Substituent Effect of (Triphenylphosphinemethylene)boranes on Latent Catalytic Activity for Polyaddition of Bisphenol A Diglycidyl Ether with Bisphenol A: Model System of Epoxy−Novolac Resin

Minoru Kobayashi,[†] Fumio Sanda,[‡] and Takeshi Endo*

Fundamental Research Laboratory, Sumitomo Bakelite Co., Ltd., 495 Akiba-cho, Totsuka-ku, Yokohama 245-0052, Japan, and Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503, Japan

Received July 23, 2001; Revised Manuscript Received October 12, 2001

ABSTRACT: The substituent effect of (triphenylphosphinemethylene)boranes, $Ph_3P-CH(R')-BR_3$ [(triphenylphosphinemethylene)borane (**I$_H$**), (triphenylphosphineformylmethylene)trifluoroborane (**II$_F$**), (triphenylphosphineacetylmethylene)trifluoroborane (**III$_F$**), (triphenylphosphineacetylmethylene)triphenylborane (**III$_{Ph}$**), and (triphenylphosphinacetylmethylene)borane (**III$_H$**)], as thermally latent catalysts was examined in the polyaddition of bisphenol A diglycidyl ether with bisphenol A. Introduction of an acyl group on the ylide moiety was effective to enhance the catalytic activity. Thermal latency of the (triphenylphosphinemethylene)boranes was discussed from the viewpoint of the catalytic mechanism with the substituent effect on both ylide and borane.

Introduction

Epoxy resin has excellent thermal, mechanical, electrical, and chemical properties such as superior adhesion, insulation, permeability, corrosion resistance, and stress resistance, ensuring its applications to a wide variety of industrial fields.[1] Especially, in electrical and electronical industries, the good combination of these properties makes it a predominant thermosetting resin as fundamental material. It is important to select an appropriate catalyst, which can speed up the reaction to increase the molding cycle for large mass production. It provides tighter control for reaction selectivity to enhance consistency and reliability of final products.[2] A recent important subject on catalysts is “latency” , which can achieve one-pot curing systems. “Latent catalysts” are inert under normal conditions such as ambient temperature and light but show activity by appropriate external stimulation such as heating and photoirradiation.[3] Development of efficient latent catalysts is desirable for enhancement of both storage stability and handling of thermosetting resin, because they can simplify operation of curing process to achieve one-pot curing systems. Several types of thermally latent catalysts are developed and industrially utilized for adhesives, paintings, encapsulants, and coatings. Sulfonium salts are one of the most common latent catalysts, whose latency comes from the thermal dissociation of the carbon−sulfur bonds to afford alkyl cations.[4] Other onium salts such as iodonium,[5] ammonium,[6] pyridinium,[7] hydrazinium,[8] and phosphonium[9] salts are also developed with considering the substituents and counterions. However, salt-type latent catalysts cannot sufficiently comply with the properties specialized for recent advanced demands. Residual salts in cured resin cause undesirable properties in insulation and hygroscopicity. Besides, poor solubility of salt-type catalysts would come to diffusion control, resulting in problems in activity and reproducibility. It is desirable to design a non-salt-type latent catalyst for overcoming these problems.

We have focused on thermal dissociation of (triphenylphosphinemethylene)boranes (**I**), based on thermal reversibility of the bond formation between ylides and boranes,[10] and found that they serve as novel non-salt-type latent catalysts in the polyaddition of bisphenol A diglycidyl ether with bisphenol A.[11] Studies on their catalytic mechanism have suggested that the B−C bond is thermally dissociated in a manner similar to other latent onium catalysts. However, the catalytic activity is insufficient even at high-temperature region. This work deals with control of catalytic activity of (triphenylphosphinemethylene)boranes by introduction of substituents in the polyaddition of bisphenol A diglycidyl ether with bisphenol A, a model system of thermosetting epoxy−novolac resin.

Results and Discussion

The candidates of novel thermally latent catalysts, (triphenylphosphinemethylene)boranes (**II, III**), were synthesized by the reaction of the corresponding ylides and boranes to estimate their catalytic activities in the polyaddition of bisphenol A diglycidyl ether with bisphenol A. The polyaddition was carried out in the presence of 1 mol % of **II** and **III** in diglyme (Scheme 1).[12] Figure 1 depicts the temperature−conversion relationships in the polyaddition along with the data of **I$_H$** previously reported.[11] **II$_F$** and **III$_F$** catalyzed the reaction at the temperature higher than 120 °C, and **III$_{Ph}$** and **III$_H$** did it above 60 °C, indicating that these (triphenylphosphinemethylene)boranes served as latent catalysts of the polyaddition. Introduction of acetyl group on the ylide moiety (**III$_F$**, **III$_{Ph}$**, **III$_H$**) increased the catalytic activity to achieve high conversion of epoxide at the higher temperature region. This results may be explained by considering the catalytic mechanism as shown in Scheme 2, consisting of (i) thermal cleavage of the bond between boron and ylide carbon forming ylide and borane, (ii) protonation of the ylide forming

---

[†] Sumitomo Bakelite Co., Ltd.

