, 10, and 11, respectively. Similarly, Figure 4 shows Hammett correlations of the addition reactions of p-Y benzenethiyl radicals to ethynylbenzene.
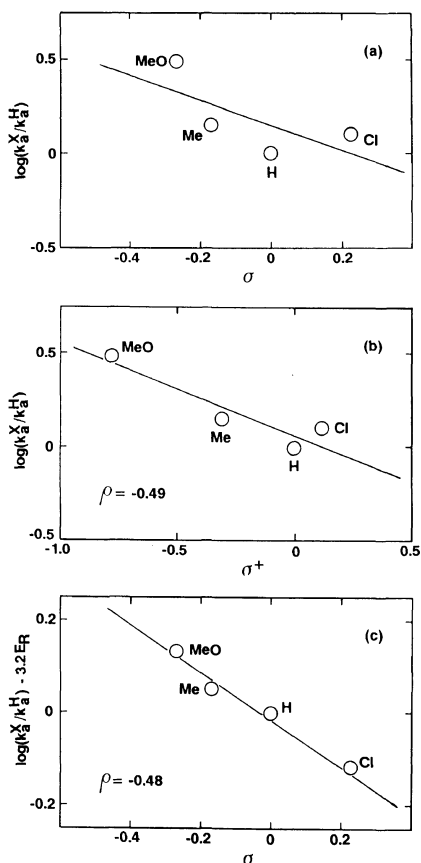
Figure 3. Hammett plots of $\log(k_a^X/K_a^H)$ of p-X ethynylbenzenes at 25°C in the dark under a nitrogen atmosphere with (a) eq 9, (b) eq 10,[7] and (c) eq 11.[8] $[X-\phi C \equiv CH]_0 = [\phi C \equiv CH]_0 = 0.15 \, \text{mol} \, l^{-1}$; $[\phi SH]_0 = 0.3 \, \text{mol} \, l^{-1}$ in benzene; $[AIBN]_0/[\phi SH]_0 = 1/100$.

Figure 4. Hammett plots of $\log(k_a^Y/K_a^H)$ of p-Y benzenethiyl radicals at 25°C in the dark under a nitrogen atmosphere with (a) eq 9, (b) eq 10,[7] and (c) eq 11.[8] $[\phi C \equiv CH]_0 = [Y-\phi SH]_0 = 0.3 \, \text{mol} \, l^{-1}$ in benzene; $[AIBN]_0/[\phi C \equiv CH]_0 = 1/100$.

The reaction constant, ρ, and resonance one, γ, obtained from Figures 3 and 4 are summarized in Table III together with the correlation coefficient, r, calculated by least squares method of the experimental data.

The reaction constant obtained with eq 10 for the addition reactions of benzenethiyl radical to p-X ethynylbenzenes ($\rho = -0.49$) and of p-Y benzenethiyl radicals to ethynylbenzene ($\rho = +1.33$) was nearly equal to the reference value ($\rho = -0.44^{3b}$, $\rho = +1.38^{3a}$, $+1.42^{3b}$, respectively) obtained by a flash photolysis method in the same reaction at 23°C in benzene or cyclohexane. Better correlation has been
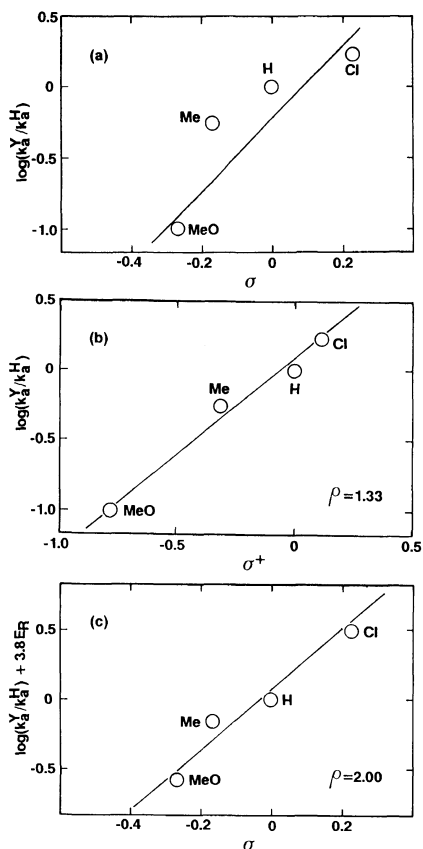
obtained with eq 10 and 11 rather than eq 9 because the correlation coefficient, r, for eq 10 and 11 is nearly one. It is noticed that the rates of these reactions are controlled not only by a polar term but also by a resonance term. Similar results were reported for the addition reactions of substituted benzenethiyl radicals not only to ethynylbenzenes but also to ethynyl compounds such as 1-pentyne and methylpropiolate by Ito *et al.*[3] Higashiura[10] has also reported that the addition reaction of polystyryl radical and poly(MMA) radical to substituted ethynylbenzenes did not obey eq 9 and 10 but eq 11. In the present study, the substituent effect of these addition reactions is

