

## Novel Conjugated Polymer Containing Aromatic Ring and Selenium in Backbone. Kinetics of Substituent Effect on the Addition Reaction of Benzeneselenols to Ethynylbenzenes as a Model for Addition Polymerization

Nobuki METAKA, Eiichi KOBAYASHI,\* Sadahito AOSHIMA,  
and Junji FURUKAWA

*Department of Industrial Chemistry, Faculty of Science and Technology,  
Science University of Tokyo, Noda, Chiba 278, Japan*

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**ABSTRACT:** Substituent effect on the addition reaction of benzeneselenols to ethynylbenzenes was investigated as a model for addition polymerization to give conjugated polymer containing aromatic ring and selenium atom in the backbone. The addition reaction of benzeneselenols to ethynylbenzenes having *p*-methoxy, *p*-methyl, *p*-chloro, and *p*-H substituent groups occurred readily without appreciable side reactions. Adducts of the anti-Markownikoff's structure were obtained in >99% yield. Relative reactivity of the addition step of the benzeneseleno radical to substituted ethynylbenzenes, which is the rate-determining step, was found to decrease in the order of *p*-methoxy, *p*-methyl, *p*-chloro, and *p*-H. Relative reactivity of substituted benzeneseleno radicals to ethynylbenzene, on the contrary, increased in the above order. These relative reactivities were better correlated by the modified Hammett's equation containing a resonance effect than by the simple Hammett's equation. These results indicate that a perturbation between SOMO of benzeneseleno radical and HOMO of ethynylbenzene in the transition state is an important controlling factor for the addition reaction. The substituent effect of the chain transfer step between  $\beta$ -phenylselenostyrylene radical ( $\text{C}_6\text{H}_5\text{-}\dot{\text{C}}\text{=CH-Se-C}_6\text{H}_5$ ) and *p*-Y benzeneselenols was also determined. The experimental data were compared with the energy levels of HOMO, SOMO, and LUMO calculated by CACHE system (PM3). The results were also compared with those of the addition reactions of benzenethiol to ethynylbenzene and benzeneselenol to styrene. The transition state of the addition reaction of benzeneselenol to ethynylbenzene was found to be similar to that of benzenethiol to ethynylbenzene and benzeneselenol to styrene.

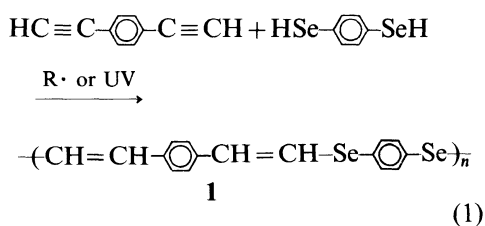
**KEY WORDS** Addition Polymerization / Addition Reaction / Reaction Mechanism / Kinetics / Substituent Effect / Hammett Correlation / Molecular Orbital Calculation / Benzeneselenol Derivatives / Ethynylbenzene Derivatives / Selenium-Containing Polymer /

Radical addition reactions of active hydrogen-containing compounds such as thiols, carbothioic acids, and phosphines to olefins or acetylenes were widely investigated to synthesize various polysulfides, polythioesters, and polyphosphines.

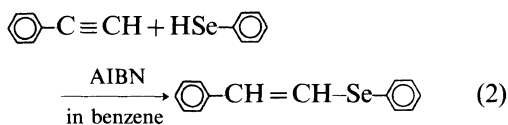
A novel polymer containing an aromatic ring and selenium atom was also synthesized by an

addition polymerization (so called polyaddition) of 1,4-benzenediselenol (BDSe) to 1,4-diethynylbenzene (DEB) in solution<sup>1</sup> and solid state,<sup>2</sup> as shown in eq 1. However, a detailed mechanism for the addition polymerization is still unclear since the polymerization proceeds heterogeneously and the polymer **1** is insoluble in conventional organic solvents.

\* To whom all correspondence should be addressed.



In the previous study,<sup>3</sup> as a model for the addition polymerization the addition reaction of benzeneselenol (BSe) to ethynylbenzene (EB) was investigated (eq 2). The addition reaction initiated with 2,2'-azobisisobutyronitrile (AIBN) preferentially occurred



without side reactions such as oligomerization of EB and coupling reaction of benzeneseleno radicals, and the adduct of the anti-Markownikoff's structure was obtained. The reaction proceeded by a radical mechanism and the rate-determining step of the reaction was estimated as the addition step of benzeneseleno radical to EB.<sup>3</sup>

In this article, to make clear the transition state of the reaction in detail substituent effects on the addition reactions of various BSe to EBs were investigated mainly by a kinetic method. The experimental data were compared with the energy levels of HOMO, SOMO, and LUMO calculated by CAChe system (PM3). The results were also compared with those of the addition reactions of benzenethiol to EB and BSe to styrene.