[‡] Tokyo Institute of Technology.

* To whom all correspondence should be addressed. Present address: Department of Polymer Science and Engineering, Faculty of Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa, Yamagata 992-8510, Japan.

10.1021/ma0113069 CCC: $22.00 © 2002 American Chemical Society
Published on Web 12/11/2001

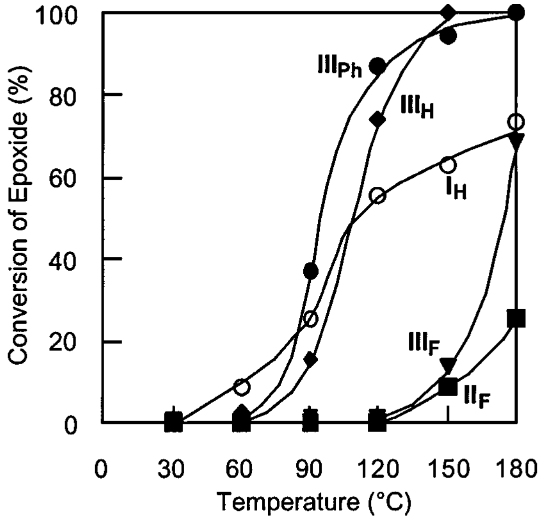
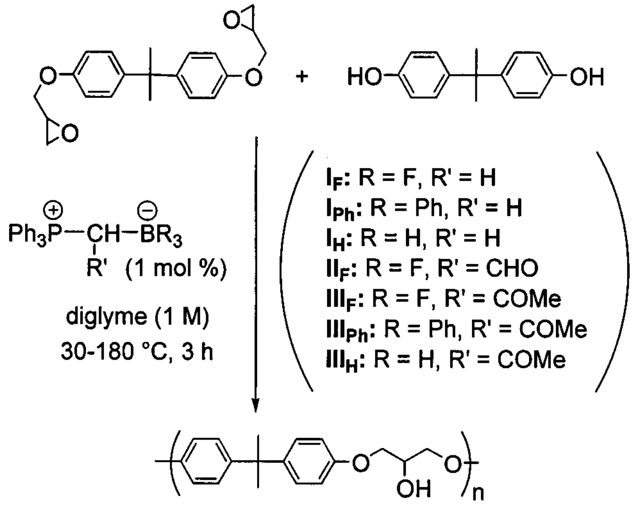


Figure 1. Temperature–conversion relationships in the polyaddition of bisphenol A diglycidyl ether with bisphenol A in the presence of **I**–**III** (1 mol %) in diglyme (1 M) for 3 h.

Scheme 1



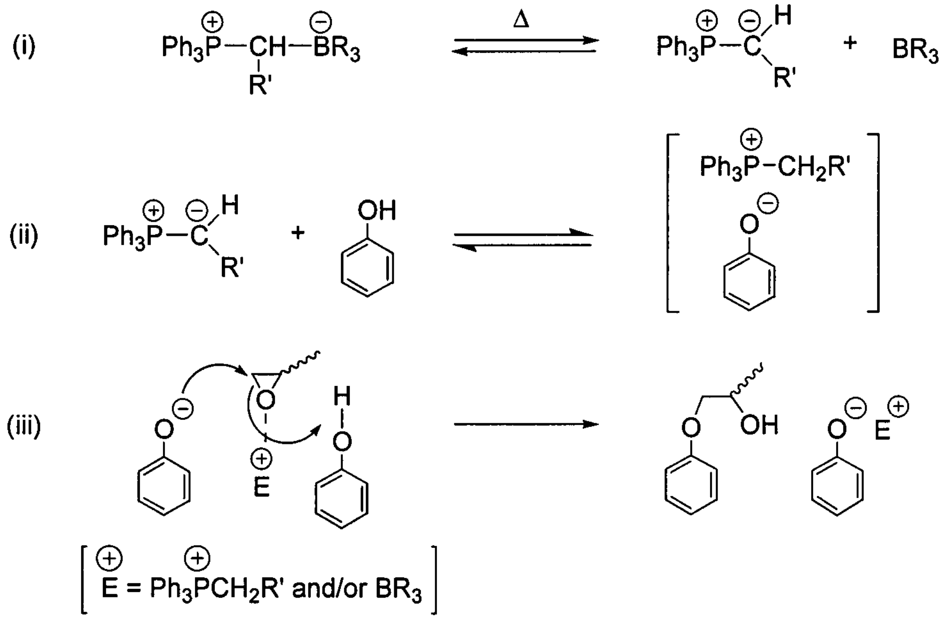
phosphonium phenoxide, and (iii) attack of phenoxide to epoxide activated by phosphonium cation and/or borane. It is considered that electron-withdrawing acetyl and formyl groups promote the B–C bond cleavage in step i because the anion of ylide formed is stabilized by the electron-withdrawing substituent R′. In step iii, the electron-withdrawing substituent R′ is also effective in activating the epoxide. **II$_F$** with a formyl group showed catalytic activity lower than **III$_F$** with an acetyl group. The formylmethylenetriphenylphosphorane part of **II$_F$** may more strongly interact with the trifluoroborane part than acetylmethylenetriphenylphosphorane of **III$_F$** to retard the B–C bond cleavage in step i because formylmethylenetriphenylphosphorane is more basic than acetylmethylenetriphenylphosphorane.[13] This result agreed with the substituent effect of benzylsulfonium salts, whose substituents accelerating the C–S bond fission enhance the activity.[3d]