Table III. Hammett parameters obtained from Figures 3 and 4 in the addition reaction of benzenethiyl radicals to ethynylbenzenes at 25°C in the dark under a nitrogen atmosphere

Hammett's equation No.	p-X Ethynylbenzenes			p-Y Benzenethiyl radicals		
	ρ	γ	r^a	ρ	γ	r^a
(9) $\rho\sigma$	−0.65		0.67	2.20		0.89
(10) $\rho\sigma^+$	−0.49		0.92	1.33		0.99
	(−0.44[3b])			(1.38[3a], 1.42[3b])		
(11) $\rho\sigma + \gamma E_R$	−0.48	3.2	0.99	2.00	−3.8	0.98

[a] Correlation coefficient.

better correlated with Yamamoto's eq 11. This may suggest that the electron on the activated complex $(X-\phi\dot{C}=CH\cdots S\phi-Y)$ formed in the transition state of the reactions is stabilized by resonance with the substituents p-X and p-Y on the radicals. Such an idea has been proposed for the substituent effect of the copolymerization of styrenes.[11] That is, the relative reactivity of the addition reaction of p-X substituted polystyryl radicals to styrene obeyed the simple Hammett's eq 9. The relative reactivity of the reaction between polystyryl radical and p-Y substituted styrene did not obey eq 9 but eq 11. The electron on the intermediate styryl radical $(\sim CH_2CH(\phi X)CH_2\dot{C}H(\phi Y))$ formed in the transition state is not stabilized by resonance with the substituent p-X but with the substituent p-Y.

The reaction constants, ρ, between benzenethiyl radical and p-X ethynylbenzenes were negative and those between p-Y benzenethiyl radicals and ethynylbenzene were positive as shown in Table III. This indicates that the benzenethiyl radical is regarded as an electrophilic one. That is, perturbation between SOMO of benzenethiyl radical and HOMO of ethynylbenzene in the transition state is the important controlling factor for reactivity. Accordingly, reactivity increases when the level of HOMO in the ethynyl compounds rises and/or the level of SOMO in the benzenethiyl radical lowers (see Scheme 1). That is, an ethynyl compound having a large electron-donating group $(+I)$ or high
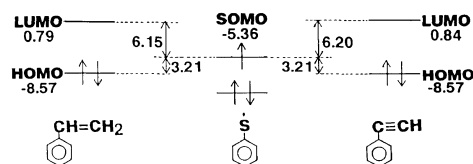
Scheme 1. Energy levels (atomic unit, 1 a.u. = 27.211 eV) of frontier orbitals in the addition step of benzenethiyl radical to styrene and ethynylbenzene.

