Application of Phosphonium Ylides to Latent Catalysts. 2. Kinetic Study on the Thermal Latency of the Phosphonium Ylides in the Polyaddition of Bisphenol A Diglycidyl Ether with Bisphenol A

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ABSTRACT: Substituent effects of phosphonium ylides $Ph_3PC(H)COR$ ($\mathbf{1_R}$) were kinetically studied in the reaction of glycidyl phenyl ether (GPE) with 2,6-dimethylphenol in the presence of the phosphonium ylide catalysts, (formylmethylene)triphenylphosphorane ($\mathbf{1_H}$), (acetylmethylene)triphenylphosphorane ($\mathbf{1_{Me}}$), (benzoylmethylene)triphenylphosphorane ($\mathbf{1_{Ph}}$), and (pivaloylmethylene)triphenylphosphorane ($\mathbf{1_{tBu}}$) for molecular design of excellent latent catalysts. Both the activation energy (E_a) and frequency factor (A) of the reaction increased with the bulkiness of the acyl group of **1**. Further, the catalytic activity was examined in the polyaddition of bisphenol A diglycidyl ether with bisphenol A in the presence of phosphonium ylide catalysts. The catalytic activity decreased with the bulkiness of the acyl group of **1**, but the latency, i.e., the starting temperature, of the epoxide conversion was little affected. On the other hand, the introduction of acetyl and cyano groups into the catalysts as the electron-withdrawing moieties shifted the temperature−conversion curves to higher temperature region compared with the case of **1**. The thermal latency of the phosphonium ylides was discussed from the viewpoint of the catalytic mechanism with the kinetic data.

Introduction

Catalysts are important in chemical reactions because they decrease the activation energies, resulting in the acceleration of reactions. “Latent catalysts” are inert under normal conditions, ambient temperature or room light, but show activity under appropriate external stimulation such as heating and irradiation with light.[1] Latent catalysts are widely utilized for various polymeric materials such as thermosetting resins, adhesives, paintings, inks, and photoresists, since they can control the activation steps of polymerization and curing. Control of activation steps is important to initiate polymerization at the desired temperature. The activation step of thermally latent cationic catalysts, e.g., iodonium,[2] sulfonium,[2−7] ammonium,[8,9] and pyridinium salts,[10,11] corresponds to the cleavage of the bond between a heteroatom and a carbon atom. The temperature at which bond cleavage takes place depends on the substituents of the catalysts, resulting in the difference of the latency, that is, initiating temperature of the polymerization. In addition, kinetic studies, especially of the activation energy (E_a) and frequency factor (A), are important for a detailed discussion on latency. Papas and Hill have reported that sulfonium salts are promising candidates for latent catalysts, because the polymerization of epoxides show large E_a and A factor.[1b] A large E_a is necessary for latency, i.e., large difference between the reaction rates at the temperatures T_1 and T_2 (eq 1.1). Although a large E_a causes the decrease of a reaction rate constant (k) as shown in the Arrhenius' equation, a large A factor can compensate to achieve a practical reaction rate (eq 1.2).

$$\ln(k_1/k_2) = E_a(1/T_2 - 1/T_1) \qquad (1.1)$$

$$\ln k = \ln A - E_a/RT \qquad (1.2)$$

We have recently reported that phosphonium ylides serve as novel thermally latent catalysts in the polyaddition of bisphenol A diglycidyl ether with bisphenol A as a model system for epoxy−novolac resins.[12] The catalytic activities of the phosphonium ylides increased with the electron-withdrawing character of the acyl group, but the starting temperatures of the epoxide conversion were constant (90 °C) irrespective of the substituents. This results might suggest that the control of latency of phosphonium ylides would be possible. In this work, we disclose kinetic parameters and substituent effects of phosphonium ylides for molecular design of excellent latent catalysts.

