

Relationship of Structure and Properties of Phosphine-Containing Catalysts in Reactions with Epoxy and Phenol Compounds

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ABSTRACT: Triphenylphosphine (TPP) derivatives, which are catalysts of reactions with epoxy and phenol compounds, were investigated regarding the melting behavior and catalyst effect. The melting behavior was measured by differential scanning calorimetry (DSC), and the relationship of melting behavior (melting point and heat of fusion) and chemical structure were discussed using the heat of formation calculated by a semiempirical method. Two schemes are proposed for the reactions with epoxy and phenol compounds: a complex formation scheme, and an ionic scheme. The ionic scheme was the predominant route in the reactions with epoxy and phenol compounds in the bulk state at high temperature (180°C) on the basis of DSC measurements of the curing reaction and the semiempirical calculation of the heat of formation of products and partial charge of the phosphine group in the TPP derivatives. Consequently, the reaction rate of epoxy and phenol compounds decreased by introducing electron-withdrawing substituents such as chlorine in the basic catalyst. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2335–2341, 2002

Key words: melting point; epoxy; curing reaction; semi-empirical calculation; phosphine-containing catalyst

INTRODUCTION

Epoxy resin has been widely used in electronics applications because its crosslinked network structure provides excellent heat-resistant and good electrical properties.¹ Epoxy resin, with phenol as a hardener, is applied in encapsulating mold material for semiconductor packaging. A basic catalyst is commonly used in the curing reaction with epoxy and phenol. Representative basic catalysts are tertiary amine, imidazole, and tertiary phosphate. Among them, the tertiary phosphate-catalyzed cured product has particularly good electrical properties under high humidity

condition. Triphenylphosphine is the most usable of the tertiary phosphate compounds.²

Epoxy resin has been generally used with amine as hardener, and its reactions have been reported on extensively.³ In recent years, details of the reaction mechanism with epoxy and phenol have also been studied.^{4–7} Some articles have treated phosphine compounds as catalysts in reactions with epoxy and phenol compounds.^{8,9} However, the relationship between catalytic properties and chemical structure of phosphine compounds has not been considered in detail.

In this article, triphenylphosphine derivatives were investigated regarding melting behavior and catalyst effect dependence on the substituent groups. Moreover, the reaction scheme with epoxy and phenol catalyzed triphenylphosphine deriva-

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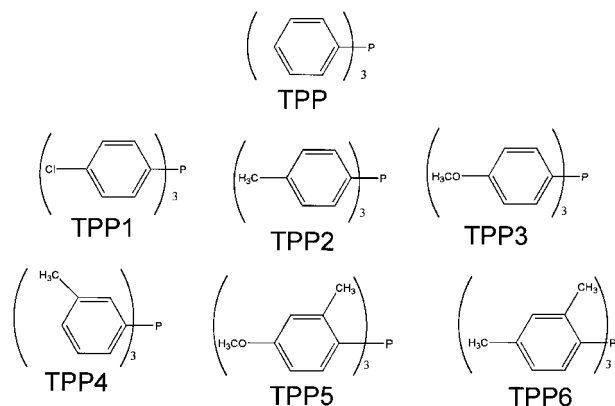


Figure 1 Chemical structures of TPP (triphenylphosphine) derivatives.

tives in the bulk state at high temperature was clarified by DSC (differential scanning calorimetry) measurements and a semiempirical calculation.

EXPERIMENTAL

Materials

Commercially available epoxy and the phenol resins were used. The *o*-cresol novolac-type epoxy (ESCN-190-2) was purchased from Sumitomo Chemical, and the phenol novolac was purchased from Meiwa Chemical and used without further purification. The triphenylphosphine (TPP) and its derivatives were purchased from Hokko Chemical Industry Co., Ltd. These compounds were purified by water and methanol. Chemical structures of TPP derivatives are listed in Figure 1.