resonance stabilizing group $(+R)$ accelerates the addition reaction. A thiol compound containing a large $-I$ and/or $-R$ group increases the reactivity. This idea explains the high reactivity of 9,10-anthracenedithiol and 9,10-diethynylanthracene.[12]
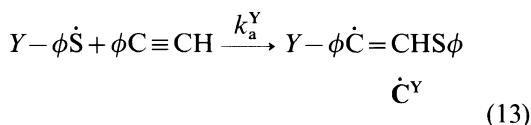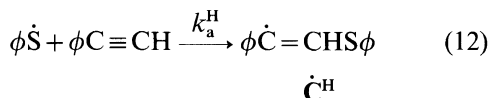
In the case of the polyaddition of BDT to DEB, it can be regarded as the addition reaction of thiophenol having a para thiol group to ethynylbenzene containing a para ethynyl group. σ^+ for the p-thiol and p-ethynyl substituents have been reported as 0.019[13] and 0.179,[14] based on rates of solvolysis of cumyl chlorides and benzyl chlorides, respectively. The estimated reactivity of the addition reaction of BDT to DEB from Figures 3b or 4b using the above σ^+ is about four times higher than the reactivity of the addition reaction of thiophenol to ethynylbenzene.

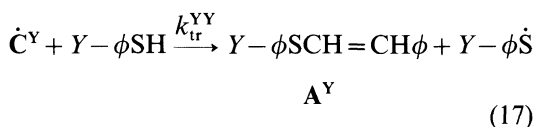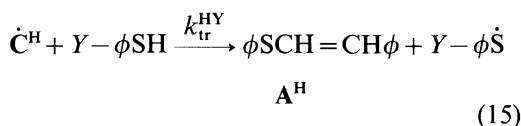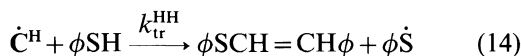*Substituent Effect on the Chain Transfer Step*

The substituent effect on the chain transfer step which is hydrogen abstraction from p-Y thiophenols by the β-phenylthiostyrylene radical $(\phi\dot{C}=CHS\phi)$ is also evaluated. The relative

rates of the reaction were estimated by competitive reactions of thiophenol and p-Y derivatives to ethynylbenzene. The main elementary reactions of the addition reaction are shown in eq 12—17,

Addition Reaction

$$\phi\dot{S} + \phi C \equiv CH \xrightarrow{k_a^H} \phi\dot{C} = CHS\phi \qquad (12)$$
$$\dot{C}^H$$

$$Y - \phi\dot{S} + \phi C \equiv CH \xrightarrow{k_a^Y} Y - \phi\dot{C} = CHS\phi$$
$$\dot{C}^Y$$
$$(13)$$

Chain Transfer Reaction

$$\dot{C}^H + \phi SH \xrightarrow{k_{tr}^{HH}} \phi SCH = CH\phi + \phi\dot{S} \qquad (14)$$

$$\dot{C}^H + Y - \phi SH \xrightarrow{k_{tr}^{HY}} \phi SCH = CH\phi + Y - \phi\dot{S}$$
$$A^H$$
$$(15)$$

$$\dot{C}^Y + \phi SH \xrightarrow{k_{tr}^{YH}} Y - \phi SCH = CH\phi + \phi\dot{S} \qquad (16)$$

$$\dot{C}^Y + Y - \phi SH \xrightarrow{k_{tr}^{YY}} Y - \phi SCH = CH\phi + Y - \phi\dot{S}$$
$$A^Y$$
$$(17)$$

where k_a^H, k_a^Y, $\cdots$, k_{tr}^{YY} are reaction rate constants for each the elementary reaction. The relative rate of the adduct formation is expressed under a steady state assumption as eq 18,

$$\frac{d[A^Y]/dt}{d[A^H]/dt} = \frac{d[A^Y]}{d[A^H]} = \frac{k_a^Y[\phi C \equiv CH][Y - \phi\dot{S}]}{k_a^H[\phi C \equiv CH][\phi\dot{S}]}$$