## EXPERIMENTAL

### Reagents

EB (Tokyo Kasei Kogyo Co.) was obtained commercially. *p*-ChloroEB (*p*-ClEB) was prepared from *p*-chlorostyrene provided by Hokko Chem. Co. by bromination and then elimination of hydrogen bromide.<sup>4</sup> *p*-Methyl and *p*-methoxyEBs were synthesized according

to the literature.<sup>5</sup> BSe was prepared according to the literature.<sup>6</sup> *p*-Chloro, *p*-methyl, and *p*-methoxyBSe were synthesized in a similar manner as BSe. These reagents were purified more than twice by vacuum distillation over calcium hydride under nitrogen atmosphere before use. Benzene (Nacalai Tesque Inc.) as a reaction solvent was distilled over calcium hydride and degassed to exclude oxygen under reduced pressure for 20 min before use. AIBN (Wako Pure Chemical Industries Ltd.) was recrystallized from methanol. *n*-Hexadecane and *n*-heptadecane (Tokyo Kasei Kogyo Co., each) as internal references for GC were purified by vacuum distillation under nitrogen atmosphere. Nitrogen gas (99.99%) was purified as shown in the previous paper.<sup>7</sup>

### Kinetics of Addition Reaction

In a two-neck flask with a three-way stopcock and a septum cap, each benzene solution of EBs, BSe, AIBN, *n*-hexadecane, and *n*-heptadecane was prepared by a semi-closed syphon method using a stainless pipe under highly purified nitrogen atmosphere.<sup>3</sup> The reaction was carried out by introducing each solution into a reaction vessel by the syphon method. The reaction temperature was maintained at 58°C. The course of the reaction was monitored every *ca.* 5 min by measurement of the concentration of the adducts by GC.

### Measurements

For characterization of the products and for monitoring the course of the reaction, the following instruments were used: <sup>1</sup>H NMR: JEOL PMX-60si and JEOL JNM-EX400 (solvent, CDCl<sub>3</sub>, internal reference, tetramethylsilane (TMS)); IR: Hitachi 260-50 spectrophotometer; EI MS: Shimadzu GCMS-QP2000A. Gas chromatograms (GC) were measured on a Shimadzu GC-4BPF equipped with a flame ionization detector (FID) and a Silicone GE SE-30 column (2 m) at 240°C under nitrogen carrier gas. The energy levels of orbitals of BSe, EB, benzeneseleno radical, *β*-phenylselenostyr-

ylene radical, and styrene were calculated by the CACHE system (PM3).

## RESULTS AND DISCUSSION

### Adducts Syntheses of Benzeneselenols and Ethynylbenzenes

The addition reaction of BSe to EB by AIBN occurred without appreciable side reactions to give an adduct of the anti-Markownikoff's structure quantitatively.<sup>3</sup>

The adducts syntheses of various BSe and EBs were carried out with AIBN initiator at 60°C in benzene under nitrogen atmosphere. *p*-Chloro, *p*-methyl, and *p*-methoxy derivatives of BSe and EB were used as a monomer. The addition reactions completed for 2 h and the adducts were obtained in >99% yield. All adducts were pale yellowish solid at room temperature. Melting points of the adducts were unclear, since the adducts were mixture of *cis* and *trans* isomers. The <sup>1</sup>H NMR spectra of the adducts appeared at  $\delta$  6.63–6.92 ppm due to *cis*-vinylene protons, at  $\delta$  6.79–7.19 ppm due to *trans*-vinylene protons, and  $\delta$  at 7.11–7.65 ppm due to aromatic ring protons. In the IR spectra of the adducts, the structure was also confirmed by *cis*- and *trans*-vinylene absorptions at 1335–1345 and 940–960 cm<sup>-1</sup>, respectively. These spectra indicate that the all adducts have the anti-Markownikoff's structure. Table I summarizes *m/z*, Se wt%, <sup>1</sup>H NMR, and IR spectral data of the adducts.

### Substituent Effects on the Addition Step

Substituent effects on the addition step of *para*-substituted (*p*-Y) benzeneseleno radicals to *para*-substituted (*p*-X) EB which is the rate-determining step<sup>3</sup> were investigated, because the substituent effects are known to give important informations on a transition state of the rate-determining step.

The relative rate in the addition step of the benzeneseleno radical to *p*-X EBs can be evaluated by a competitive reaction, and is expressed in eq 3,<sup>7</sup>

$$\frac{k_a^X}{k_a^H} = \frac{[\text{X-C}_6\text{H}_4\text{-CH=CH-Se-C}_6\text{H}_5][\text{C}_6\text{H}_5\text{-C}\equiv\text{CH}]_0}{[\text{C}_6\text{H}_5\text{-CH=CH-Se-C}_6\text{H}_5][\text{X-C}_6\text{H}_4\text{-C}\equiv\text{CH}]_0} \quad (3)$$

where  $k_a^X$  and  $k_a^H$  are the rate constants in the addition step of benzeneseleno radical to *p*-X EB and *p*-H EB, respectively. Therefore,  $k_a^X/k_a^H$  is readily calculated by determination of the concentration of both adducts.

In the addition step of *p*-Y benzeneseleno radical to EB, the reaction rates,  $R^Y$  and  $R^H$ , were estimated individually by first order plots of the adduct formation of *p*-Y BSe to EB and *p*-H BSe to EB, respectively. The relative rate,  $k_a^Y/k_a^H$ , is expressed in eq 4,<sup>7</sup>

$$\frac{R^Y}{R^H} = \frac{k_a^Y}{k_a^H} \left( \frac{k_4^Y}{k_4^H} \right)^{0.5} \approx \frac{k_a^Y}{k_a^H} \quad (4)$$

where  $k_a^Y$  is the rate constant in the addition step of *p*-Y benzeneseleno radical to EB,  $k_4^Y/k_4^H$  means the ratio of coupling reaction rate constants between *p*-Y benzeneseleno radicals and between *p*-H benzeneseleno radicals, respectively. The relative rate of the addition step,  $k_a^Y/k_a^H$  can be represented by  $R^Y/R^H$  assuming that the coupling reaction rate  $k_4^Y$  equals  $k_4^H$ . The relative rates,  $k_a^X/k_a^H$ , and  $k_a^Y/k_a^H$ , are summarized in Table II.