The resin compositions were prepared as follows. A mixture of an equivalent molar ratio of epoxy and phenol compounds was dissolved in acetone homogeneously and 1 mol % of each TPP derivative was added as a catalyst. The powder samples were obtained by eliminating solvent *in vacuo* at room temperature.

Apparatus

DSC (differential scanning calorimetry) was performed on a Du Pont 910. The measurement of melting point was carried at a heating rate of 5 K·min⁻¹ in air. The curing reaction was measured at a heating rate of 5, 10, and 20 K·min⁻¹ in air. The sample weight was about 5 mg.

The partial electron charge of phosphine and heat of formation were calculated with a semiempirical method, PM3 (Parametric Method 3). The

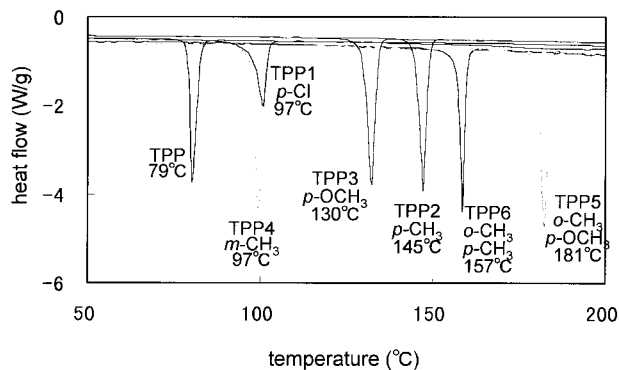


Figure 2 DSC curves showing melting behavior of TPP derivatives.

PM3 is the latest method of MNDO (Modified Neglect of Diatomic Overlap) developed by Stewart.¹⁰ The PM3 is well-suited for chemical structures involving phosphorus.¹¹

RESULTS AND DISCUSSION

Melting Behavior

The melting behavior of TPP derivatives measured by DSC is shown in Figure 2. The melting points of TPP derivatives could be changed drastically by the introduction of substituent groups on their phenyl rings. The melting point of TPP without any substituents was 79°C, while melting points of all TPP derivatives with substituents were higher. The melting points of two-substituent derivatives (TPP5 and TPP6) were higher than those of monosubstituent derivatives (TPP1, TPP2, TPP3, and TPP4).

Figure 3 shows the relationship between melting point and molecular weight for these TPP derivatives. The melting point tended to increase

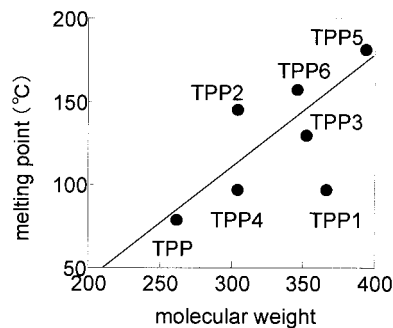


Figure 3 Relationship between melting point and molecular weight of TPP derivatives.

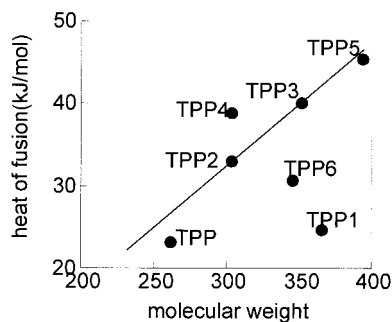


Figure 4 Relationship between heat of fusion and molecular weight.

as the molecular weight was higher. Because a compound with high molecular weight tends to have relatively high cohesive energy, it has a high melting point. This tendency is shown again in the relationship between heat of fusion and molecular weight (Fig. 4). However, the chlorine substituent (TPP1) showed different behavior from other alkyl or alkoxy substituents. TPP1 had both a relatively low melting point and a low heat of fusion despite its comparatively high molecular weight. This means the cohesive energy of the chlorine effect on melting behavior (melting point and heat of fusion) is different from that of the alkyl or alkoxy groups. It is presumed that the cohesive energy of chlorine is relatively low compared with alkyl or alkoxy groups. Another explanation is that the chlorine substituent interferes sterically with stacking of phenyl groups in an intermolecular interaction. TPP1 may have a different packing structure in the crystalline state compared with other TPP derivatives.