Results and Discussion

The relationships between the kinetic parameters and the steric effect of the acyl groups of phosphonium ylides were examined in the reaction of glycidyl phenyl ether (GPE) with 2,6-dimethylphenol at 80−100 °C in the presence of 1 mol % of (formylmethylene)triphenyl-phosphorane ($\mathbf{1_H}$), (acetylmethylene)triphenylphosphorane ($\mathbf{1_{Me}}$), (benzoylmethylene)triphenylphosphorane ($\mathbf{1_{Ph}}$), and (pivaloylmethylene)triphenylphosphorane ($\mathbf{1_{tBu}}$) (Scheme 1). The addition reaction proceeded homogeneously, and its conversion was monitored by ^{1}H NMR spectroscopy. Figure 1 depicts the time−conversion relationships of the reaction with 1 mol % of $\mathbf{1_{Me}}$ at 80, 90, and 100 °C, exhibiting a linear plot in the initial stage at every temperature, from which the reaction rate constants (k_{obs}) can be estimated according to a first-order rate equation.[13] Figure 2 depicts the Arrhenius' plot of the data from Figure 1. Table 1 summarizes the

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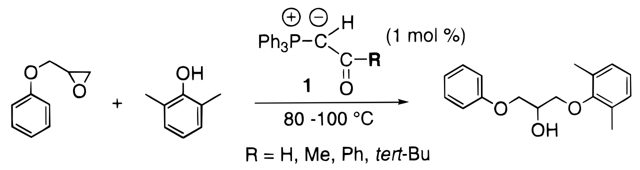
Scheme 1



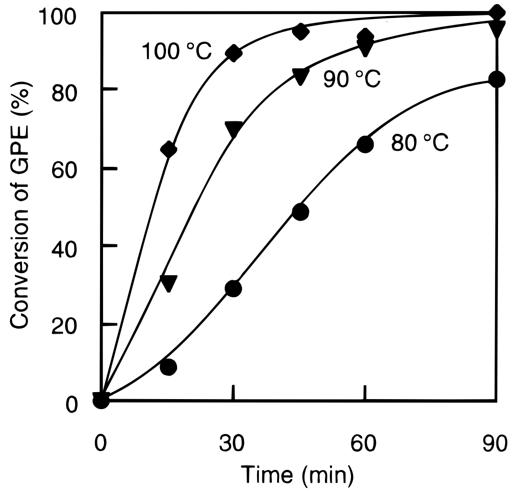


Figure 1. Time−conversion relationships in the reaction of GPE with 2,6-dimethylphenol in the presence of $\mathbf{1}_{\mathbf{Me}}$ (1 mol %) at 80, 90, and 100 °C.

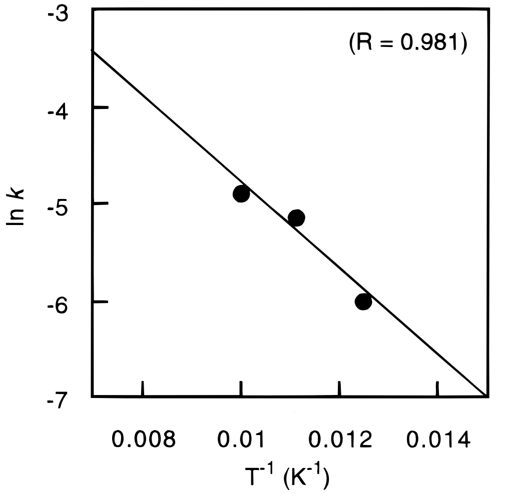


Figure 2. Arrhenius plots in the reaction of GPE with 2,6-dimethylphenol in the presence of $\mathbf{1}_{\mathbf{Me}}$ (1 mol %). The data were calculated from the time−conversion curves (Figure 1) in the early stage using a first-order rate equation.