In the case of EB,  $k_a^X/k_a^H$  decreases in the order of *p*-methoxy, *p*-methyl, *p*-chloro, and *p*-H. On the other hand,  $k_a^Y/k_a^H$  increases in the order of *p*-methoxy, *p*-methyl, *p*-chloro, and *p*-H. That is, electron-donating *p*-X groups on EBs increase the reaction rate, while the electron-donating *p*-Y groups on BSe decrease the reaction rate.



These relative rates were correlated by Hammett's eq 5 and 6.<sup>8</sup>

$$\log(k/k_0) = \rho\sigma \quad (5)$$

$$\log(k/k_0) = \rho\sigma + \gamma E_R \quad (6)$$

In eq 6,  $\sigma$  and  $E_R$  are polar and resonance

Table I. Syntheses of adducts of *p*-X EBs and *p*-Y BSe's by AIBN at 60°C in benzene for 2 h under nitrogen atmosphere<sup>a</sup>

X-  -C≡CH	Y-  -SeH	Yield <sup>b</sup> %	<i>m/z</i> (Calcd)	Se wt% (Calcd)	<sup>1</sup> H NMR Spectra <sup>c</sup>		IR Spectra <sup>d</sup>	
					ppm	cm <sup>-1</sup>		
H-	H-	>99	259 (259)	30.6 (30.5)	6.70–7.19 (m, 2H, vinylene) 7.11–7.58 (m, 10H, aromatic rings)	940, 1340 (–CH=CH–) 2960–3110 (=CH–)		
CH <sub>3</sub> –	H–	>99	273 (273)	29.3 (28.9)	2.35 (s, 3H, CH <sub>3</sub> ) 6.70–7.60 (m, 11H, aromatic rings and vinylene)	960, 1340 (–CH=CH–), 2900 (–CH <sub>3</sub> ) 2960–3060 (=CH–)		
Cl–	H–	>99	293 (293)	27.0 (26.9)	6.75–7.18 (m, 2H, vinylene) 7.20–7.65 (m, 9H, aromatic rings)	960, 1340 (–CH=CH–), 1100 (C–Cl) 3000–3080 (=CH–)		
CH <sub>3</sub> O–	H–	>99	289 (289)	27.0 (27.3)	3.82 (s, 3H, CH <sub>3</sub> O) 6.63–7.65 (m, 11H, aromatic rings and vinylene)	960, 1335 (–CH=CH–), 2830 (–CH <sub>3</sub> O) 1250 (>C–O–C), 2890–3070 (=CH–)		
H–	CH <sub>3</sub> –	>99	273 (273)	28.5 (28.9)	2.35 (s, 3H, CH <sub>3</sub> ) 6.70–7.59 (m, 11H, aromatic rings and vinylene)	960, 1340 (–CH=CH–), 2900 (–CH <sub>3</sub> ) 2960–3060 (=CH–)		
H–	Cl–	>99	293 (293)	27.0 (26.9)	6.69–7.15 (m, 2H, vinylene) 7.12–7.56 (m, 9H, aromatic rings)	960, 1345 (–CH=CH–), 1095 (C–Cl) 2980–3090 (=CH–)		
H–	CH <sub>3</sub> O–	>99	289 (289)	27.5 (27.3)	3.81 (s, 3H, CH <sub>3</sub> O) 6.68–7.56 (m, 11H, aromatic rings and vinylene)	960, 1340 (–CH=CH–), 2830 (–CH <sub>3</sub> O) 1250 (>C–O–C), 2890–3100 (=CH–)		

<sup>a</sup>[*p*-X EB]<sub>0</sub> = [*p*-Y BSe]<sub>0</sub> ≈ 1.0 mol l<sup>-1</sup>, [AIBN]<sub>0</sub> ≈ 0.01 mol l<sup>-1</sup>. <sup>b</sup>By GC. <sup>c</sup>In CDCl<sub>3</sub>, reference, TMS. <sup>d</sup>KBr method.

