Addition Reaction of Phenylphosphines to Styrenes as the Model of Polyaddition. Study on the Rate-Determining Step and Substituent Effect

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ABSTRACT: The addition reactions of phenylphosphine or diphenylphosphine to styrenes or α -methylstyrene were carried out to know the reaction mechanism and the transition state of the addition reaction. Phenylphosphine having two reactive hydrogens added to two styrenes, and the 1:2 adduct [$\phi\text{CH}_2\text{CH}_2\text{P}(\phi)\text{CH}_2\text{CH}_2\phi$] of the anti-Markownikoff's structure was obtained in a 94% yield. But, a little amount of the by-product containing styrene-styrene unit was produced as compared with the reaction of thiophenol to styrene. Such a side reaction was suppressed by using α -methylstyrene instead of styrene. The kinetics of the addition reaction of the P-H group to the vinyl group was investigated in detail by the addition reaction of diphenylphosphine to styrene, to give scarcely by-product. The rate-determining step of the reaction was the chain transfer step between the intermediate carbon radical ($\phi\dot{\text{C}}\text{HCH}_2\text{P}\phi_2$) and diphenylphosphine. In the para substituent effect of styrenes on the chain transfer step, fairly good linear correlation was obtained with modified Hammett's equation including the resonance effect. The rate-determining step and the substituent effect on this reaction were found to be similar to those of the addition reaction of thiophenol to styrenes. The results were also compared with the polyaddition of phenylphosphine to 1,4-divinylbenzene or 1,4-diisopropenylbenzene.

KEY WORDS Kinetics / Polyaddition / Addition Reaction / Reaction Mechanism / Rate-Determining Step / Substituent Effect / Hammett Correlation / Phenylphosphine / Diphenylphosphine / Styrene Derivatives /

Primary and secondary phosphines have been known to add to alkenes, similar to the addition reactions of thiols to alkenes. The radical addition initiated by UV light,¹ radical initiator,² or X-ray² is the convenient way of carrying out the addition reaction. For example, bis(2-cyanoethyl)phosphine reacted with 1-octene in the presence of AIBN at 75–140°C to give the tertiary phosphine in a 74% yield.² Such the addition reaction seems to proceed by a radical chain mechanism.³ However, no extensive investigation about the addition mechanism has been undertaken.

In the present paper, two model addition reactions were investigated in detail to know the polymerization mechanism and the polymer structure of phenylphosphine (PH) with 1,4-divinylbenzene (DVB) or 1,4-diisopropenylbenzene (DIPB). The model addition reactions of PH to styrene (St) and to α -methylstyrene (MSt) were studied to make clear the reaction behavior with primary phosphines and olefins. The detailed kinetic behavior such as the rate-determining step and substituent effect on the addition reaction of P-H group to vinyl group were also inves-

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tigated by the model addition reaction of diphenylphosphine (DPH) to St. These results were discussed by comparing with the addition reaction of thiophenol (TP) to St⁴ and with the polyaddition of PH to DVB⁵ or DIPB.⁵

EXPERIMENTAL

Reagents

PH⁶ and DPH⁷ were prepared by reduction of dichlorophenylphosphine (Tokyo Chem. Ind. Co., Ltd.) and chlorodiphenylphosphine provided by Hokko Chem. Ind. Co., Ltd. using LiAlH₄ (Yoneyama Reagent Ind. Co., Ltd.), respectively. St (Wako Pure Chemical Industries, Ltd.) and MSt (Nacalai Tesque Inc.) were obtained commercially. *p*-Chloro St was provided by Hokko Chem. Ind. Co., Ltd. *p*-Methyl and *p*-methoxy Sts were prepared according to the literature.⁸⁻¹⁰ The reagents were purified by vacuum distillation under a nitrogen atmosphere before use. Toluene (Nacalai Tesque Inc.) as a reaction solvent was distilled over CaH₂ and then degassed several times by vacuum for 20 min before use to exclude oxygen. 2,2'-Azobisisobutyronitrile (AIBN, Wako Pure Chemical Industries, Ltd.) was used as received. Nitrogen gas was purified as shown in the previous paper.⁴

Addition Reaction

The typical addition reaction was carried out as follows: in a 50 ml round-bottomed flask equipped with a three-way stopcock, the toluene solutions of DPH, St, AIBN, and decane or *cis*-decalin as an internal reference for GC were charged by a hypodermic syringe under a nitrogen atmosphere. The reaction was carried out at 60°C. The reaction course was monitored every *ca.* 10 min by measurement of the concentration of DPH by GC.