Table 1. Activation Energy (E_a) and Frequency Factor (A) in the Reaction of GPE with 2,6-Dimethylphenol in the Presence of 1 (1 mol %) at 80−100 °C

substituent (R) of **1**	E_a [kJ/mol]	A [s^{-1}]
tert-Bu	7.4	1.61×10
Ph	6.2	1.01×10
Me	3.8	1.29
H	2.2	2.04×10^{-3}
Ph_4P^+ ^-Br	1.2	2.48×10^{-2}
Ph_3P	0.7	1.79×10^{-2}

E_a and A factors of the reaction with $\mathbf{1}_{\mathbf{H}}$, $\mathbf{1}_{\mathbf{Me}}$, $\mathbf{1}_{\mathbf{Ph}}$, and $\mathbf{1}_{\mathbf{tBu}}$. Both the E_a and A factors increased with the bulkiness of the acyl group of the phosphonium ylide **1** in the order of *tert*-Bu > Ph > Me > H. Triphenylphosphine and tetraphenylphosphonium bromide, common catalysts for curing of epoxy−novolac resins, showed smaller E_a than the phosphonium ylides **1**. These simple phosphorus catalysts cannot serve as latent catalyst because they show catalytic activities even at room temperature. These E_a data may explain the advantage of the phosphonium ylides **1** for thermal latency.

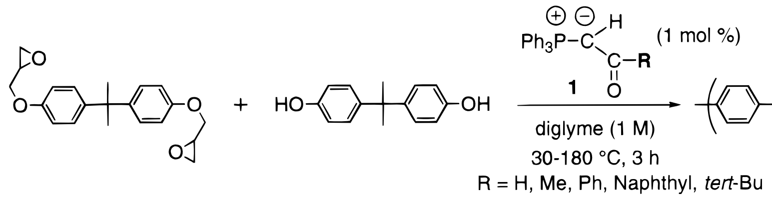
Further, the polyaddition of bisphenol A diglycidyl ether with bisphenol A was carried out in diglyme (1 M) in the presence of 1 mol % of phosphonium ylides **1** (Scheme 2). The M_n and M_w/M_n of the obtained polyether were 5500−7200 and 1.08−1.10 at 50−60% conversion, respectively, independent of the catalyst. Figure 3 depicts the temperature−conversion relationships in the polyaddition for 3 h with $\mathbf{1}_{\mathbf{Me}}$, $\mathbf{1}_{\mathbf{Ph}}$, (naphthoyl)methylenetriphenylphosphorane ($\mathbf{1}_{\mathbf{NA}}$), and $\mathbf{1}_{\mathbf{tBu}}$ as the catalyst. The catalytic activity decreased with the bulkiness of the acyl group of the phosphonium ylide in the order of H > Me > Ph, naphthyl > *tert*-Bu, but the latency, i.e., starting temperature, of the epoxide conversion was little affected in the polyaddition.

Next, acetyl and cyano groups were introduced as electron-withdrawing moieties into phosphonium ylides to examine the electronic effect of the substituents (Chart 1). Figure 4 depicts the temperature−conversion relationships in the polyaddition with $\mathbf{1}_{\mathbf{Me}}$, (diacetylmethylene)triphenylphosphorane (**2**), (acetylcyanomethylene)triphenylphosphorane (**3**), and (dicyanomethylene)triphenylphosphorane (**4**) as the catalysts. The temperature−conversion curves (catalytic activities) of **2**−**4** shifted to higher temperature region compared with $\mathbf{1}_{\mathbf{Me}}$ keeping the slopes.