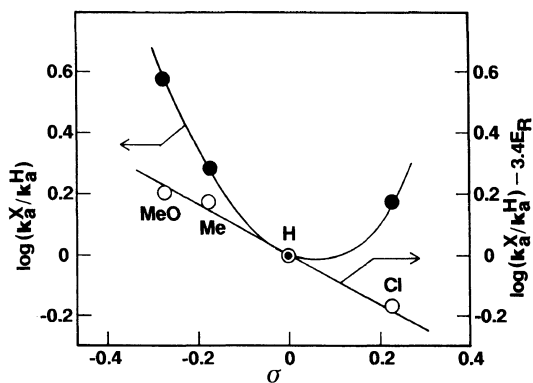
**Table II.** Relative rates ( $k_a^X/k_a^H$  and  $k_a^Y/k_a^H$ ) of the addition step and ( $k_{tr}^{HY}/k_{tr}^{HH}$ ) of the chain transfer step in the addition reactions of  $p$ -Y BSe to  $p$ -X EBs at 58°C in the dark under nitrogen atmosphere

X--C≡CH or Y--SeH	$k_a^X/k_a^H$ <sup>a</sup>	$k_a^Y/k_a^H$ <sup>b</sup>	$k_{tr}^{HY}/k_{tr}^{HH}$ <sup>c</sup>
CH <sub>3</sub> O-	3.77	0.10	1.47
CH <sub>3</sub> -	1.93	0.47	1.22
H-	1.00	1.00	1.00
Cl-	1.49	0.70	1.07

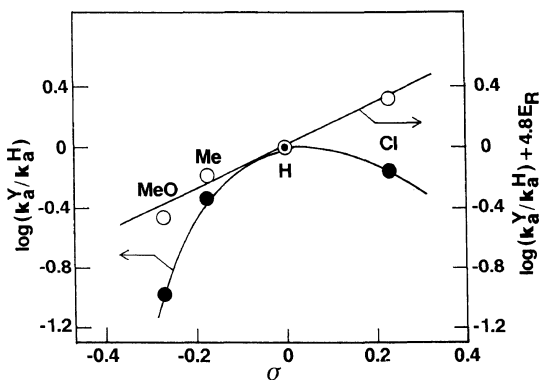
<sup>a</sup>  $[p\text{-X EB}]_0 = [p\text{-H EB}]_0 = 7.0 \times 10^{-2} \text{ mol l}^{-1}$ ;  $[\text{BSe}]_0 = 7.3 \times 10^{-2} \text{ mol l}^{-1}$ ;  $[\text{AIBN}]_0 = 6.4 \times 10^{-4} \text{ mol l}^{-1}$  in benzene. <sup>b</sup>  $[\text{EB}]_0 = 7.0 \times 10^{-2} \text{ mol l}^{-1}$ ;  $[p\text{-Y BSe}]_0$  or  $[p\text{-H BSe}]_0 = 7.0 \times 10^{-2} \text{ mol l}^{-1}$ ;  $[\text{AIBN}]_0 = 7.0 \times 10^{-4} \text{ mol l}^{-1}$  in benzene. <sup>c</sup>  $[\text{EB}]_0 = [p\text{-Y BSe}]_0 = [p\text{-H BSe}]_0 = 7.0 \times 10^{-2} \text{ mol l}^{-1}$ ;  $[\text{AIBN}]_0 = 7.0 \times 10^{-4} \text{ mol l}^{-1}$  in benzene. See latter section.

substituent constants,  $\rho$  and  $\gamma$  are reaction constants giving the susceptibility of the polar and resonance effects caused by the substituents, respectively. That is,  $\rho\sigma$  shows a polar term and  $\gamma E_R$  is a resonance term. Figure 1 shows Hammett plots of the addition step of benzeneseleno radical to  $p$ -X EBs according to eq 5 and 6. Similarly, Figure 2 shows Hammett correlations of the addition step of  $p$ -Y benzeneseleno radicals to EB.

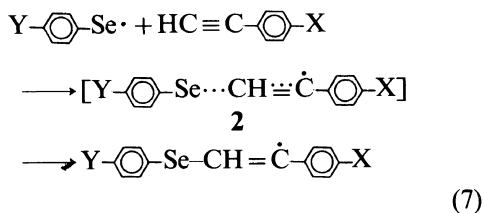
The lines with ● and ○ in Figures 1 and 2 were correlated by eq 5 and 6, respectively. Better correlation was obtained by eq 6 rather than by eq 5 in both the cases. Consequently, the addition reaction rate of BSe to EBs is controlled by both polar and resonance terms. Contribution of both polar and resonance terms has been already discussed on the hydrogen transfer step between polystyryl radical or poly(methyl methacrylate) [poly(MMA)] radical and  $p$ -substituted cumenes or toluenes.<sup>9</sup> The activated complex **2** formed in the transition state of the reaction may be stabilized by resonance with the substituents  $p$ -X and  $p$ -Y.



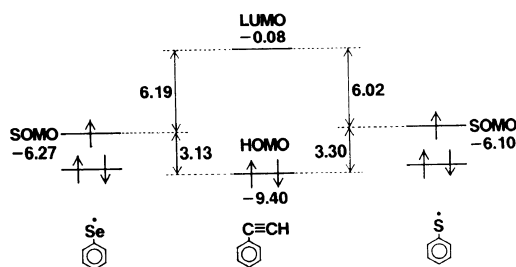
**Figure 1.** Hammett plots of  $\log(k_a^X/k_a^H)$  between  $p$ -X ethynylbenzenes and BSe at 58°C in the dark under nitrogen atmosphere with ●, eq 5 and ○, eq 6<sup>8</sup>;  $\rho = -0.83$ .  $[p\text{-X EB}]_0 = [p\text{-H EB}]_0 = 7.0 \times 10^{-2} \text{ mol l}^{-1}$ ;  $[\text{BSe}]_0 = 7.3 \times 10^{-2} \text{ mol l}^{-1}$ ,  $[\text{AIBN}]_0 = 6.4 \times 10^{-4} \text{ mol l}^{-1}$  in benzene, internal reference for GC;  $n$ -hexadecane.