Next, **III$_F$**, **III$_{Ph}$**, and **III$_H$**, all of which have the same ylide part (acetylmethylenetriphenylphosphorane), were compared to elucidate the effect of borane part. It is considered that the initiating temperature of the reaction depends on the B–C bond strength as reported.[11] **III$_F$** initiated the reaction at the highest temperature among the three catalysts, presumably due to the high Lewis acidity of trifluoroborane, which tightly bonds to the ylide. Meanwhile, **III$_{Ph}$** and **III$_H$** did not exhibit significant difference concerning the initiating temperature. This is reasonably understood from the slight difference of Lewis acidities between triphenylborane and BH_3. In fact, the ^{13}C NMR chemical shifts of the ylide carbons (**III$_F$**, 71.3; **III$_{Ph}$**, 65.1; **III$_H$**, 63.6 ppm) well agreed with the tendency. **III$_{Ph}$** showed activity higher than **III$_H$** as shown in Figure 1.

Summary

We could demonstrate that triphenylphosphinemethyleneboranes served as non-salt structure thermally latent catalysts in the polyaddition of bisphenol A diglycidyl ether with bisphenol A. Introduction of an acyl group on the ylide moiety was effective to enhance the catalytic activity. On the basis of substituent effect on the ylide and borane parts, we can conclude that it is

Scheme 2



necessary to consider the ease of B−C bond cleavage of (triphenylphosphinemethylene)boranes as well as Lewis acidity of the phosphonium ion formed for designing catalysts, which show excellent latency as well as activity.

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. Melting points were measured on a Yanaco micro melting point apparatus. Elemental analysis was carried out with a Yanaco CHN Corder MT-5 and an SX-Elements micro analyzer YS-10.

Materials. Bisphenol A diglycidyl ether (Epikote 828), bisphenol A, and diglyme were purchased from Shell Chemical Co. Ltd., Wako Pure Chemical Industries Co. Ltd., and Tokyo Chemical Industry Co., Ltd., respectively, and used as received without purification. Formylmethylenetriphenylphosphorane, acetylmethylenetriphenylphosphorane, and methoxycarbonylmethylenetriphenylphosphorane were purchased from Aldrich Chemical Co. Ltd. and used as received.

Synthesis of (Triphenylphosphineformylmethylene)trifluoroborane (II$_\mathbf{F}$). To a filtered solution of 7.94 mmol of formylmethylenetriphenylphosphorane in 200 mL of toluene was added a solution of equivalent amount of boron trifluoride diethyl etherate with stirring at ambient temperature for 1 h. The resulting brown precipitate was filtered and washed with ethyl acetate and recrystallized from chloroform to give 330 mg of **II$_\mathbf{F}$**. Yield 11%, mp 168−169 °C. ^{1}H NMR (CDCl$_3$): δ 7.77 (dd, J = 7.5, 2.0 Hz, 1 H, −formyl), 7.66−7.26 (m, 15 H, −phenyl), 5.26 (dd, J = 16.5, 13.0 Hz, 1 H, −methine). ^{13}C NMR (CDCl$_3$): δ 170.8 (d, J = 20.2 Hz, carbonyl), 134.5 (d, J = 3.6 Hz, *p*-phenyl), 133.4 (d, J = 11.0 Hz, *m*-phenyl), 130.0 (d, J = 11.0 Hz, *o*-phenyl), 121.1 (d, J = 91.5 Hz, *ipso*-phenyl), 73.5 (d, J = 109.7 Hz, methine). ^{31}P NMR (CDCl$_3$): δ 20.1. IR (KBr): 3437, 1607, 1484, 1440, 1335, 1289, 1104, 973, 859, 756, 722, 693, 597, 552, 518 cm^{-1}. Anal. Calcd for C$_{20}$H$_{17}$BF$_3$OP: C, 64.55; H, 4.60. Found: C, 64.24; H, 4.63.