Measurements

Gas chromatograms were recorded on a Shimadzu GC-4BMPF equipped with a flame ionization detector (FID) and a Silicone GE

SE-30 column (2 m) under a nitrogen carrier gas at 300°C of the injection temperature. The GC conditions are as follows: the addition reaction of PH to St or MSt: nitrogen carrier gas, 27 ml min⁻¹; column temp, 100→270°C; int. ref., decane for St or *cis*-decalin for MSt; the addition reactions of DPH to St derivatives: nitrogen carrier gas, 27 ml min⁻¹; column temp, 190°C; int. ref., decane for *p*-methoxy St or *cis*-decalin for the others; the competitive addition reaction of DPH to MSt and St or of DPH and PH to St: nitrogen carrier gas, 27 ml min⁻¹; column temp, 100→270°C; int. ref., *cis*-decalin. ¹H NMR spectra were measured on a JEOL JNM-FX90Q or a JEOL JNM-EX400 in CDCl₃ with the chemical shift δ from tetramethylsilane (TMS) as 0 ppm. IR spectra were recorded on a Hitachi 260-50 spectrophotometer by a liquid film or a KBr method. FD mass spectra were obtained on a JEOL JMS-MX110. The molecular weight distribution (MWD) curves were measured using GPC in chloroform on a JASCO TRI ROTAR instrument equipped with a polystyrene gel column (Shodex K-2002, inner diameter 20 mm; length 300 mm) and a refractive index detector. The MW was determined based on the polystyrene calibration. Phosphorus content of the adducts was determined by the phosphovanadomolybdic acid method^{11,12} as described in the previous paper.⁵

The simulation curves of the adduct formations of PH to St or MSt were obtained by the laboratory made program¹³ based on the algorithm theory. The concentrations of the substances in the simulation curves were calculated by the equation on the consecutive reaction with A→B→C.

RESULTS AND DISCUSSION

Addition Reaction Behavior of PH to St or MSt

Addition Reaction of PH to St. Primary phosphines add to twice molar olefins, and unsymmetrical secondary and tertiary phos-

phines are obtained.² But, the addition reaction of PH to St has not been reported. The reaction perhaps occurs because the chain transfer constant of PH determined in the polymerization of St at 60°C has been reported to be about 44¹⁴ as same order as that of thiophenol.¹⁵ In this work, to know the structure of the product of PH and St, and the relative reactivity of the two P-H groups in the PH, the addition reaction of PH to St was investigated in detail. This information is helpful to understand the polymerization behavior of PH to DVB and the polymer structure.

PH (0.5 mol l⁻¹) was reacted with twice molar quantity of St (1.0 mol l⁻¹) in the presence of AIBN radical initiator (0.01 mol l⁻¹) at 60°C in toluene under a nitrogen atmosphere. Figure 1 shows the typical time-courses of the remaining monomers or the yields of **1** and **2** for the addition reaction, confirmed by GC analysis. Both PH and St decreased without an induction period and were almost consumed for 10 h and 20 h, respectively. The yield of the adduct **1** increased with reaction time until 3 h, and then decreased. On the other hand, the yield of the adduct **2** increased monotonously with reaction time. The retention times of **1** and **2** by GC were *ca.* 32 min and *ca.* 47 min, respectively.

Figure 1. Time-courses of the remaining monomers or the yields of **1** and **2** for addition reaction of PH to St at 60°C in toluene under a nitrogen atmosphere. $[PH]_0 = 0.5 \text{ mol l}^{-1}$; $[St]_0 = 1.0 \text{ mol l}^{-1}$; $[AIBN]_0 = 0.01 \text{ mol l}^{-1}$; int. ref. for GC, decane. $\circ$, PH; $\bullet$, St; $\square$, $\phi\text{CH}_2\text{CH}_2\text{PH}\phi$ (**1**); $\triangle$, $\phi\text{CH}_2\text{CH}_2\text{P}(\phi)\text{CH}_2\text{CH}_2\phi$ (**2**).

The crude product obtained by removal of toluene from the reaction mixture for 1 day at room temperature under reduced pressure without any pretreatment was analyzed by GPC as shown in Figure 2. The crude product contained 94 wt% of adduct **2** and 6 wt% of oligomer **3**. Any by-products such as teromers of styrene with higher molecular weight than the oligomer **3** were not confirmed.