**Figure 2.** Hammett plots of  $\log(k_a^Y/k_a^H)$  between  $p$ -Y benzeneseleno radicals and EB at 58°C in the dark under nitrogen atmosphere with ●, eq 5 and ○, eq 6<sup>8</sup>;  $\rho = 1.42$ .  $[\text{EB}]_0 = [p\text{-Y BSe}]_0$  or  $[p\text{-H BSe}]_0 = 7.0 \times 10^{-2} \text{ mol l}^{-1}$ ;  $[\text{AIBN}]_0 = 7.0 \times 10^{-4} \text{ mol l}^{-1}$  in benzene, internal reference for GC;  $n$ -heptadecane.



The polar reaction constant ( $\rho = -0.83$ ) with eq 6 for the addition step of benzeneseleno



**Scheme 1.** Energy levels (eV) of orbitals in the addition step of benzeneseleno radical or benzenethiyl radical to ethynylbenzene.

radical to *p*-X EBs was negative, whereas that ( $\rho = 1.42$ ) for the addition step of *p*-Y substituted benzeneseleno radicals to EB was positive. These results indicate that the perturbation between SOMO of benzeneseleno radical and HOMO of EB in the transition state is the important factor for reactivity control in the adduct formation. That is, benzeneseleno radical is electrophilic one. The interpretation is also consistent with the molecular orbital calculation by CAChe system (PM3): the energy gap between SOMO level of benzeneseleno radical and HOMO level of EB (3.13 eV) is smaller than that between the SOMO and LUMO levels (6.19 eV) as shown in Scheme 1.

The resonance reaction constant ( $\gamma = 3.4$ ) for addition step of benzeneseleno radical to *p*-X EBs was positive, whereas that ( $\gamma = -4.8$ ) for the addition step of *p*-Y benzeneseleno radicals to EB was negative. The signs of  $\gamma$  were discussed by Otsu *et al.*<sup>9</sup>: when  $\gamma > 0$ , the resonance stabilization by the substituent in the transition state was larger than that in the initial state, when  $\gamma < 0$ , the resonance stabilization in the transition state was smaller than that in the initial state. Accordingly, the resonance stabilization by the *p*-X substituent on EB in the transition state is larger than that in the initial state. On the other hand, the resonance stabilization by *p*-Y substituent on benzeneseleno radical in the transition state is smaller than that in the initial state.

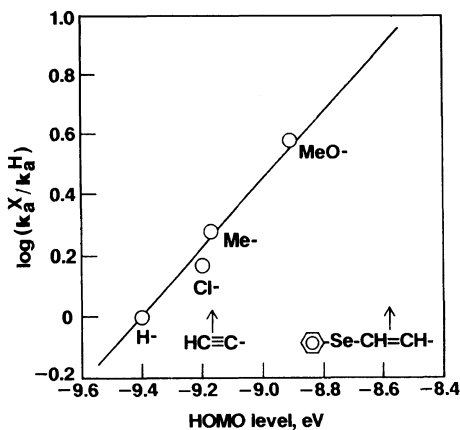
Consequently, the reactivity of addition step

increases when the HOMO level of EBs rises and/or the SOMO level of benzeneseleno radicals lowers (Scheme 1). Therefore, the overall addition reaction rate of BSe to EB accelerates by introducing a largely electron donating (+I) group and/or highly resonance stabilizing (+R) group into the *para* position of EB, and large -I group and/or -R group into the *para* position of BSe.

#### Reactivity of Addition Polymerization of BDSe to DEB

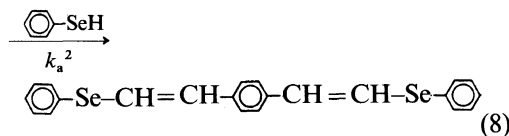
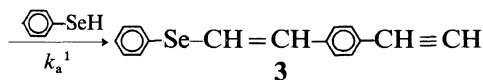
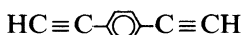
Reactivity of addition polymerization of BDSe to DEB could be estimated on the basis of the above substituent effect. BDSe and DEB are regarded as the BSe having *p*-selenol group and EB having *p*-ethynyl group.  $\sigma$  for the *p*-ethynyl group has been reported as 0.233<sup>10</sup> by *pKa* method.  $\sigma$  for the *p*-selenol group has not been reported and is thought to be a positive, since  $\sigma$  for the *p*-thiol group is 0.150<sup>11</sup> and the value of electronegativity of selenium atom (2.4) approximately equals to that of sulfur atom (2.5). Though  $E_R$  for the *p*-ethynyl and the *p*-selenol groups are unclear,  $E_R$  for the *p*-ethynyl group is expected to be positive, because the *p*-ethynyl group on EB has a planner and  $\pi$ -conjugated structure, and  $E_R$  for the *p*-selenol group is also thought to be positive since the *p*-hydroxy group is positive. Accordingly, by assuming that the resonance terms for the *p*-ethynyl and the *p*-selenol groups are compensated each other, the reactivity of the addition polymerization of BDSe to DEB is estimated to be 1.4 times that of the model addition reaction of BSe to EB. Figure 3 shows that the relationship between HOMO level of *p*-X EBs calculated by CAChe system (PM3) and the rate of the addition reactions of BSe to *p*-X EBs.