$$= \frac{k_{tr}^{HY}[Y - \phi SH](k_{tr}^{YH}[\phi SH] + k_{tr}^{YY}[Y - \phi SH])}{k_{tr}^{YH}[\phi SH](k_{tr}^{HH}[\phi SH] + k_{tr}^{HY}[Y - \phi SH])}$$
$$(18)$$

where $[A^Y]$ means the concentrations of the adducts of p-Y thiophenol to ethynylbenzene. Here, the authors approximate $k_{tr}^{HY} = ak_{tr}^{HH}$ and $k_{tr}^{YH} = bk_{tr}^{HH}$, where a and b are proportional

constants, and k_{tr}^{HH}, k_{tr}^{HY}, and k_{tr}^{YH} mean the rate constants of chain transfer reactions between $\dot{C}^H$ and ϕSH, $\dot{C}^H$ and $Y - \phi SH$, $\dot{C}^Y$ and ϕSH as shown in eq 14, 15, and 16, respectively. In this way, k_{tr}^{YY} may be expressed as abk_{tr}^{HH}, where k_{tr}^{YY} is the chain transfer rate constant between $\dot{C}^Y$ and $Y - \phi SH$. This is because $Y - \phi SH$ has a times higher reactivity than ϕSH in the chain transfer reaction with $\dot{C}^H$, and $\dot{C}^Y$ has b times higher reactivity than $\dot{C}^H$ in the ϕSH, so that the reaction between $\dot{C}^Y$ and $Y - \phi SH$ may occur at ab times faster than that between $\dot{C}^H$ and ϕSH. Accordingly, eq 18 can be expressed to be eq 19.

$$\frac{d[A^Y]}{d[A^H]} = a\frac{[Y - \phi SH]}{[\phi SH]} = \frac{k_{tr}^{HY}[Y - \phi SH]}{k_{tr}^{HH}[\phi SH]} \quad (19)$$

Eq 19 is integrated to eq 20.

$$\frac{k_{tr}^{HY}}{k_{tr}^{HH}} = \frac{[A^Y][\phi SH]_0}{[A^H][Y - \phi SH]_0} \qquad (20)$$

The relative rates, k_{tr}^{HY}/k_{tr}^{HH}, of the chain transfer step are calculated readily by determination of both adducts. However, the relative rate determined with eq 20 may have some error, because the hydrogen transfer between two thiophenols such as $\phi\dot{S} + Y - \phi SH \rightleftharpoons \phi SH + Y - \phi\dot{S}$ is not regarded in the equation. Gleicher[15] already reported that the relative rate of the hydrogen abstraction in a radical chain reaction was determined by a similar method using competitive reactions.

These k_{tr}^{HY}/k_{tr}^{HH} data are summarized in Table II and plotted with Hammett's eq 9—11 as shown in Figure 5. The reaction constant, resonance reaction constant, and correlation coefficient obtained from Figure 5 are summarized in Table IV. Better correlation was obtained with eq 11 rather than eq 9 and 10, since the correlation coefficient for eq 11 is nearly one. That is, a resonance effect as well as a polar effect are important factors to control reactivity in the chain transfer reaction. In the chain transfer reaction between a polystyryl radical and cumene derivatives,[16] the sub-
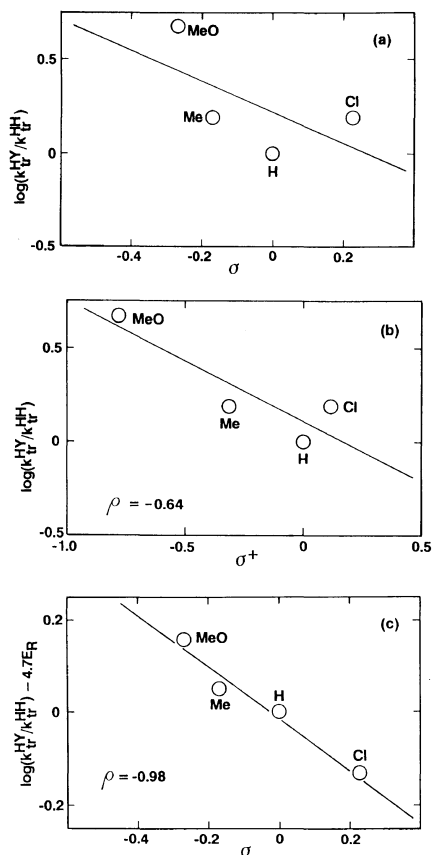
Figure 5. Hammett plots of $\log(k_{tr}^{HY}/K_{tr}^{HH})$ of p-Y thiophenols at 25°C in the dark under a nitrogen atmosphere with (a) eq 9, (b) eq 10[7], and (c) eq 11.[8] $[\phi C \equiv CH]_0 = 0.3 \, mol \, l^{-1}$; $[Y - \phi SH]_0 = [\phi SH]_0 = 0.15$ $mol \, l^{-1}$ in benzene; $[AIBN]_0/[\phi C \equiv CH]_0 = 1/100$.