The adduct **2** isolated by vacuum distillation

Figure 2. MWD curve of the products obtained for addition reaction of PH to St for 1 day at 60°C in toluene under a nitrogen atmosphere. $[PH]_0 = 0.5 \text{ mol l}^{-1}$; $[St]_0 = 1.0 \text{ mol l}^{-1}$; $[AIBN]_0 = 0.01 \text{ mol l}^{-1}$.

Figure 3. ¹H NMR spectra of (a) the isolated adduct **2** and (b) the isolated adduct **1** of PH and St in CDCl₃ (JEOL JNM-EX400). **2**, $\phi\text{CH}_2\text{CH}_2\text{P}(\phi)\text{CH}_2\text{CH}_2\phi$; **1**, $\phi\text{CH}_2\text{CH}_2\text{PH}\phi$.

(bp 167–168°C/0.04 mmHg) was colorless transparent liquid. The ^1H NMR spectrum of the **2** shows signals at δ 1.94–2.08 ppm (m, 4H, $-\text{CH}_2\text{P}-$) and 2.57–2.73 ppm (m, 4H, ϕCH_2-) due to methylene protons, and at δ 7.09–7.58 ppm (15H) due to benzene ring protons (Figure 3(a)). The spectrum also indicates the absence of the signals of unreacted P–H group or any by-products formed by the side reactions such as Markownikoff's type reactions. The phosphorus content (found 9.7 wt%; calcd 9.7 wt%), the molecular weight [MW, 300 (GPC); 318 (FD mass); 318 (calcd)], and the proton ratio of methylene and benzene ring in the ^1H NMR spectrum were almost equal to those calculated based on the 1:2 adduct of PH and St. These results indicate that the **2** is the 1:2 adduct of PH and St and has the anti-Markownikoff's structure. The oligomer **3** is estimated to be 1:3 adduct of PH and St, because its molecular weight (calcd 422) was

found to be 400 by GPC and 422 from the molecular ion peak in the FD mass spectrum.

On the other hand, the 1:1 adduct **1** was synthesized with equimolar amounts (1.0 mol l^{-1}) of PH and St under the similar conditions for 1 day, and isolated by vacuum distillation (yield = 28%). The product **1** is confirmed to be 1:1 adduct of PH and St by ^1H NMR (Figure 3(b)), IR, and GC analyses. Table I summarizes the bp, m/z , Pwt%, IR, and ^1H NMR spectral data of the 1:1 and 1:2 adducts (**1** and **2**). Consequently, both two hydrogens in PH can be reacted with St. PH adds to St at first to form the 1:1 adduct **1**, and the 1:2 adduct **2** is finally obtained by the addition reaction of **1** to St (eq 1): the reaction is $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ type.

To make clear the polymerization behavior of PH and DVB, or to obtain the 1:1 adduct

Figure 4. Evaluation of k_2/k_1 by the computer simulation curve fitting method. $\square$ and $\triangle$ are the experimental data for the **1** and **2**, taking from the Figure 1, respectively, in the addition reaction of PH to St in toluene at 60°C under a nitrogen atmosphere ($[\text{PH}]_0 = 0.5 \text{ mol l}^{-1}$; $[\text{St}]_0 = 1.0 \text{ mol l}^{-1}$; $[\text{AIBN}]_0 = 0.01 \text{ mol l}^{-1}$). The curves were drawn by taking $k_2/k_1 = a, 0.3$; $b, 0.4$; $c, 0.5$; $d, 0.6$; $e, 0.7$; $f, 0.5$.

1, containing the active P–H group, in a high yield, it is necessary to know the ratio of the apparent second addition rate constant (k_2) to the apparent first addition rate constant (k_1), k_2/k_1 . The k_2/k_1 was determined by comparing the experimental data with the computer simulation curve.¹³ Figure 4 shows the yields of **1** and **2** adducts and the computer simulation curves. The yield of **1** or **2** was calculated based on the initial concentration of PH. The calculated curves with k_2/k_1 of 0.50 almost fit with the experimental points. That is, the reactivity of first addition of PH to St is higher than that of second addition of $\phi\text{CH}_2\text{CH}_2\text{PH}\phi$ to St ($k_1 > k_2$).