Linear correlation was recognized between HOMO level of *p*-X EBs and relative rate. To estimate the ratio of the second addition rate constant ( $k_a^2$ ) to the first addition rate constant ( $k_a^1$ ) in eq 8, HOMO levels of DEB and 4-( $\beta$ -*cis*-selenophenylethenyl)-1-ethynylben-



**Figure 3.** Relationship between HOMO level of *p*-X ethynylbenzenes calculated by CAChe system (PM3) and the relative rate of the addition reactions of benzeneselenol to *p*-X ethynylbenzenes at 58°C in benzene under nitrogen atmosphere.  $[p\text{-X EB}]_0 = [p\text{-H EB}]_0 = 7.0 \times 10^{-2} \text{ mol l}^{-1}$ ;  $[\text{BSe}]_0 = 7.3 \times 10^{-2} \text{ mol l}^{-1}$ ;  $[\text{AIBN}]_0 = 6.4 \times 10^{-4} \text{ mol l}^{-1}$ .

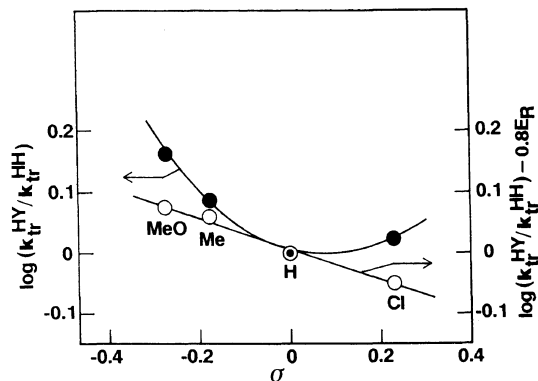
zene (**3**) were calculated to be  $-9.17$  and  $-8.58$  eV, respectively.



Therefore, the reactivity ratios of the addition reactions of BSe to DEB and BSe to **3**, respectively, are 1.8 times and 8.3 times toward the addition reaction of BSe to EB. Consequently, the ratio of  $k_a^2$  to  $k_a^1$  is estimated to be 4.6.

#### Substituent Effects on the Chain Transfer Step

The substituent effect on the chain transfer step which is hydrogen abstraction from *p*-Y BSeS by  $\beta$ -phenylselenostyrylene radical ( $\text{C}_6\text{H}_5-\dot{\text{C}}=\text{CH}-\text{Se}-\text{C}_6\text{H}_5$ ) was also investigated. The relative rate of the chain transfer step was evaluated by a competitive addition of *p*-H BSe and *p*-Y BSeS to EB, and is expressed in eq 9,<sup>7</sup>



**Figure 4.** Hammett plots of  $\log(k_{\text{tr}}^{\text{HY}}/k_{\text{tr}}^{\text{HH}})$  between *p*-Y benzeneselenols and EB at 58°C in the dark under nitrogen atmosphere with  $\bullet$ , eq 5 and  $\circ$ , eq 6;  $\rho = -0.26$ .  $[\text{EB}]_0 = [p\text{-Y BSe}]_0 = [p\text{-H BSe}]_0 = 7.0 \times 10^{-2} \text{ mol l}^{-1}$ ;  $[\text{AIBN}]_0 = 7.0 \times 10^{-4} \text{ mol l}^{-1}$  in benzene, internal reference for GC; *n*-heptadecane.

$$\frac{k_{\text{tr}}^{\text{HY}}}{k_{\text{tr}}^{\text{HH}}} = \frac{[\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{Se}-\text{C}_6\text{H}_4-\text{Y}][\text{C}_6\text{H}_5-\text{SeH}]_0}{[\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{Se}-\text{C}_6\text{H}_5][\text{Y}-\text{C}_6\text{H}_4-\text{SeH}]_0} \quad \mathbf{(9)}$$

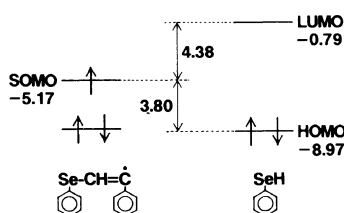
where  $k_{\text{tr}}^{\text{HY}}$  or  $k_{\text{tr}}^{\text{HH}}$  is the rate constant in the chain transfer step between  $\beta$ -phenylselenostyrylene radical and *p*-Y BSeS or *p*-H BSe, respectively. Therefore,  $k_{\text{tr}}^{\text{HY}}/k_{\text{tr}}^{\text{HH}}$  is calculated readily by determination of the concentration of both adducts. These  $k_{\text{tr}}^{\text{HY}}/k_{\text{tr}}^{\text{HH}}$  were summarized in Table II. Figure 4 shows the Hammett correlation of the chain transfer step by eq 5 and 6. Better correlation was obtained with eq 6 rather than by eq 5. That is, the rate of the chain transfer step between  $\beta$ -phenylselenostyrylene radical and BSeS is controlled by both the polar and resonance effects. Similar result has been discussed on the substituent effect of the chain transfer step between polystyryl radical and cumenes.<sup>12</sup> In the chain transfer step between  $\beta$ -phenylselenostyrylene radical and *p*-Y BSeS, the polar reaction constant ( $\rho = -0.26$ ) is negative and the resonance reaction constant ( $\gamma = 0.8$ ) is positive. Accordingly, a perturbation between SOMO of  $\beta$ -phenylselenostyrylene radical and HOMO of BSe in the transition state is the important controlling factor for the chain transfer step.

