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Application of (Triphenylphosphinemethylene)boranes to Thermally Latent Catalysts for Polyaddition of Bisphenol A Diglycidyl Ether with Bisphenol A: Model System of Epoxy−Novolac Resin

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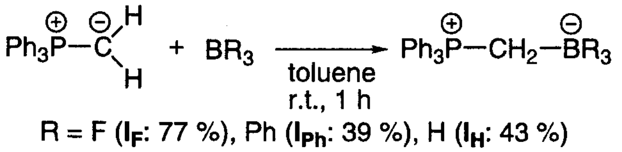
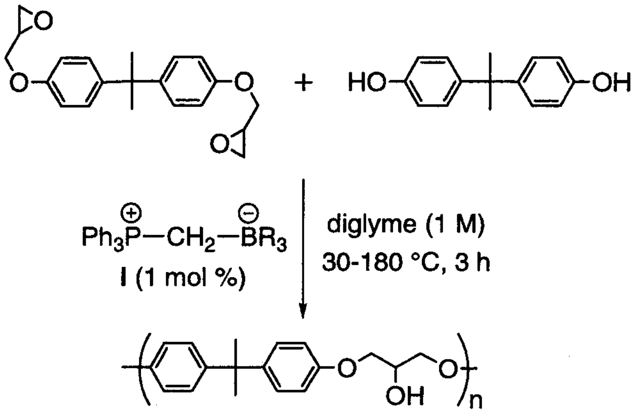
Introduction. “Latent catalysts” are inert under normal conditions such as ambient temperature and light but show activity by appropriate external stimulation such as heating and photoirradiation.[1] Development of efficient latent catalysts is desirable for enhancement of both storage stability and handling of thermosetting resins, because they can simplify the operation of the curing process to achieve one-pot curing systems. Many efforts have been made to comply with a wide variety of demands from the market. As a result, latent catalysts are widely utilized in the industrial fields of adhesives, paintings, coatings, inks, and photoresists.[2] Several types of onium salts such as iodonium,[2] sulfonium,[2,3] ammonium,[4] and pyridinium salts[5] have been reported as excellent thermally latent cationic catalysts, where the latency comes from the thermal dissociation of the carbon−heteroatom bonds to afford alkyl cations. However, these onium salts are sometimes poorly soluble in monomers and organic solvents,[6] resulting in problems in reproducibility. In electronic components, the residual hygroscopic catalysts would cause deterioration of insulating property. It is required to design a non-salt-type latent catalyst to solve these problems. In this work, we have focused on the thermal decomposition of (triphenylphosphinemethylene)boranes on the basis of our previous work concerning phosphonium ylides as latent catalysts for the polyaddition of bisphenol A diglycidyl ether with bisphenol A.[7] The structures of (triphenylphosphinemethylene)boranes have been reported by the X-ray diffraction technique, where both the phosphorus and boron atoms have nearly tetrahedral orbital hybridizations.[8] The bonds between the boranes and ylide carbons are composed of $p\pi-p\pi$ orbital overlap, nearly corresponding to freely rotational single bonds.[8a,b] Therefore, these bonds would be thermally cleaved in a fashion similar to other latent onium catalysts. This communication deals with (triphenylphosphinemethylene)boranes as novel thermally latent catalysts in the polyaddition of bisphenol A diglycidyl ether with bisphenol A, a model system of thermosetting epoxy−novolac resins.

Scheme 1



Scheme 2



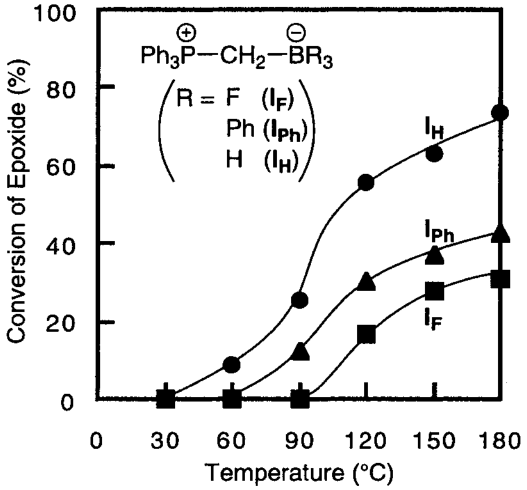


Figure 1. Temperature−conversion relationships in the polyaddition of bisphenol A diglycidyl ether with bisphenol A in the presence of **I** (1 mol %) in diglyme (1 M) for 3 h.

Results and Discussion. The candidate thermally latent catalysts, (triphenylphosphinemethylene)trifluoroborane ($\mathbf{I_F}$), (triphenylphosphinemethylene)triphenylborane ($\mathbf{I_{Ph}}$), and (triphenylphosphinemethylene)borane ($\mathbf{I_H}$), were synthesized by the reaction of triphenylphosphinemethylene with the corresponding boranes in toluene at room temperature for 1 h (Scheme 1).[9] The catalysts were obtained as air-stable white solids, which were insoluble in water but soluble in chloroform, methanol, and acetone.