Table IV. Hammett parameters obtained from Figure 5 in the chain transfer reaction among thiophenols and β-phenylthiostyrylene radical at 25°C in the dark under a nitrogen atmosphere

Hammett's equation No.	p-Y Thiophenols		
	ρ	γ	r^a
(9) $\rho\sigma$	−0.81		0.61
(10) $\rho\sigma^+$	−0.64		0.88
(11) $\rho\sigma + \gamma E_R$	−0.98	4.7	0.98

[a] Correlation coefficient.
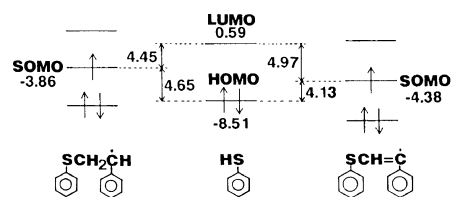
Scheme 2. Energy levels (atomic unit, 1 a.u. = 27.211 eV) of frontier orbitals in the chain transfer step of β-phenylthiostyryl and β-phenylthiostyrylene radicals to thiophenol.

stituent effect on the reaction did not obey eq 9 and 10 but eq 11. The electron is transferred from the polystyryl radical to cumenes in a transition state, since the reaction constant was positive $(\rho = 0.7)$.[17] In these chain transfer reactions between β-phenylthiostyrylene radical $(\phi \dot{C} = CHS\phi)$ and p-Y thiophenols, the reaction constant is negative, −0.98 (see Table IV). Consequently, the electron transfers from thiophenol to $\phi \dot{C} = CHS\phi$ in a transition state. Accordingly, the chain transfer reactivities of thiophenols toward the radical increased as electron-donating p-Y substituents in thiophenol. It was also found that a perturbation between SOMO of β-phenylthiostyrylene radi-

cal and HOMO of thiophenol in the transition state is the important controlling factor for reactivity (see Scheme 2).

Comparison between Styrene and Ethynylbenzene

The authors reported that thiophenol added quantitatively to both styrene and ethynylbenzene by the anti-Markownikoff's orientation, but the rate-determining steps of both reactions were quite different and the reasons were unclear.[2,4] Here, the authors discuss the reasons by comparison with the substitutent effects of styrenes and ethynylbenzenes.