As described above, the latency of the phosphonium ylides was not affected by the steric factor of the substituent, but by the electronic factor. This difference between the steric and electronic effects of the substituents is explained from the viewpoint of the catalytic mechanism of the phosphonium ylide. Scheme 3 illustrates a plausible mechanism of the polyaddition of bisphenol A diglycidyl ether with bisphenol A catalyzed with a phosphonium ylide. The ylide may be protonated by a phenolic proton to form the corresponding phosphonium salt (Scheme 3, first step), which may catalyze the addition of a phenoxide species with an epoxide as a Lewis acid (Scheme 3, second step). In the protonation step (first step), the equilibrium may lie to the ylide rather than the phosphonium phenoxide, resulting in the excellent catalytic latency. In this mechanism, the carbanionic and phosphonium cationic parts of the ylide play different roles, i.e., the abstraction of the phenolic proton and the activation of the epoxide, respectively. The increase of E_a with the bulkiness of the acyl group in Table 1 indicates that the rate-determining step is the activation of the epoxide by the phosphonium cation (second step), because this step should be affected by the steric factor of the phosphonium cation much more than the protonation step. For this reason, the difference of E_a seemed not to affect the latency of the phosphonium ylide, but the catalytic activity. The introduction of electron-withdrawing groups should decrease the basicity of the anionic part of the ylide to retard the protonation, resulting in the shift of the catalytic activity to higher temperature region as shown in Figure 4.

It is common for anionic catalysts to decrease in activity with the decrease of the basicity. Therefore, introduction of the electron-withdrawing groups may decrease the catalytic activity. In this work, simultaneous control of both latency and the high activity could

Scheme 2



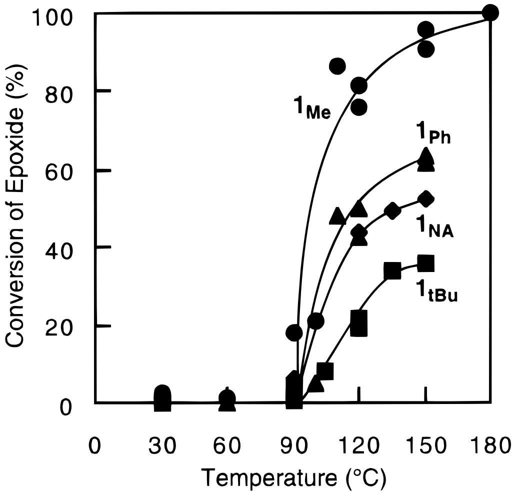


Figure 3. Temperature−conversion relationships in the polyaddition of bisphenol A diglycidyl ether with bisphenol A in the presence of ylides **1** (1 mol %) in diglyme (1 M) for 3 h.

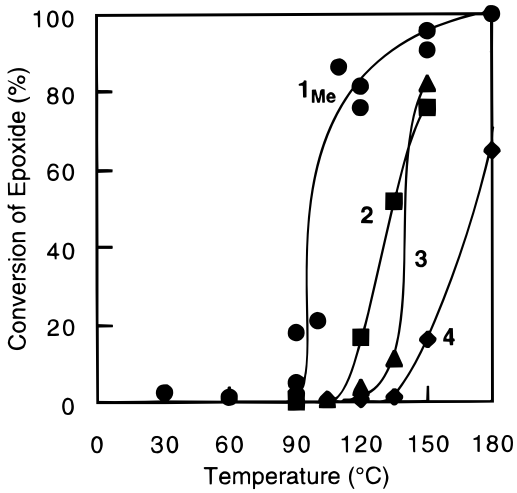
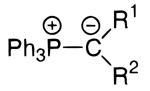


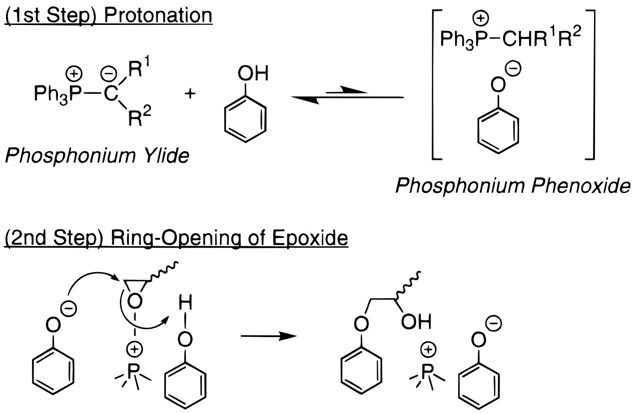
Figure 4. Temperature−conversion relationships in the polyaddition of bisphenol A diglycidyl ether with bisphenol A in the presence of ylides $\mathbf{1}_{\mathrm{Me}}$**, 2, 3,** and **4** (1 mol %) in diglyme (1 M) for 3 h.