The interpretation is also consistent with the molecular orbital levels calculated by CAChe system (PM3), since the energy gap between SOMO level of  $\beta$ -phenylselenostyrene radical and HOMO level of BSe (3.80 eV) is smaller than that between the SOMO and LUMO levels (4.38 eV) as shown in Scheme 2.

#### Comparative Study between BSe and BT or EB and St

**Comparison between BSe and BT.** The substituent effect on the addition and chain transfer steps in the addition reactions of BSe or BT to EB is summarized in Table III. The rate-determining step of both reactions is addition one of benzeneseleno radical or benzenethiyl radical<sup>13</sup> to EB.

In the addition step, the transition states are thought to be much alike, since the polar



**Scheme 2.** Energy levels (eV) of orbitals in the chain transfer step between  $\beta$ -phenylselenostyrene radical (intermediate for *cis* adduct) and benzeneselenol.

reaction constant,  $\rho$ , and the resonance reaction constant,  $\gamma$ , of both addition reactions have the same sign. But, absolute  $\rho$  value ( $\rho = -0.83$ ) for the addition step of benzeneseleno radical to *p*-X EBs is about twice that ( $\rho = -0.48^7$ ) for benzenethiyl radical. The experimental data suggest that SOMO level of the benzeneseleno radical is lower than that of the benzenethiyl radical. This interpretation is consistent with the data calculated by CAChe system (PM3), in which SOMO levels of the benzeneseleno and benzenethiyl radicals are  $-6.27$  eV and  $-6.10$  eV, respectively (Scheme 1). The resonance reaction constant ( $\gamma = 3.4$ ) for the addition step of benzeneseleno radical to *p*-X EBs is nearly equal to that ( $\gamma = 3.2^7$ ) for benzenethiyl radical, indicating that the resonance stabilization by *p*-X substituent on EB in the transition state is larger than that in the initial state. On the other hand,  $\rho$  value ( $\rho = 1.42$ ) for the addition step of *p*-Y benzeneseleno radicals to EB is 1.4 times smaller than that ( $\rho = 2.00^7$ ) for *p*-Y benzenethiyl radicals. That is, the polar effect by *p*-Y substituent on benzeneseleno radicals is smaller than that for *p*-Y benzenethiyl radicals, since  $2sp^2$  orbital of carbon atom of benzene ring overlaps with  $4p$  orbital of selenium atom looser than  $3p$  orbital of sulfur atom. The resonance reaction constant ( $\gamma = -4.8$ ) for the addition step of

**Table III.** Hammett parameters<sup>a</sup> obtained by the addition reaction of BSe to EBs and benzenethiols to EBs in benzene under nitrogen atmosphere

Elementary Reaction	Benzeneselenol-Ethynylbenzene		Benzenethiol-Ethynylbenzene <sup>e</sup>	
Addition	$X-\text{C}_6\text{H}_4-\text{C}\equiv\text{CH}$ $+ \text{C}_6\text{H}_5-\text{Se}\cdot$	$\text{C}_6\text{H}_5-\text{C}\equiv\text{CH}$ $+ Y-\text{C}_6\text{H}_4-\text{Se}\cdot$	$X-\text{C}_6\text{H}_4-\text{C}\equiv\text{CH}$ $+ \text{C}_6\text{H}_5-\text{S}\cdot$	$\text{C}_6\text{H}_5-\text{C}\equiv\text{CH}$ $+ Y-\text{C}_6\text{H}_4-\text{S}\cdot$
	$-0.83\sigma + 3.4E_R^b$	$1.42\sigma - 4.8E_R^c$	$-0.48\sigma + 3.2E_R$	$2.00\sigma - 3.8E_R$
Chain Transfer	$\text{C}_6\text{H}_5-\dot{\text{C}}=\text{CH}-\text{Se}-\text{C}_6\text{H}_5$ $+ Y-\text{C}_6\text{H}_4-\text{SeH}$		$\text{C}_6\text{H}_5-\dot{\text{C}}=\text{CH}-\text{S}-\text{C}_6\text{H}_5$ $+ Y-\text{C}_6\text{H}_4-\text{SH}$	
	$-0.26\sigma + 0.8E_R^d$		$-0.98\sigma + 4.7E_R$	

<sup>a</sup> Eq 6,  $\log(k/k_0) = \rho\sigma + \gamma E_R$ . <sup>b</sup> From Figure 1. <sup>c</sup> From Figure 2. <sup>d</sup> From Figure 3. <sup>e</sup> Reference 7.



*p*-Y benzeneseleno radicals to EB is 1.3 times that ( $\gamma = -3.8^7$ ) for *p*-Y benzenethiyl radicals, indicating that the resonance stabilization by *p*-Y substituent on BSe in the transition state is smaller than that in the initial state, and difference in resonance stabilization in the transition state and in the initial state is larger than that by *p*-Y substituent on BT.