The substituent effect on the addition step and chain transfer reaction according to Hammett's equations is summarized in Table V. However, the results obtained by eq 9 are not quoted in the table, since the correlation coefficient r was less than 0.97. In both the addition step and chain transfer reaction, the

Table V. Comparison of the substituent effect on the addition step and chain transfer reaction between styrenes and ethynylbenzenes in benzene under a nitrogen atmosphere by use of Hammett's equations

Elementary reaction	Equation No.[a]	Styrene at 50°C		Ethynylbenzene at 25°C	
		$X-\phi CH=CH_2$[b] $+\phi\dot{S}$	$\phi CH=CH_2$ $+Y-\phi\dot{S}$	$X-\phi C\equiv CH$ $+\phi\dot{S}$	$\phi C\equiv CH$ $+Y-\phi\dot{S}$
Addition	(10)	—[f]	$1.37\sigma^{+}$[c]	—[f]	$1.33\sigma^{+}$
	(11)	$-0.34\sigma+1.8E_R$	$2.42\sigma-1.8E_R$[d]	$-0.48\sigma+3.2E_R$	$2.00\sigma-3.8E_R$
		$\phi SCH_2\dot{C}H\phi-X$[e] $+\phi SH$	$Y-\phi SCH_2\dot{C}H\phi$[e] $+Y-\phi SH$	$\phi SCH=\dot{C}\phi-X$ $+\phi SH$	$\phi SCH=\dot{C}\phi$ $+Y-\phi SH$
Chain	(10)	$-0.60\sigma^{+}$	$0.64\sigma^{+}$		—[f]
transfer	(11)	$-0.99\sigma+2.3E_R$	$1.30\sigma-1.0E_R$		$-0.98\sigma+4.7E_R$

[a] Eq 10, $\rho\sigma^{+}$; eq 11, $\rho\sigma+\gamma E_R$.

[b] This Hammett correlation was similarly determined based on the unpublished experimental data in competitive reactions of thiophenol to p-X styrenes.

[c] Value quoted from ref 18 at 23°C.

[d] Values were calculated based on the data of the ref 18 at 23°C.

[e] Reference 2.

[f] The equations were omitted from the table, since the value of r was less than 0.97.

substituent effect is more reasonably evaluated by eq 10 and 11 including the resonance effect.

The transition states of the addition step of thiyl radical to styrenes or ethynylbenzenes are thought to be much alike, since the reaction constants, ρ, obtained from eq 10 and 11 are little changed. For example, the reaction constant ($\rho=2.42$) in eq 11 for the addition step of p-Y benzenethiyl radical to styrene is nearly equal to the reaction constant ($\rho=2.00$) in the case of ethynylbenzene. ρ of the addition step among benzenethiyl radical to both p-X styrenes and ethynylbenzenes were negative but ρ of the same step of p-Y benzenethiyl radicals to both monomers were positive. This indicates that the benzenethiyl radical is electrophilic. That is, a perturbation between SOMO of p-Y benzenethiyl radical and HOMO of styrene or ethynylbenzene in the transition state is the important controlling factor for the reactivity of the addition step (see Scheme 1). The inductive effect of the p-Y substituent on the

benzenethiyl radicals is evidently observed at the addition step to styrene and ethynylbenzene. However, the I-effect of the p-X substituent on the styrenes and ethynylbenzenes at the addition step to the benzenethiyl radical is not so prominent, since the absolute values of ρ for Y substituent on the thiophenols were much larger than those for X substituent. The resonance reaction constant, γ, obtained by eq 11 in the styrene system is nearly half that in the ethynylbenzene system. This indicates that the addition step of the p-Y benzenethiyl radical to ethynylbenzene is more stabilized by the resonance effect than to styrene in the transition state. That is, the β-phenylthiostyrylene radical ($\phi\dot{C}=CHS\phi$) has more resonance stability than the β-phenylthiostyryl radical ($\phi\dot{C}HCH_2S\phi$). γ for X substituent were positive and those for Y substituent, negative in both styrene and ethynylbenzene systems. Otsu et al.[9,20] discussed the signs of γ: in the case of $\gamma>0$ the R-effect by the substituent in the transition

Table VI. ρ and γ obtained for the substituent effect on the addition and chain transfer reactions of various polystyryl radicals to substituted monomers using eq 11