The above relationship of melting behavior (melting point and heat of fusion) and chemical structures was examined from a different viewpoint. The heat of formation of TPP derivatives was estimated by a semiempirical calculation with PM3 method. The melting point was higher as the heat of formation became lower, as shown in Figure 5. Because the low heat of formation means a compound is stable, its melting point is relatively high. TPP2 and TPP6 had relatively high melting points compared with other derivatives. They have *p*-substituent methyl groups. The *p*-substituent methyl group may enhance intermolecular interaction in the crystalline state due to hyperconjugation. The calculated heat of formation roughly expressed the cohesive energy of TPP derivatives. The stable structure of TPP derivatives went with high melting point. Simi-

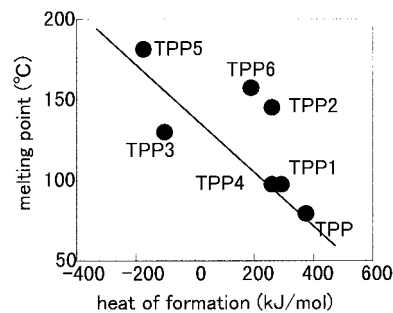


Figure 5 Relationship between melting point and calculated heat of formation.

larly, the heat of fusion was higher as the heat of formation became lower, as shown in Figure 6. This relationship was seen with not only alkyl or alkoxy groups, but also chlorine. The melting behavior (melting point and heat of fusion) was well explained by the calculated heat of formation, which was related to the cohesive energy of TPP derivatives.

Curing Reaction Mechanism

A representative reaction mechanism of epoxy and phenol with basic catalyst is shown in Figure 7. The phenol compound produces an adduct with a basic catalyst like the TPP derivatives. This reaction proceeds easily as the neutralization of Lewis acid and base, and is a spontaneous exothermic process. The proposed next step can proceed by two different processes.¹² One is the complex formation scheme that is reaction with the above adduct and epoxy.¹³ This scheme leads to a complex of the three compounds. The complex formation process is the rate-determining step. Finally, the reaction with epoxy and phenol occurs with elimination of the base catalyst. The

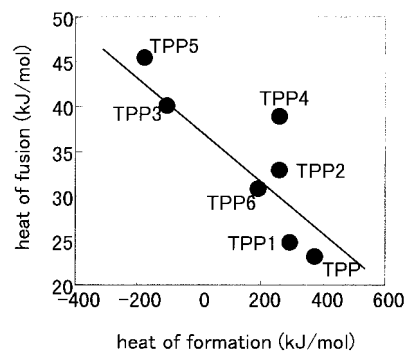


Figure 6 Relationship of heat between fusion and calculated heat of formation.

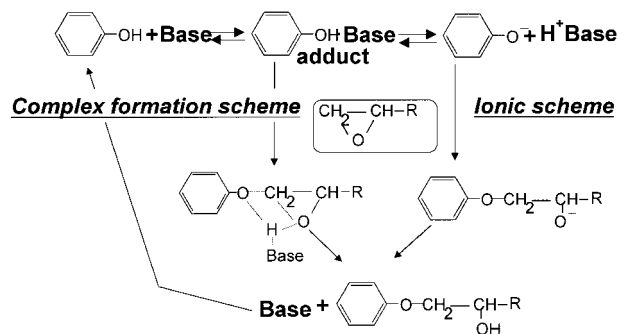


Figure 7 Scheme for epoxy and phenol reaction with basic catalyst.

other process is the ionic scheme in which the above adduct is separated into a phenoxy anion and a cationic hydrogenated basic species.¹⁴ This ion formation step is the rate-determining step. Then the phenoxy anion attacks the epoxy ring and withdraws the hydrogen cation from the basic species. The final product is the same as in the complex formation scheme. The TPP derivatives act as the basic catalyst in both schemes.