Addition Reaction of PH to MSt. It was mentioned above that the PH added to St in a high yield, but oligomer **3** containing two St units as the by-product was also formed by reaction between the intermediate carbon

Table I. The addition reaction of PH to St^a or MSt^b at 60°C in toluene under a nitrogen atmosphere

Initial Rate k_2/k_1^c $\text{mol l}^{-1} \text{s}^{-1}$	Yield ^d %	bp °C/mmHg	m/z (Calcd)	P/wt% ^e (Calcd)	¹ H NMR Spectra ^f		IR Spectra ^g cm ⁻¹	
					ppm			
St	35	167—168 /0.04	318 (318)	9.7 (9.7)	1.94—2.08 (m, 4H, CH ₂ P) 2.57—2.73 (m, 4H, ϕ CH ₂) 7.09—7.58 (m, 15H, C ₆ H ₅)		1430 (CH ₂ P) 3015, 3050 (C ₆ H ₅)	
					1.92—2.12 (m, 2H, CH ₂ P) 2.59—2.76 (m, 2H, ϕ CH ₂) 3.83, 4.36 (m, 1H, PH, $J_{P-H} = 211 \text{ Hz}$) 7.05—7.44 (m, 10H, C ₆ H ₅)		1435 (CH ₂ P) 2280 (P-H) 3015, 3050 (C ₆ H ₅)	
	0.50	28 ⁱ	82—83 /0.03	— (214)	14.3 (14.5)			
MSt	7 ^j	175—176 /0.03	346 (346)	8.9 (9.0)	1.14—1.37 (m, 6H, CH ₃) 1.58—2.07 (m, 4H, CH ₂) 2.51—2.85 (m, 2H, CH) 6.95—7.53 (m, 15H, C ₆ H ₅)		1440 (CH ₂ P) 2960 (CH ₃) 3030, 3060 (C ₆ H ₅)	
	0.45	35 ⁱ	86—87 /0.01	— (228)	13.4 (13.6)	1.31 (ABq, 3H, CH ₃) 1.90—2.32 (m, 2H, CH ₂) 2.51—2.85 (m, 1H, CH) 7.09—7.46 (m, 10H, C ₆ H ₅) 3.73, 4.26 (m, 1H, PH, $J_{P-H} = 211 \text{ Hz}$)		1435 (CH ₂ P) 2280 (P-H) 2960 (CH ₃) 3025, 3060 (C ₆ H ₅)

[PH]₀ = 0.5 mol l⁻¹, [St]₀ = [MSt]₀ = 1.0 mol l⁻¹.^a For 1 day; [AIBN]₀ = 0.01 mol l⁻¹.^b For 5 days; [AIBN]₀ = 0.04 mol l⁻¹.^c Computer simulation curve fitting method.^d By GC and GPC analyses.^e Phosphovanadomolybdic acid method.^f JEOL JNM-EX 400: solv., CDCl₃; ref., TMS.^g Liquid film method.^h [PH]₀ = 1.0 mol l⁻¹.ⁱ Isolated yield by vacuum distillation.^j [AIBN]₀ = 0.01 mol l⁻¹.

radical and St instead of PH. It is well known that homopolymerization of MSt hardly occurs over the ceiling temperature, that is, $\sim\text{CH}_2\dot{\text{C}}\phi(\text{CH}_3)$ adds hardly to MSt. In the present study, the addition reaction of PH to MSt examined under the similar conditions to the St system ($[\text{PH}]_0 = 0.5 \text{ mol l}^{-1}$, $[\text{MSt}]_0 = 1.0 \text{ mol l}^{-1}$; $[\text{AIBN}]_0 = 0.01 \text{ mol l}^{-1}$). The reaction proceeded very slowly and saturated for 5 days with remaining the unreacted MSt (*ca.* 20%). However, the addition reaction of PH to MSt was completed for 5 days with increasing the AIBN concentration (0.04 mol l^{-1}). The apparent initial rate of PH concentration decay of MSt system was five times less than that of St as shown in Table I. Low reactivity of MSt was also estimated by competitive reaction of DPH to MSt and St. That is, the relative addition reactivity of DPH to MSt and St was 0.09. The crude product of PH and MSt obtained by removal of toluene at room temperature under reduced pressure contained 98 wt% of the adduct and 2 wt% of oligomer. The adduct was confirmed to be the 1:2 adduct of PH and MSt [MW, 340 (GPC); 346 (FD mass); 346 (calcd)], as shown in the Table 1. The oligomer may be the 1:3 adduct of PH and MSt because of its fair agreement of the molecular weight found by GPC and FD mass spectrum with the calculated one [MW, 500 (GPC); 464 (FD mass); 464 (calcd)]. The ratio of the apparent second addition rate to the apparent first addition one, k_2/k_1 , was also determined by the computer simulation curve fitting method to be 0.45. The value is almost equal to that of the St system (0.5). That is, by the α -methyl group on the MSt, the addition reactivity of PH to MSt becomes much lower than that of PH to St, thus the k_2/k_1 for the MSt system is little changed. Consequently, PH can add to St as well as MSt by anti-Markownikoff's type to give the 1:2 adduct of PH and St or MSt in a high yield. By-product was diminished by using MSt instead of St.