Reactions	Radicals	Substituted monomers	ρ	γ	Ref
Addition[a]	p-OCH$_3$ Polystyryl	Styrenes	0.6	1.4	19
reaction	Polystyryl	Styrenes	0.85	1.5	19
	p-Cl Polystyryl	Styrenes	0.15	1.5	19
	p-CN Polystyryl	Styrenes	−0.25	0.7	19
Chain transfer[b]	p-OCH$_3$ Polystyryl	Cumenes	1.0	1.3	16a
reaction	p-CH$_3$ Polystyryl	Cumenes	0.8	1.1	16b
	Polystyryl	Cumenes	0.7	1.0	16c
	p-Cl Polystyryl	Cumenes	0.2	1.0	16d

[a] ex. $\sim \dot{C}H(\phi) + X - \phi - CH = CH_2 \rightarrow \sim CH(\phi)CH_2\dot{C}H(\phi - X)$.
[b] ex. $\sim \dot{C}H(\phi) + (CH_3)_2CH(\phi - X) \rightarrow \sim CH_2(\phi) + (CH_3)_2\dot{C}\phi - X$.

state was larger than that in the initial state. The R-effect in the transition state was smaller in the case of $\gamma < 0$. Accordingly, γ in this study suggest that the R-effect by the X substituent in the transition state is larger than that in the initial state, and the R-effect by the Y substituent in the transition state is smaller than that in the initial state.

In the chain transfer step, the reaction constants, ρ, obtained from styrene or ethynylbenzene system by eq 11 have opposite signs. The reaction constant of the chain transfer reaction among $\phi\dot{C}HCH_2S\phi$-Y and p-Y thiophenol in styrene system is a positive, 1.30, ρ of the same step in the ethynylbenzene system is a negative, −0.98. ρ of radical reactions changes surely from positive to negative. For example, in the case of the substituent effect on the addition reaction of polystyryl radical to substituted styrenes (Table VI) ρ obtained by eq 11 changed greatly by attacking radicals.[19] On the substituent effect on the chain transfer reactions of polystyryl radicals and cumenes,[16,20] similar results were observed as shown in Table VI. Otsu et al.[18] claimed that ρ obeyed the polarity of the substituents on the attacking radicals. Accordingly, the β-phenylthiostyryl radical ($\phi\dot{C}HCH_2S\phi$) is nucleophilic and the β-phenylthiostyrylene radical ($\phi\dot{C} = CHS\phi$) is electrophilic. In the styrene system, the controlling factor of the reactivity is perturbation between SOMO of $\phi\dot{C}HCH_2S\phi$ and LUMO of thiophenol, whereas perturbation between SOMO of $\phi\dot{C} = CHS\phi$ and HOMO of thiophenol is the important factor in the ethynylbenzene system. These ideas well coincide with the MO calculation indicated in Scheme 2. γ of the ethynylbenzene system (+4.7) is also much larger than that of the styrene system (−1.0) in the chain transfer reaction. That is, the chain transfer step of the ethynylbenzene system is more resonance stabilized than that of the styrene system in the transition state. The sign of γ suggests that in the styrene system, the R-effect by the Y substituent on the thiophenol in the transition state is smaller than that in the initial state and that in the transition state is larger in the ethynylbenzene system.

It was confirmed that perturbation between SOMO of benzenethiyl radical and HOMO of styrene and ethynylbenzene is an important controlling factor for the reactivity of the addition step, since energy gaps among SOMO level of benzenethiyl radical and HOMO levels of both monomers (3.21 a.u.) are smaller than the LUMO levels (>6.15 a.u.) as shown in the Scheme 1. In the chain transfer step, SOMO of the intermediate carbon radicals