The solvent has a great effect on the above reaction scheme in a solution reaction.¹⁵ The complex formation scheme is predominant in nonpolar solvents such as xylene. In this case, the reaction is third order, and the reaction rate is proportional to the concentrations of the epoxy, phenol, and basic catalyst. The Hammett equation coefficient is positive in this reaction mechanism. This means the reaction rate becomes higher by introducing electron-withdrawing groups. It is presumed that the activation energy of the complex formation becomes lower by introducing electron-withdrawing groups into the basic catalyst. On the other hand, the ionic scheme is carried out in polar solvents such as nitrobenzene. In this case, the reaction is second order, and the reaction rate is related to the concentrations of the epoxy and base. In polar solvent, ionic species, which are the phenoxy anion and hydrogenated base cation, form easily, and are relatively stable. In this scheme, the Hammett equation coefficient is negative; introduction of the electron-withdrawing group reduces the reaction rate. It is presumed that the introduction of electron-withdrawing groups reduces the electron density of the lone pair on the phosphine, and basicity of the catalyst becomes weak.

Then it is necessary to decide which is the predominant scheme in the bulk curing reaction with the multifunctional epoxy, multifunctional

phenol, and phosphine-containing basic catalyst. The bulk curing reaction does not use any solvent, and is a model for encapsulating mold material used in semiconductor packaging. In general, the reaction temperature is about 180 °C for the encapsulating mold process. The curing reaction in the bulk state was investigated by DSC and the semiempirical calculation with PM3 method.

Preparation of the sample for DSC was described in the Experimental section. The epoxy used had the multifunctional *o*-cresol novolac-type structure. The phenol hardener was also of the multifunctional type, phenol novolac. The two compounds were combined in a molar equivalent ratio. The catalyst was added as 1 mol % of the above equivalent value.

Example DSC results of the resin composition samples are shown in Figure 8. The heating rates were 5, 10, and 20 K·min⁻¹. Although the height of heat flow of the peak differed with the heating rate, the total heat of reaction in the curing process was almost the same despite the different heating rate. The total molar heat of reaction in the curing process was almost 75–85 kJ·mol⁻¹, independent of not only heating rate, but also TPP structure. The peak temperature of the curing reaction varied with the heating rate. The

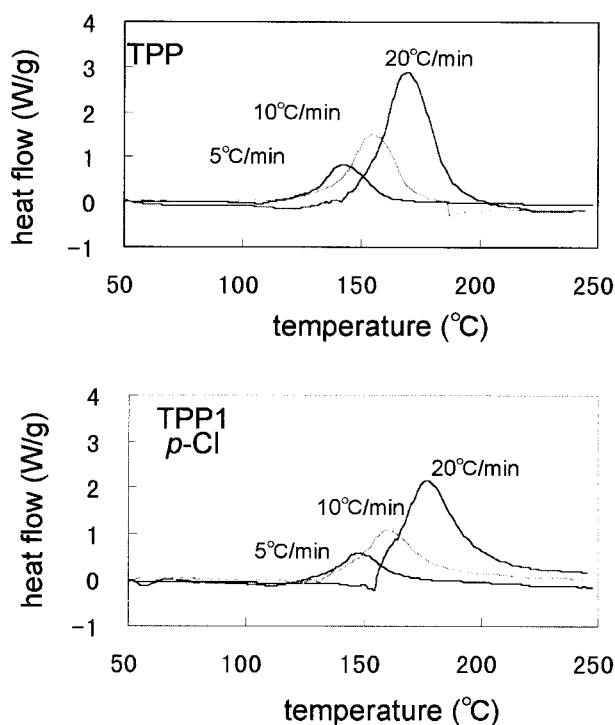


Figure 8 Typical DSC curves of reaction process of epoxy and phenol with TPP and TPP1.