The authors estimate the polyaddition

behavior of PH to DVB or DIPB based on the above mentioned results of the model adduct formations. The apparent polyaddition reactivity of PH to DVB is larger than that of PH to DIPB.⁵ The polymer of PH and DVB or DIPB is sure to have the anti-Markownikoff's structure. That is, the polymers have the alternating structure of PH and DVB or DIPB units. However, a minor homosequence of DVB–DVB or DIPB–DIPB unit is probably formed in the polymer main chain by the side reaction between the intermediate carbon radical and DVB or DIPB instead of PH, so that the pendant vinyl or isopropenyl group was formed along with the two terminal groups. The pendant vinyl or isopropenyl group thus formed induces polymer cross-linkage. In the case of polyaddition of PH to DVB, the polymer of the molecular weight of about 4×10^3 may have potentially only one pendant vinyl group according to the calculation based on the by-product content in the model addition reaction of PH to St. Similarly, in the case of polyaddition of PH to DIPB, only one pendant isopropenyl group may be contained in the polymer of the molecular weight of about 1×10^4 . That is, the polymer of DVB and PH having the molecular weight of 1×10^4 might be expected to have the cross-linked structure and become insoluble in conventional organic solvents,⁵ on the contrary, the cross-linked polymer is scarcely obtained in the polyaddition with DIPB.⁵

Reaction Mechanism

As the kinetic investigation for the model addition reactions, the reaction order, the rate-determining step, and the substituent effect on the addition reaction were determined. Such kinetic data have been reported hardly yet. The model addition reaction of DPH, containing mono P–H group, to St is chosen for the kinetic investigation, since the addition reaction of PH is proceeding in two steps and is complicated. The addition reaction of DPH (1.0 mol l^{-1}) to St (1.0 mol l^{-1}) was carried out with AIBN

Figure 5. Competitive addition reaction of DPH (●) and PH (○) to St at 60°C in toluene under a nitrogen atmosphere $[\text{DPH}]_0 = [\text{PH}]_0 = 0.5 \text{ mol l}^{-1}$; $[\text{St}]_0 = 2.5 \text{ mol l}^{-1}$; $[\text{AIBN}]_0 = 0.01 \text{ mol l}^{-1}$.

Figure 6. Time-yield curves of the adduct formation of DPH to St by changing the initial concentration of St at 60°C in toluene under a nitrogen atmosphere. $[\text{DPH}]_0 = 1.08 \text{ mol l}^{-1}$; $[\text{AIBN}]_0 = 0.01 \text{ mol l}^{-1}$; int. ref. for GC, *cis*-decalin. $[\text{St}]_0$ (mol l⁻¹): □, 2.03; △, 1.50; ○, 1.01; ■, 0.73; ●, 0.51.

initiator (0.01 mol l^{-1}) in toluene at 60°C under a nitrogen atmosphere. The reaction was completed for 1 day without appreciable side reactions, and the adduct of the anti-Markownikoff's structure was obtained in a 97% yield (Table II in the latter section). The relative addition reactivity of DPH to PH was also examined by the competitive reaction of DPH and PH to St under the similar conditions. The apparent decreasing rate of the PH concentration was twice larger than that of the DPH concentration as shown in Figure 5. Accordingly, the addition reaction of DPH to St is suggested to proceed by a similar mechanism to the addition reaction of PH to

Figure 7. Time-yield curves (a) of the adduct formation of DPH to St by changing the initial concentration of DPH and the reaction order (b) of DPH at 60°C in toluene under a nitrogen atmosphere. $[\text{St}]_0 = 1.01 \text{ mol l}^{-1}$; $[\text{AIBN}]_0 = 0.01 \text{ mol l}^{-1}$; int. ref. for GC, *cis*-decalin. $[\text{DPH}]_0$ (mol l⁻¹): □, 2.01; △, 1.41; ○, 1.08; ■, 0.69; ●, 0.51.