makes perturbation with the frontier orbitals of thiophenol (Scheme 2). The rate-determining step in the styrene system was confirmed to be the chain transfer step,[4] because the energy gap (4.45 a.u.) between SOMO level of $\phi\dot{C}HCH_2S\phi$ and LUMO level of thiophenol in the chain transfer step is greater than that (3.21 a.u.) between the SOMO level of benzenethiyl radical and HOMO level of styrene in the addition step. In the ethynylbenzene system the energy gap of the chain transfer step (4.13 a.u.) is also greater than that of the addition step (3.21 a.u.). However, the rate-determining step was the addition of benzenethiyl radical to ethynylbenzene. The reason for the discrepancy between the kinetic data and MO calculation may be that the thiophenol and ethynylbenzene form the CT complex[21] and the addition reaction of thiophenol to ethynylbenzene occurs in a cage of the CT complex. That is, the chain transfer reaction may occur very rapidly by a sort of cage effect. The MO calculation of the CT complex may be useful to decide final consideration.

REFERENCES

1. E. Kobayashi, T. Ohashi, and J. Furukawa, *Makromol. Chem.*, **189**, 541 (1986); E. Kobayashi, T. Ohashi, and J. Furukawa, *J. Polym. Sci., A. Polym. Chem. Ed.*, **25**, 2077 (1987); E. Kobayashi, *Kobunshi*, **38**, 836 (1989).
2. E. Kobayashi, T. Obata, S. Aoshima, and J. Furukawa, *Polym. J.*, **22**, 1035 (1990).
3. a) O. Ito, R. Omori, and M. Matsuda, *J. Am. Chem. Soc.*, **104**, 3934 (1982); b) O. Ito, M. Daniela, and C. M. Fleming, *J. Chem. Soc., Perkin Trans. 2*, 689 (1989).
4. E. Kobayashi, T. Obata, S. Aoshima, and J. Furukawa, *Polym. J.*, **22**, 803 (1990).
5. A. S. Hay, *J. Org. Chem.*, **25**, 637 (1960).
6. D. J. Dawson, J. D. Frazier, P. J. Brock, and R. J. Twieg, *Polym. Mater. Sci. Eng.*, **55**, 401 (1986).
7. W. Schoeniger, *Mikrochim. Acta*, 123 (1955).
8. H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).
9. T. Yamamoto and T. Otsu, *J. Soc. Org. Chem. Jpn.*, **23**, 643 (1965).
10. K. Higashiura and M. Oiwa, *J. Polym. Sci., A. Polym. Chem. Ed.*, **6**, 1857 (1968).
11. M. Kinoshita and M. Imoto, *Kogyo Kagaku Zasshi*, **68**, 2454 (1965).
12. E. Kobayashi, J. Jiang, S. Aoshima, and J. Furukawa, *Polym. J.*, **22**, 146 (1990).
13. C. G. Swain and E. C. Lupton, Jr., *J. Am. Chem. Soc.*, **90**, 4328 (1968).
14. J. A. Landgrebe and R. H. Rynbrandt, *J. Org. Chem.*, **31**, 2585 (1966).
15. G. J. Gleicher, *J. Org. Chem.*, **33**, 332 (1968).
16. a) T. Yamamoto, T. Otsu, and M. Imoto, *Kogyo Kagaku Zasshi*, **70**, 203 (1967); b) *ibid.*, **69**, 990 (1966); c) T. Yamamoto, *Bull. Chem. Soc. Jpn.*, **40**, 642 (1967); d) *Polym. Letter*, **4**, 1039 (1966).
17. M. Imoto, *Kagaku*, **29**, 958 (1974).
18. O. Ito and M. Matsuda, *J. Am. Chem. Soc.*, **101**, 5732 (1979).
19. M. Imoto, M. Kinoshita, and M. Nishigaki, *Makromol. Chem.*, **94**, 238 (1966).
20. T. Otsu, *Kogyo Kagaku Zasshi*, **70**, 1854 (1967).
21. E. Kobayashi, Y. Terada, T. Ohashi, and J. Furukawa, *Polym. J.*, **23**, 267 (1991).