Table I Reaction Peak Temperature at Various Heating Rates of TPP Derivatives

Catalyst	Reaction Peak Temperature (°C)		
	Heating Rate (K.min ⁻¹)		
	5	10	20
TPP	142	156	169
TPP1 (<i>p</i> -Cl)	149	161	177
TPP2 (<i>p</i> -CH ₃)	142	155	170
TPP3 (<i>p</i> -OCH ₃)	143	155	171
TPP4 (<i>m</i> -CH ₃)	142	153	168
TPP5 (<i>m</i> -CH ₃ , <i>p</i> -OCH ₃)	143	156	168
TPP6 (<i>m</i> -CH ₃ , <i>p</i> -OCH ₃)	144	155	169

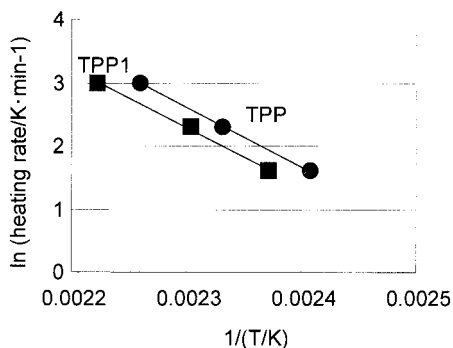
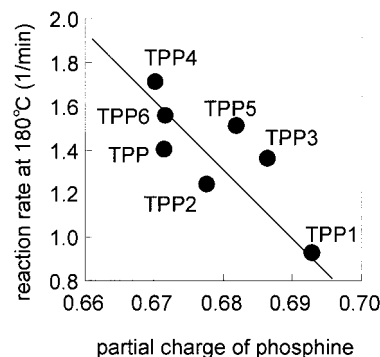
peak temperature became higher with increasing heating rate. The DSC measurement results are summarized in Table I. The activation energy was obtained by measurements with different heating rate, as shown in Figure 9.¹⁶ The reaction rate $k(T)$ is given by the following expression.

$$k(T) = A \exp(-Ea/RT) \quad (1)$$

Here, A is the frequency factor, Ea is the activation energy, R is the gas constant, and T is temperature.

As shown in Table I, the reaction peak temperature of TPP derivatives was almost the same except for TPP1, which included the chlorine substituent. The reaction of epoxy and phenol with TPP derivative catalysts occurred above 100°C and the peak temperature was about 140–180°C. TPP1 had almost a 10°C higher peak temperature compared with the other TPP derivatives.

As shown in Figure 9, the activation energy (Ea) and the frequency factor (A) were obtained

**Figure 9** Arrhenius plot of reaction process.**Figure 10** Relationship between estimated reaction rate and calculated electron density of phosphine of catalyst.

by the Arrhenius plot. Moreover, the reaction rate at 180°C was estimated with the above Ea and A . The reaction with TPP1 had the lowest rate. The introduction of chlorine substituent on the catalyst structure reduced the curing reaction rate in the bulk state of epoxy and phenol at high temperature (180°C).

Next, an explanation of the above catalyst structure effect on the curing reaction was attempted using the partial charge of phosphine and the heats of reaction calculated by the semiempirical method, PM3. The relationship between the estimated curing reaction at 180°C and the calculated partial charge of phosphine of basic catalyst is shown in Figure 10. The reaction rate tended to decrease with larger positive partial charge of phosphine. In the other words, the reaction rate was lowered by the introduction of an electron-withdrawing substituent group in the basic catalyst. The relationship of the reaction peak temperature at 10 K · min⁻¹ heating rate and the partial charge is also shown in Figure 11. Similarly, the peak temperature became higher when the catalyst had electron-withdrawing substituent. These results indicated that the Hammett equation coefficient was negative, and the predominant reaction scheme of epoxy and phenol with basic catalyst in the bulk state (which means without any solvent) at high temperature was the ionic route mechanism. The ionic state was presumed to be relatively stable compared with the complex made from the three compounds at high temperature.