St or MSt. The addition reaction of DPH to St can be utilized for the kinetic investigation as a model of polyaddition of PH to DVB.

Reaction Order and Rate-Determining Step. The reaction order of the addition reaction of DPH to St was determined by the similar method to that mentioned in the previous paper.^{4,16} As shown in Figure 6 the rate of addition reaction was found to be independent of the St concentration. On the other hand, the typical time-yield curves and the reaction order of DPH in Figure 7(a) and 7(b), respectively, indicate that the addition rate depends on the first order of the DPH concentration. The kinetic order of AIBN was determined to be approximately 0.5. Therefore, the rate equation can be as follows;

$$\text{Rate} = k[\phi_2\text{PH}]^1[\phi\text{CH}=\text{CH}_2]^0[\text{AIBN}]^{0.5} \quad (2)$$

Table II. Synthesis of adducts of DPH and *p*-substituted Sts at 60°C in toluene for 1 day under a nitrogen atmosphere

<i>p</i> -X Sts	Yield ^a		bp	mp	P/wt% ^b (Calcd)	¹ H NMR Spectra ^c		IR Spectra ^d	
	%	°C/mmHg				ppm		cm ⁻¹	
H	97	144–145 /0.03	28.0–28.5		10.9 (10.7)	2.15–2.85 (m, 4H, CH ₂) 7.05–7.55 (m, 15H, benzene ring)		1435 (CH ₂ P) 3020, 3050 (benzene ring)	
CH ₃	99	155–156 /0.08	44.2–44.8		10.1 (10.2)	2.30 (s, 3H, CH ₃) 2.26–2.83 (m, 4H, CH ₂) 7.05–7.55 (m, 14H, benzene ring)		1440 (CH ₂ P) 2930 (CH ₃) 3020, 3050 (benzene ring)	
Cl	96	166–169 /0.06	°	°	9.7 (9.5)	2.17–2.86 (m, 4H, CH ₂) 6.97–7.66 (m, 14H, benzene ring)		680 (C–Cl) 1440 (CH ₂ P) 3035, 3060 (benzene ring)	
CH ₃ O	99	159–161 /0.07	°	°	9.5 (9.7)	3.73 (s, 3H, CH ₃) 2.17–2.86 (m, 4H, CH ₂) 6.71–7.60 (m, 14H, benzene ring)		1440 (CH ₂ P) 1250 (O–CH ₃), 2840 (CH ₃ O) 3010, 3050 (benzene ring)	

^a By GC analysis.^b Phosphovanadomolybdic acid method.^c JEOL-FX90Q: solv., CDCl₃; ref., TMS.^d KBr method.^e The adduct has not been crystallized yet, since it is very viscous liquid.

where k is the overall reaction rate constant in toluene at 60°C. The rate equation is similar to that of the addition reaction of TP to St.⁴ That is, the addition reaction of DPH to St progresses by the radical chain mechanism, and the rate-determining step is the chain transfer step between the intermediate carbon radical ($\dot{C}$, $\phi\dot{C}HCH_2P\phi_2$) and DPH. The elementary reactions and theoretical rate equations were mentioned already in the previous paper.^{4,16}

Substituent Effect. The addition reactions of DPH to St derivatives such as *p*-methoxy, *p*-methyl, and *p*-chloro Sts were also carried out under the similar conditions to the addition reaction of DPH to St to give the adducts of the anti-Markownikoff's structure in 96–99% yields as shown in Table II. Table II summarizes bp, mp, Pwt%, ¹H NMR, and IR spectral data of the adducts isolated by vacuum distillation.