Chart 1



$\mathbf{1}_{\mathbf{Me}}$: R^1 = H, R^2 = COMe
2: R^1 = COMe, R^2 = COMe
3: R^1 = COMe, R^2 = CN
4: R^1 = CN, R^2 = CN

Scheme 3



be achieved by the introduction of electron-withdrawing groups into the phosphonium ylides, probably due to the decrease of the basicity of the carbanionic site and the increase of the Lewis acidity of the phosphonium cationic site.

Summary

This work demonstrated the relationships between the substituent effects of the phosphonium ylides and latency in the reaction of GPE with 2,6-dimethylphenol and in the polyaddition of bisphenol A diglycidyl ether with bisphenol A. Both the activation energy (E_a) and frequency factor (A) increased with the bulkiness of the acyl group of the phosphonium ylide in the kinetic studies on the addition of GPE with 2,6-dimethylphenol. The bulkiness of the acyl group did not affect the latency but affected the catalytic activity in the polyaddition of bisphenol A diglycidyl ether with bisphenol A. The steric factor of the substituents seemed to affect the interaction between the phosphonium cationic site of the ylide with the epoxide but might not affect the protonated reaction. For this reason, the E_a might be correlated with the catalytic activity of phosphonium ylide, but not with latency. The introduction of acetyl and cyano groups into phosphonium ylides as electron-withdrawing moieties shifted the temperature−conversion curve to higher temperature region.

Experimental Section

Measurements. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL JNM EX-400 spectrometer, using tetramethylsilane (TMS) and phosphoric acid as internal and external standards in chloroform-*d* ($CDCl_3$) at 27 °C, respectively. IR spectra were obtained with a JEOL JIR-5300. Number-average molecular weights (M_n's) and polydispersity ratios (M_w/M_n's) were estimated by gel permeation chromatography (GPC) on a Tosoh HPLC HLC-8020 system with a data processor, equipped with three consecutive polystyrene gel columns (TSK gel, G5000H, G4000H, G2500H), using LiBr solution in *N*,*N*-dimethylformamide (5.8 mM) as an eluent, a flow rate of 1.0 mL/min, polystyrene calibration, and refractive index (RI) and ultraviolet (UV) detectors.

Materials. GPE and 2,6-dimethylphenol were purchased from Tokyo Chemical Industry Co., Ltd., and GPE was purified by distillation over CaH_2. Bisphenol A diglycidyl ether (Epikote

828) and bisphenol A were purchased from Shell Chemical Co. Ltd. and Wako Pure Chemical Industries Co. Ltd., respectively, and used as received without purification. Diglyme, triphenylpnosphine, and tetraphenylphosphonium bromide were purchased from Tokyo Chemical Industry Co., Ltd., and used as received. (Formylmethylene)triphenylphosphorane ($\mathbf{1_H}$) and (acetylmethylene)triphenylphosphorane ($\mathbf{1_{Me}}$) were purchased from Aldrich Chemical Co., Ltd., and used as received. (Benzoylmethylene)triphenylphosphorane ($\mathbf{1_{Ph}}$), (pivaloylmethylene)triphenylphosphorane ($\mathbf{1_{tBu}}$), (naphthoylmethylene)triphenylphosphorane ($\mathbf{1_{NA}}$), (diacetylmethylene)triphenylphosphorane (**2**), (acetylcyanomethylene)triphenylphosphorane (**3**), and (dicyanomethylene)triphenylphosphorane (**4**) were synthesized in the general method according to the literature.[12,14,15]