Table II summarizes the calculated heats of reaction of two processes: the adduct formation with phenol and catalyst, and the dissociation to phenolate and hydrogenated base. The heat of

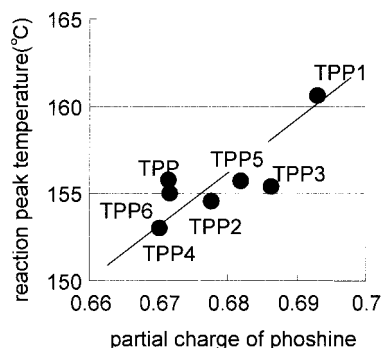


Figure 11 Relationship between reaction peak temperature and calculated electron density of phosphine of catalyst.

reaction of the adduct formation process (ΔH_1) was positive or small negative value. This indicated an exothermic spontaneous reaction at room temperature. The dissociation process had a highly negative heat of reaction (ΔH_2). This was a highly endothermic process, and the process was promoted by heating. The total heat of reaction ($\Delta H = \Delta H_1 + \Delta H_2$) was almost 400–450 kJ \cdot mol $^{-1}$, which gave $\Delta T \sim 50$ K. It seemed that temperatures over 80°C were required for the promotion of the reaction. As shown in Figure 8, the curing reaction occurred above 100°C. It was considered that the dissociation process was the rate-determining step.

The relationship of reaction rate, and the above total heat of formation in the ionic scheme (ΔH), is shown in Figure 12. The reaction rate tended to be low on increasing the heat of reaction, which

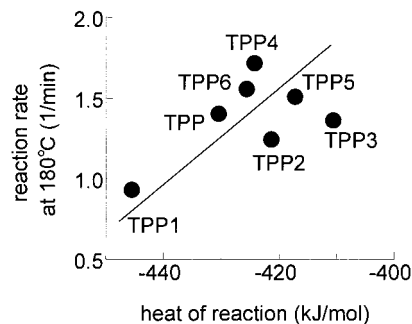


Figure 12 Relationship between estimated reaction rate and calculated heat of reaction.

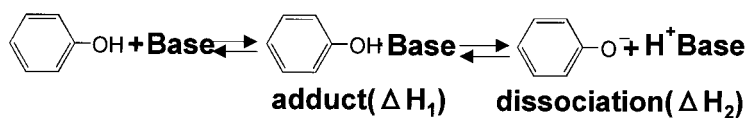
means that the dissociation process was more endothermic. This result also supports the predominant route being ionic.

CONCLUSIONS

The substituent effects of triphenylphosphine (TPP) on melting behavior and catalyst activity derivatives were investigated. The melting point and heat of fusion were consistent with the heat of formation calculated by a semiempirical method. The bulk curing reaction of epoxy and phenol with basic catalyst, such as TPP derivatives, was examined as a model investigation of encapsulating materials for semiconductor devices. The curing reaction occurred above 100°C and the reaction rate depended on the catalyst chemical structure. This curing reaction behavior was also explained by the relationship between

Table II Calculation Results in Heats of Reaction of Adduct Process and Dissociation Process

Catalyst	ΔH_1 (kJ/mol)	ΔH_2 (kJ/mol)	$\Delta H = \Delta H_1 + \Delta H_2$ (kJ/mol)
TPP	96.6	-527.1	-430.5
TPP1 (<i>p</i> -Cl)	5.9	-451.4	-445.6
TPP2 (<i>p</i> -CH ₃)	-0.4	-420.9	-421.3
TPP3 (<i>p</i> -OCH ₃)	15.9	-426.4	-410.5
TPP4 (<i>m</i> -CH ₃)	8.4	-432.6	-424.3
TPP5 (<i>m</i> -CH ₃ , <i>p</i> -OCH ₃)	5.9	-423.0	-417.2
TPP6 (<i>m</i> -CH ₃ , <i>p</i> -CH ₃)	-16.3	-409.2	-425.5



the electron density of the phosphine of the catalyst and the heat of reaction estimated by the semiempirical method. The curing reaction rate decreased with substitution of electron-withdrawing substituents on the basic catalyst.

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