The above procedure is representative of that used in the preparation of other ylides.

(Triphenylphosphineacetylmethylene)trifluoroborane (III$_\mathbf{F}$). Yield 26%, mp 159−161 °C. ^{1}H NMR (CDCl$_3$): δ 7.70−7.26 (m, 15 H, −phenyl), 4.53 (d, J = 22.0 Hz, 1 H,−methine), 2.38 (s, 3 H, −methyl). ^{13}C NMR (CDCl$_3$): δ 182.1 (carbonyl), 133.5 (d, J = 3.6 Hz, *p*-phenyl), 133.2 (d, J = 9.1 Hz, *m*-phenyl), 129.5 (d, J = 12.8 Hz, *o*-phenyl), 122.5 (d, J = 91.4 Hz, *ipso*-phenyl), 71.3 (d, J = 98.8 Hz, methine), 22.7 (d, J = 12.8 Hz, methyl). ^{31}P NMR (CDCl$_3$): δ 14.6. IR (KBr): 3059, 1567, 1441, 1366, 1318, 1185, 1080, 1007, 894, 857, 758, 723, 691, 633, 596, 539, 513 cm^{-1}. Anal. Calcd for C$_{21}$H$_{19}$BF$_3$OP: C, 65.32; H, 4.96. Found: C, 65.55; H, 5.04.

(Triphenylphosphineacetylmethylene)triphenylborane (III$_\mathbf{Ph}$). Yield 65%, mp 105−107 °C. ^{1}H NMR (CDCl$_3$): δ 7.80−7.70 (m, 30 H, −phenyl), 4.24 (d, J = 22.0 Hz, 1 H,−methine), 1.71 (s, 3 H, methyl). ^{13}C NMR (CDCl$_3$): δ 188.4 (carbonyl), 133.6, 133.4 (d, J = 11.0 Hz), 133.0 (d, J = 16.4 Hz), 129.3 (d, J = 11.0 Hz), 128.4 (d, J = 12.8 Hz), 127.9, 126.3 (d, J = 27.5 Hz), 123.9 (d, J = 71.3 Hz), 65.1 (d, J = 98.8 Hz, methine), 25.9 (d, J = 14.6 Hz, methyl). ^{31}P NMR (CDCl$_3$): δ 13.7. IR (KBr): 3062, 2997, 1535, 1482, 1436, 1402, 1179, 1110, 981, 870, 790, 704, 691, 632, 594, 519 cm^{-1}. Anal. Calcd for C$_{39}$H$_{34}$BOP: C, 83.58; H, 6.11. Found: C, 84.96; H, 6.58.

(Triphenylphosphineacetylmethylene)borane (III$_\mathbf{H}$). Yield 58%, mp 193−195 °C. ^{1}H NMR (CDCl$_3$): δ 7.7−7.5 (m, 15 H, −phenyl), 4.17 (d, J = 23.6 Hz, 1 H, −methine), 2.32 (s, 3 H, −methyl), 2.2 (brs, 3H, −hydride). ^{13}C NMR (CDCl$_3$): δ 188.6 (carbonyl), 133.1 (d, J = 11.0 Hz, *m*-phenyl), 132.9 (*p*-phenyl), 129.2 (d, J = 12.8 Hz, *o*-phenyl), 124.1 (d, J = 91.5 Hz, *ipso*-phenyl), 63.6 (d, J = 104.3 Hz, methine), 22.1 (d, J = 12.8 Hz, methyl). ^{31}P NMR (CDCl$_3$): δ 14.9. IR (KBr): 3370, 2274, 1540, 1440, 1413, 1152, 1107, 995, 863, 757, 720, 692, 573, 502 cm^{-1}. Anal. Calcd for C$_{21}$H$_{22}$BOP: C, 75.93; H, 6.68. Found: C, 75.86; H, 6.10.