In the chain transfer step, the transition states are also thought to be much alike, since  $\rho$  and  $\gamma$  of both the steps have the same sign. However, absolute  $\rho$  value ( $\rho = -0.26$ ) for the chain transfer step between the  $\beta$ -phenylselenostyrene radical ( $\text{C}_6\text{H}_5\text{-}\dot{\text{C}}=\text{CH-Se-C}_6\text{H}_5$ ) and *p*-Y BSe is about four times smaller than that ( $\rho = -0.98^7$ ) for the  $\beta$ -phenylthiostyrene radical ( $\text{C}_6\text{H}_5\text{-}\dot{\text{C}}=\text{CH-S-C}_6\text{H}_5$ ) and *p*-Y BTs. The result also suggests that the polar effect by *p*-Y substituent on BSe is smaller than that for *p*-Y BTs. Small polar effect of *p*-Y substituent on BSe may also be caused by weak overlap between  $2sp^2$  orbital of carbon atom and  $4p$  orbital of selenium atom. The resonance reaction constant ( $\gamma = 0.8$ ) for the chain transfer step between  $\beta$ -phenylselenostyrene radical and *p*-Y BSe is six times smaller than that ( $\gamma = 4.7^7$ ) for  $\beta$ -phenylthiostyrene radical and *p*-Y BT, indicating that resonance stabilization by *p*-Y substituent on BSe in the transition state is larger than that in the initial state, and difference in resonance stabilization in the transition state and in the initial state is much smaller than that by *p*-Y BT.

In the addition reaction of BSe to EB similar to that of BT to EB, energy gap (3.13 eV) between SOMO level of benzeneseleno radical

and HOMO level of EB is smaller than that (3.80 eV) between SOMO level of  $\beta$ -phenylselenostyrene radical and HOMO level of BSe. However, the rate-determining step was the confirmed experimentally to be the addition step. The energy levels of SOMO, HOMO, and LUMO are probably altered by the CT interaction.<sup>14</sup> CT interaction of BSe and EB was suggested by diffuse reflectance spectrum of the thin layer mixture of BDSe and DEB,<sup>2</sup> thus the chain transfer step of the reaction may occur very rapidly in a sort of cage effect.

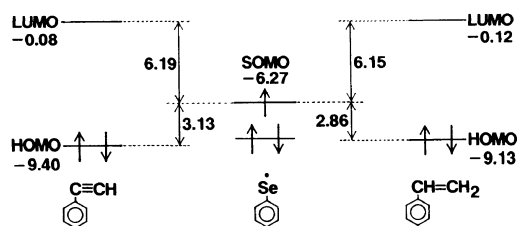
*Comparison between EB and St.* The substituent effect on the addition step in the addition reactions of BSe to EB or St is summarized in Table IV. The rate-determining step of both the reactions is addition one of benzeneseleno radical to EB or St.<sup>15</sup> The transition states in the addition step are much alike because  $\rho$  and  $\gamma$  of both addition reactions have the same sign. However, absolute  $\rho$  value ( $\rho = -0.83$ ) for the addition step of benzeneseleno radical to *p*-X EBs is larger than that ( $\rho = -0.46^{15}$ ) for *p*-X St. The experimental data suggest that energy gap between SOMO level of benzeneseleno radical and HOMO level of EB is smaller than that between SOMO level of benzeneseleno radical and HOMO level of St. However, this interpretation is in conflict with the data calculated by CAChe system (PM3) as shown in Scheme 3.

The reason for the discrepancy between the calculated data and experimental data can be explained on the basis of the changes of SOMO level of benzeneseleno radical and HOMO level of EB by a CT interaction as mentioned above.

**Table IV.** Hammett parameters<sup>a</sup> obtained by the addition reaction of BSe to EBs and BSe to styrenes in benzene under nitrogen atmosphere

Elementary reaction	Benzeneselenol-Ethynylbenzene	Benzeneselenol-Styrene <sup>c</sup>
Addition	$\text{X-C}_6\text{H}_4\text{-C}\equiv\text{CH} + \text{C}_6\text{H}_5\text{-Se}\cdot$	$\text{X-C}_6\text{H}_4\text{-CH}=\text{CH}_2 + \text{C}_6\text{H}_5\text{-Se}\cdot$
	$-0.83\sigma + 3.4E_R^b$	$-0.46\sigma + 1.6E_R$

<sup>a</sup> Eq 6,  $\log(k/k_0) = \rho\sigma + \gamma E_R$ . <sup>b</sup> From Figure 1. <sup>c</sup> Reference 15.



**Scheme 3.** Energy levels (eV) of orbitals in the addition step of benzeneseleno radical to ethynylbenzene or styrene.

The resonance reaction constant ( $\rho=3.4$ ) for the addition step of benzeneseleno radical and *p*-X EBs is about twice that ( $\rho=1.6^{15}$ ) for *p*-X St, indicating that an activated complex containing EB in the transition state is more resonance-stabilized by the *p*-X substituent than that containing St.

### CONCLUSION

The mechanism for the addition reaction of BSe to EB was investigated on the basis of Hammett correlation. The controlling factor for the addition reaction is found to be perturbation between SOMO level of  $\beta$ -phenylselenostyrylene radical and HOMO level of

EB, which is also supported by the quantum chemical calculation by CAChe system (PM3).

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