(Pivaloylmethylene)triphenylphosphorane ($\mathbf{1_{tBu}}$). Yield 82%, mp 168−171 °C. ^{1}H NMR ($CDCl_3$): δ 7.7−7.4 (m, 15 H), 3.78 (d, J = 24.4 Hz, PC*H*−), 1.20 (s, 9 H, *tert-Bu*). ^{13}C NMR ($CDCl_3$): δ 200.3 (−*C*O−), 133.0, 131.7, 128.6, 127.5, 47.2 (d, J = 109.7 Hz, P*C*H−), 40.5 (−*C*(CH$_3$)$_3$), 28.8 (−C(*C*H$_3$)$_3$). ^{31}P NMR ($CDCl_3$): δ 16.4. IR (KBr) 1529 (−CO−), 1508, 1480, 1435, 1393, 1375, 1314, 1233, 1107, 902, 883, 752, 713, 694, 561, 524 cm^{-1}. Anal. Calcd for $C_{24}H_{25}OP$: C, 79.98; H, 6.99. Found: C, 79.94; H, 7.04.

(Naphthoylmethylene)triphenylphosphorane ($\mathbf{1_{NA}}$). Yield 80%, mp 195−196 °C. ^{1}H NMR ($CDCl_3$): δ 8.5−7.4 (m, 22 H), 4.60 (d, J = 24.4 Hz, 1 H, −PC*H*−). ^{13}C NMR ($CDCl_3$): δ 184.7 (d, J = 5.5 Hz, −*C*O−), 134−124 (14 aromatics), 51.8 (d, J = 109.8 Hz, P*C*H−). ^{31}P NMR ($CDCl_3$): δ 17.0. IR (KBr) 1649, 1595, 1510 (−CO−), 1487, 1435, 1402, 1340, 1314, 1175, 1132, 1105, 953, 900, 876, 825, 752, 716, 694, 627, 577, 525 cm^{-1}. Anal. Calcd for $C_{30}H_{23}OP$: C, 83.70; H, 5.39. Found: C, 83.48; H, 5.55.

(Diacetylmethylene)triphenylphosphorane (2). Yield 59%, mp 166−167 °C (lit.[13] 167−169 °C). ^{1}H NMR ($CDCl_3$): δ 7.7−7.6 (m, 6 H), 7.5 (m, 3 H), 7.5−7.4 (m, 6 H), 2.28 (s, 6 H, −*Me*). ^{13}C NMR ($CDCl_3$): δ 193.1 (d, J = 9.1 Hz, −*C*O−), 132.9 (d, J = 9.1 Hz), 131.5 (d, J = 3.7 Hz), 128.6 (d, J = 12.8 Hz), 126.7 (d, J = 93.3 Hz), 88.8 (d, J = 102.4 Hz, −P*C*−), 30.6 (d, J = 5.5 Hz, −*Me*). ^{31}P NMR ($CDCl_3$): δ 16.6. IR (KBr) 3459, 3063, 2992, 1601, 1557, 1481, 1437, 1364, 1323, 2354, 1101, 1059, 1022, 899, 756, 696, 635, 544, 511 cm^{-1}. Anal. Calcd for $C_{22}H_{21}O_2P$: C, 75.85; H, 6.08. Found: C, 76.40; H, 5.98.

(Acetylcyanomethylene)triphenylphosphorane (3). Yield 53%, mp 208−210 °C. ^{1}H NMR ($CDCl_3$): δ 7.7−7.5 (m, 15 H), 2.37 (s, 3 H, −*Me*). ^{13}C NMR ($CDCl_3$): δ 194.7 (−*C*O−), 133.6 (d, J = 11.0 Hz), 133.1, 129.1 (d, J = 12.8 Hz), 123.3 (d, J = 93.2 Hz), 48.8 (d, J = 126.2 Hz, −P*C*−), 27.6 (d, J = 9.1 Hz, −*Me*). ^{31}P NMR ($CDCl_3$): δ 20.7. IR (KBr): 2172 (−*CN*), 1584 (−*CO*−), 1480, 1437, 1358, 1310, 1192, 1107, 1017, 997, 930, 764, 718, 694, 604, 563, 529, 513, 496 cm^{-1}. Anal. Calcd for $C_{22}H_{18}NOP$: C, 76.96; H, 5.28; N, 4.08. Found: C, 76.84; H, 5.32, N, 3.94.