Polyaddition of Bisphenol A Diglycidyl Ether with Bisphenol A. Typical Procedure. (Triphenylphoshinemethylene)borane (**I**−**III**, 1 mol %) was dissolved into a solution (10 mL) of bisphenol A diglycidyl ether (19.0 g, 67.0 mmol) and bisphenol A (15.3 g, 67.0 mmol) in diglyme (67.0 mL, 1 M) at room temperature. The homogeneous mixture (1 mL) was placed in an ampule tube under a nitrogen atmosphere. The tube was heated at a desired 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).

References and Notes

(1) (a) May, C. A.; Tanaka, Y. *Epoxy Resins*; Marcel Dekker: New York, 1973. (b) Bauer, R. S. *Epoxy Resin Chemistry*; American Chemical Society: Washington, DC, 1978.

(2) Biernath, R. W.; Soane, D. S. In *Contemporary Topics in Polymer Science*; Salamone, J. C., Riffle, J., Eds.; Plenum Press: New York, 1992; Vol. 7.

(3) (a) Smith, J. D. B. In *Epoxy Resin Chemistry*; Bauer, R. S., Ed.; American Chemical Society: Washington, DC, 1978; Chapter 3. (b) Pappas, S. P.; Hill, L. W. *J. Coat. Technol.* **1981**, *53*, 43. (c) Muizebelt, M. J. *J. Coat. Technol.* **1985**, *57*, 43. (d) Endo, T.; Sanda, F. *Macromol. Symp.* **1996**, *107*, 237.

(4) (a) Morio, K.; Murase, M.; Tsuchiya, H.; Endo, T. *J. Appl. Polym. Sci.* **1986**, *32*, 5727. (b) Walls, E.; Lupinski, J.; Bandes, S.; Rosenfield, M. *Proc. ACS Div. Polym. Mater. Sci. Eng.* **1988**, 758. (c) Hamazu, F.; Akashi, S.; Koizumi, T.; Takata, T.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1991**, *29*, 1675. (d) Macgowen, J. A.; Mathias, L. J. *Polym. Compos.* **1997**, *18*, 348.

(5) Crivello, J. V. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 4241.

(6) (a) Uno, H.; Endo, T. *J. Polym. Sci., Part C: Polym. Lett.* **1988**, *26*, 453. (b) Uno, H.; Takata, T.; Endo, T. *Chem. Lett.* **1988**, 935. (c) Nakano, S.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 505. (d) Nakano, S.; Endo, T. *Prog. Org. Coat.* **1996**, *28*, 143.

(7) (a) Lee, S. B.; Takata, T.; Endo, T. *Macromolecules* **1990**, *23*, 431. (b) Lee, S. B.; Takata, T.; Endo, T. *Macromolecules* **1991**, *24*, 2689.

(8) Lee, S. B.; Park, Y. S.; Lee, K. W.; Endo, T. *Chem. Lett.* **1995**, 287.

(9) (a) Takuma, K.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 862. (b) Toneri, T.; Sanda, F.; Endo, T. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1957. (c) Toneri, T.; Watanabe, K.; Sanda, F.; Endo, T. *Macromolecules* **1999**, *32*, 1293.

(10) (a) Schmidbaur, H.; Muller, G.; Blaschke, G. *Chem. Ber.* **1980**, *113*, 1480. (b) Schmidbaur, H.; Muller, G. Mahrla, B. M.; Schubert, U. *Chem. Ber.* **1980**, *113*, 2575. (c) Brauer, D. J.; Burger, H.; Dittmar, T.; Pawelke, G.; Rothe, J. *J. Organomet. Chem.* **1996**, *524*, 225. (d) Doring, S.; Erker, G.; Frohlich, R.; Meyer, O.; Bergander, K. *Organometallics* **1998**, *17*, 2183. (e) Miller, N. E. *Inorg. Chem.* **1965**, *4*, 1458. (f) Mahiason, D. R.; Miller, N. E. *Inorg. Chem.* **1968**, *7*, 709.

(11) Kobayashi, M.; Sanda, F.; Endo, T. *Macromolecules* **2001**, *34*, 1134.

(12) The M_n and M_w/M_n of the polymers obtained at 180 °C were as follows: **II$_\mathbf{F}$**: 4700, 1.23; **III$_\mathbf{F}$**: 11 400, 1.41; **III$_\mathbf{Ph}$**: 12 600, 1.03; **III$_\mathbf{H}$**: 12 400, 1.55.

(13) (a) Kobayashi, M.; Sanda, F.; Endo, T. *Macromolecules* **1999**, *32*, 4751. (b) Kobayashi, M.; Sanda, F.; Endo, T. *Macromolecules* **2000**, *33*, 5384.

MA0113069