The substituent effect on the chain transfer step between $\dot{C}$ ($\phi\dot{C}HCH_2P\phi_2$) and DPH, which is the rate-determining step, was elucidated in detail. The relative rates of the step, k_{tr}^X/k_{tr}^H , were determined by the similar method to the TP-*p*-X Sts systems having the same rate-determining step.⁴ The k_{tr}^X or k_{tr}^H is the chain transfer rate constant between the *p*-X or *p*-H intermediate carbon radical and DPH, respectively. The relative rates, k_{tr}^X/k_{tr}^H , are summarized in Table III, and the plots by Hammett's equation 3 (broken line) and modified Hammett's equation 4¹⁷ (solid line) are shown in Figure 8.

$$\log(k_{tr}^X/k_{tr}^H) = \rho\sigma \quad (3)$$

$$\log(k_{tr}^X/k_{tr}^H) = \rho\sigma + \gamma E_R \quad (4)$$

Better correlation was obtained with eq 4, indicating that the chain transfer rates are controlled by both polar and resonance effects as same as mentioned in the previous paper.^{4,18}

The polar and resonance reaction constants, ρ and γ , are tentatively determined from Figure 8 to be -0.80 and -1.2 , respectively. The negative ρ value indicates that the intermediate

Table III. Relative rates (k_{tr}^X/k_{tr}^H)^a of the chain transfer step in the addition reactions of DPH to *p*-X Sts at 60°C in toluene under a nitrogen atmosphere

<i>p</i> -X Sts	k_{tr}^X/k_{tr}^H
MeO	1.18
Me	1.42
H	1.00
Cl	0.15

^a $[X-Sts]_0 = [DPH]_0 = 1.0 \text{ mol l}^{-1}$; $[AIBN]_0 = 0.01 \text{ mol l}^{-1}$.

Figure 8. Hammett plot of relative chain transfer rate constant k_{tr}^X/k_{tr}^H between *p*-X intermediate carbon radicals and DPH at 60°C in toluene under a nitrogen atmosphere by Hammett's equation 3 (---●---) and modified Hammett's equation 4 (—○—). $[X-Sts]_0 = [DPH]_0 = 1.0 \text{ mol l}^{-1}$; $[AIBN]_0 = 0.01 \text{ mol l}^{-1}$; $\log(k_{tr}^X/k_{tr}^H) = -0.80\rho - 1.2E_R$.

carbon radical $\dot{C}$ is regarded as a nucleophilic one and a perturbation between SOMO of $\dot{C}$ and LUMO of DPH in the transition state is an important factor for controlling the reactivity of the addition reaction. That is, the electron is somewhat transferred from the intermediate carbon radical $\dot{C}$ to DPH in the transition state. On the other hand, the γ is negative. Otsu *et al.*^{17,19} reported that in the case of $\gamma < 0$, the resonance effect (R-effect) by the substituent in the transition state was smaller than that in the initial state. Therefore, the chain transfer rate increases by introducing a large electron-donating group (+I), and decreases by introducing a high resonance

stabilizing group (+R or -R) into the para position of St.

In the case of the polyaddition of PH to DVB, it can be regarded as the addition reaction of PH to St containing the para vinyl group. The addition reactivity of PH to DVB is evaluated from the results in Figure 8 to be almost equal to that of PH to St, assuming $\sigma = -0.08$,²⁰ $\gamma = 0.11$ (tentative value for *p*-methoxy group¹⁵), and $\rho_{\text{PH}} = \rho_{\text{DPH}}$.

Comparison between DPH and TP⁴ in the Addition Reactions to St

Both DPH and TP added quantitatively to St and side reactions occur scarcely. The adducts had the anti-Markownikoff's structure. The addition reaction of DPH proceeded more slowly than that of TP: the addition reaction of TP was completed within 2 h⁴ in spite of the lower initial concentrations of both monomers being 0.3 mol l⁻¹. The rate-determining step of both reactions is similar chain transfer step between the each intermediate carbon radical and DPH or TP. The transition state of the chain transfer step of both systems is thought to be much alike, since ρ were negative and little changed (DPH, $\rho = -0.80$; TP, $\rho = -0.99$). Accordingly, the lower reactivity of DPH than TP may be caused by the larger energy gap between SOMO of the each intermediate carbon radical and LUMO of DPH than that of TP. On the other hand, γ of DPH-Sts was negative (-1.2), but γ of TP-Sts was positive (+2.3⁴), which suggests that in the case of DPH the R-effect of the para substituent on the St in the transition state is smaller than that in the initial state, on the contrary the R-effect in the transition state is larger in the TP system. That is, the *p*-X substituent on the St in the activated complex

of TP can be conjugated, while that of DPH is hardly conjugated.

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