The polyaddition of bisphenol A diglycidyl ether with bisphenol A was carried out in diglyme in the presence of 1 mol % of **I** (Scheme 2). The M_n and M_w/M_n of the obtained polyether were 5500−7200 and 1.1−1.4 at 50−60% conversion independent of the catalyst, respectively. Figure 1 depicts the temperature−conversion relationships in the polyaddition with **I** as the catalysts for 3 h. The activity order of the catalysts was $\mathbf{I_H} > \mathbf{I_{Ph}}$

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Scheme 3

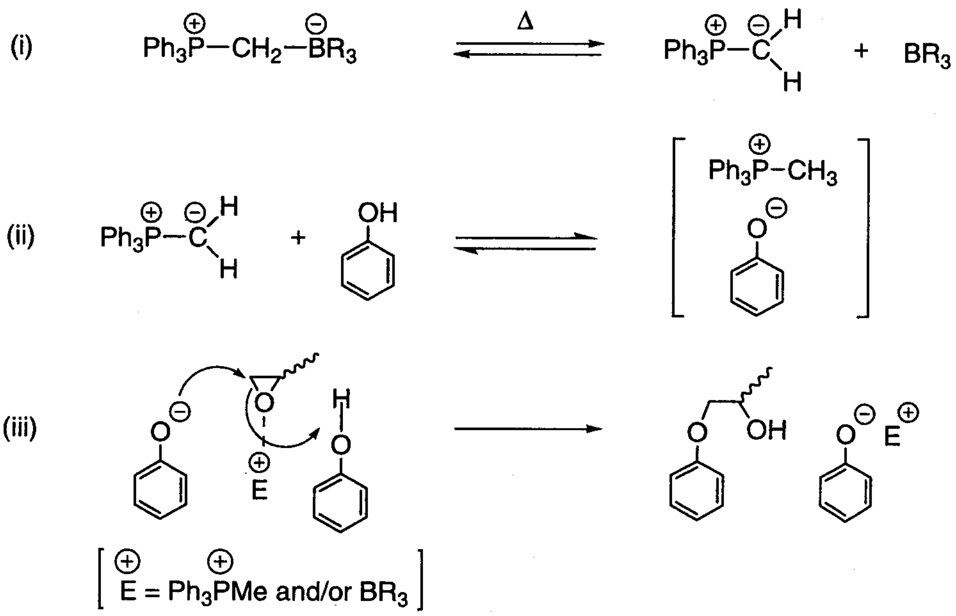

Table 1. ^{13}C NMR Chemical Shift of the Ylide Carbon and B−C Bond Length of I

catalyst	^{13}C NMR chemical shift^a (ppm)	bond length^b (Å)
$\mathbf{I_F}$	11.9	1.6919
$\mathbf{I_{Ph}}$	8.0	1.7413
$\mathbf{I_H}$	6.8	1.7454

^{a} Measured in $CDCl_3$ using TMS as an internal standard. ^{b} Distance between the borane and ylide carbon calculated by the SPARTAN program.

> $\mathbf{I_F}$, indicating that the borane substituents affected the catalytic activity.

The bond strength between the boron and ylide carbon of **I** was studied in relation to the substituent effect on the thermal stability. Table 1 summarizes the ^{13}C NMR chemical shifts of the ylide carbons and the calculated B−C bond lengths of **I**.[10] The catalyst with higher activity showed the ^{13}C NMR signal at higher field and longer B−C bond length. This tendency would reflect the electron density of the ylide carbon and orbital overlap between borane and ylide carbon, resulting in the difference in the thermal stability.

Scheme 3 illustrates a plausible catalytic mechanism. The first step is the thermal dissociation of the B−C bond of **I** to form triphenylphosphinemethylene and borane. The second step is the phenolic proton abstraction by the ylide to form phosphonium phenoxide. The third step is the attack of the phenoxide on the epoxide, which may be activated by the phosphonium and/or borane.[11]

For further investigation concerning the role of the boranes released from **I**, the polyaddition was performed in the presence of 1 mol % of boron trifuoride diethyl etherate, triphenylborane, and borane tetrahydrofuran in diglyme at 150 °C for 3 h. Triphenylborane and borane tetrahydrofuran scarcely converted the epoxide, while boron trifluoride diethyl etherate converted the epoxide quantitatively (M_n: 3200; M_w/M_n: 1.2). However, it was indicated that the structure of the obtained polymer was different from that obtained by the polyaddition using **I** on the basis of the ^{1}H NMR spectroscopic analysis. In addition, it was confirmed that the conversion of bisphenol A was only 30% despite the quantitative conversion of the epoxide.[12] In the absence of the ylide, boron trifluoride would not only activate the epoxide but also cause side reactions such as homopolymerization or cyclodimerization of the epoxide, because of its strong Lewis acidity. In the presence of the ylide, the addition of phenolate anion would be faster than the side reactions, resulting in polyaddition satisfactorily. It has been reported that triphenylborane is an effective additive for the living anionic polymerization of *tert*-butyl acrylate, forming a dormant intermediate with the acrylate oxygen atom at the propagating polymer terminal.[13] In this work, the released boranes would act as Lewis acids and activate the epoxide together with the phosphonium cation by the interaction with the oxygen atom of the oxirane ring as illustrated in Scheme 3(iii).

The thermal reversibility of the bond formation between ylides and boranes has been already reported along with the substituent effect.[8] For example, Bergender et al. have reported that $Ph_3P{-}CHPh{-}B(C_6F_5)_3$, formed from triphenylphosphinebenzylidene and tris(pentafluorophenyl)borane at 0 °C, is cleaved above 0 °C.[8d] The substituents on the boranes of **I** should affect the stability, leading to changes in catalytic activity for the polyaddition of bisphenol A diglycidyl ether with bisphenol A.

In summary, we could demonstrate that (triphenylphosphinemethylene)boranes served as novel non-salt-type thermally latent catalysts in the polyaddition of bisphenol A diglycidyl ether with bisphenol A. The borane substituents affected the catalytic activity in the order $\mathbf{I_H} > \mathbf{I_{Ph}} > \mathbf{I_F}$.

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