(Dicyanomethylene)triphenylphosphorane (4). Yield 13%, mp 188−189 °C (lit.[14] 187−188 °C). ^{1}H NMR ($CDCl_3$): δ 7.73 (td, J = 7.2, 1.6 Hz, 3 H), 7.67 (t, J = 6.6 Hz, 6 H), 7.6−7.5 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ 134.3 (d, J = 3.6 Hz), 133.6 (d, J = 11.0 Hz), 129.7 (d, J = 14.7 Hz), 121.9 (d, J = 93.2 Hz), 119.9 (d, J = 11.0 Hz. P*C*(CN)$_2$), 5.5 (d, J = 144.2 Hz. PC(*C*N)$_2$). ^{31}P NMR ($CDCl_3$): δ 27.0. IR (KBr) 3076, 2353, 2123 (−*CN*), 2013, 1813, 1585, 1481, 1435, 1314, 1231, 1186, 1161, 1107, 995, 764, 754, 723, 693, 625, 586, 546, 503 cm^{-1}. Anal. Calcd for $C_{21}H_{15}N_2P$: C, 77.29; H, 4.63; N, 8.58. Found: C, 77.36; H, 4.56; N, 8.48.

Addition Reaction of GPE with 2,6-Dimethylphenol. Typical Procedure. A ylide (0.6 mmol) was dissolved in a mixture of GPE (8.0 mL, 60 mmol) and 2,6-dimethylphenol (7.2 mg, 60 mmol) at room temperature. The solution was heated at a desirable temperature, and the conversion was monitored by ^{1}H NMR spectroscopy. ^{1}H NMR ($CDCl_3$): δ 7.30 (t, J = 7.8 Hz, 2 H, *aryl*), 6.91 (m, 6 H, *aryl*), 4.38 (m, 1 H, *methine*), 4.20 (d, J = 4.8 Hz, 2 H, *methylene*), 3.97 (d, J = 4.8 Hz, 2 H, *methylene*), 2.70 (d, J = 5.3 Hz, 1 H, −*OH*), 2.28 (s, 6 H, *methyl*).

Polyaddition of Bisphenol A Diglycidyl Ether with Bisphenol A. Typical Procedure. A ylide (0.1 mmol) was dissolved in a solution of bisphenol A diglycidyl ether (19.0 g, 67 mmol) and bisphenol A (15.3 g, 67 mmol) in diglyme (67 mL) at room temperature. The homogeneous mixture (1 mL) was fed in an ampule tube under a nitrogen atmosphere after the tube was heated at a desirable temperature in an oil bath. ^{1}H NMR ($CDCl_3$): δ 7.08 (d, J = 7.6 Hz, 4 H, *phenylene*), 6.77 (d, J = 7.6 Hz, 4 H, *phenylene*), 4.30 (br, 1 H, *methine*), 4.06 (br, 4 H, *methylene*), 2.14 (s, 6 H, *methyl*).

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(13) One of the reviewers has pointed out that the observed kinetic parameters do not represent the rate-determining step but the overall reaction. Despite the effort for elucidation of elementary reactions, the reaction intermediate (phosphonium phenoxide in Scheme 3) could not be isolated. However, we found that the ylid methine ^{1}H NMR signals of **1** broadened even at room temperature, in the reaction with equivalent amounts of substituted phenols. This indicates the presence of rapid exchange between the ylides and the phosphonium phenoxides, and the protonation step is slower compared to the ring-opening of epoxide. The overall reaction rates approximately represent those of the rate-determining step.

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