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Comparative cure behavior of DGEBA and DGEBP with 4-nitro-1,2-phenylenediamine

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Abstract

Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and advanced isoconversional kinetic analysis were used to study the curing reaction of diglycidyl ether of 4,4′-bisphenol A (DGEBA) epoxy monomer with an aromatic amine, 4-nitro-1,2-phenylenediamine (4-NPDA). The first DSC exothermic peak was assigned to the curing process of DGEBA with 4-NPDA. Kinetic analysis suggested that the effective activation energy for the cure process decreases from ≈ 120 to a practically constant value $\approx 60\ \mathrm{kJ\ mol^{-1}}$. This system was compared with diglycidyl ether of 4,4′-bisphenol (DGEBP)/4-NPDA. DGEBA/4-NPDA system shows higher reaction temperature, lower reaction rate and lower glass transition temperature under the same cure condition. This can be explained by stereochemical structure of epoxy monomer and the effect of conjugation.

Keywords: Activation energy; Differential scanning calorimetry (DSC); DGEBA

1. Introduction

Most of the commercially available epoxy resins are monomers of diglycidyl ether of 4,4′-bisphenol A (DGEBA). Although these resins have good thermal, electrical and mechanical properties, they are brittle and have poor resistance to the crack propagation. It is well known that properties of cured epoxy resin are strongly dependent on the degree of cure, and the processability is dependent on the cure rate. For this reason, it is very important to understand the cure kinetics to obtain optimum cure conditions.

In this paper, we studied the cure reaction of two epoxy monomers with 4-nitro-1,2-phenylenediamine (4-NPDA). One is monomer of DGEBA and the other is of diglycidyl ether of 4,4′-bisphenol (DGEBP), which is a new type of epoxy monomer and unavailable commercially. DGEBP is of interest because it has a mesomorphic structure that favors the formation of the liquid crystalline (LC) phase during curing [1]. The introduction of LC structure improves mechanical properties, making the material tougher. Because DGEBP is not commercially available, the kinetic and mechanistic studies of its curing process are very scarce. 4-NPDA is used as a curing agent because of its potential non-linear optical (NLO) activity. In a previous paper, the thermal properties and curing kinetics of DGEBP with 4-NPDA system were studied by DSC, TGA and advanced isoconversional kinetic analysis [2]. In this paper we use these techniques to study the thermal properties and measure the kinetics of the non-isothermal curing of DGEBA with 4-NPDA. By studying curing kinetics, reactivity, stability and glass transition temperature of DGEBA/4-NPDA system, we expect to learn more about the difference between these two epoxy materials and to better understand their application potential.

2. Experimental section

2.1. Material

The epoxy monomer used in this study was a commercial product, DER 332 resin, which is a DGEBA resin from Sigma.

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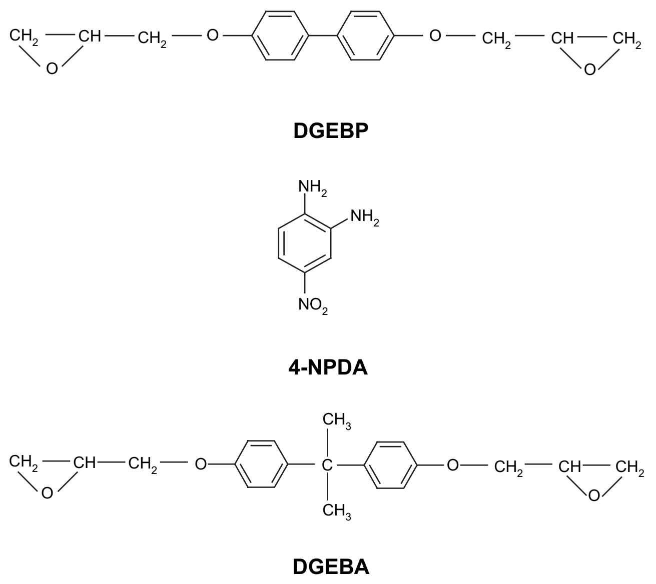

Scheme 1. Chemical structure of DGEBP, DGEBA and 4-NPDA.

It has an epoxy equivalent weight of 172–176 g eq.$^{-1}$ and was used as received. DGEBP was synthesized according to Mormann and Bröcher [3]. The molecular weight of DGEBP monomer is 298. As it has no additives, its epoxy equivalent weight is about 149 g eq.$^{-1}$ The curing agent, 4-NPDA is from Acros, and used as received. The structures of epoxy monomers and curing agent are shown in Scheme 1.

2.2. Measurements

DGEBA and DGEBP were mixed, respectively, with 4-NPDA in a stoichiometric ratio. The mixtures (about 5–7 mg for DGEBP/4-NPDA system and 10–12 mg for DGEBA/4-NPDA system) were sealed under air in aluminum pans with pinhole and cured by heating in a Mettler-Toledo DSC 822^{e}. The temperature and heat calibration of DSC were carried out by using an Indium standard. Non-isothermal experiments were performed at 2, 4, 8, 10, 12, and 14 °C min^{-1} under N_2 at 80 ml min^{-1}. The mixtures have also been studied by heating in a Mettler-Toledo TGA/SDTA 851^{e}. The experiments were performed at 2 °C min^{-1} under N_2 at 80 ml min^{-1}.

In order to measure the glass transition by DSC, the cured sample was heated and cooled between 25 °C and 210 °C at the rate of 20 °C min^{-1}. To check the reproducibility, the measurements were conducted in a continuous series of cool-and-reheat cycles without removing the sample from the DSC. The glass transition measurements were performed on freshly cured sample as well as on the sample annealed in a Thermolyne 10600 oven at 165 °C, 175 °C and 190 °C for a period up to 55 h.

3. Results and discussion

3.1. DSC and TGA data

Fig. 1 shows the DSC and TGA curves of neat DGEBA and DGEBA/4-NPDA system and TGA curve of neat 4-NPDA.

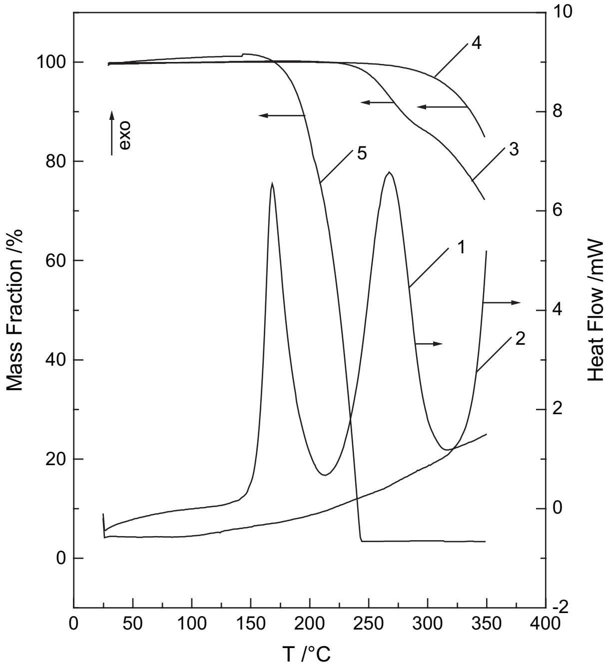

Fig. 1. DSC and TGA curves of neat DGEBA and DGEBA/4-NPDA systems and TGA curve of neat 4-NPDA at 2 °C min^{-1}. 1 – DSC curve of DGEBA/4-NPDA, 2 – DSC curve of neat DGEBA, 3 – TGA curve of DGEBA/4-NPDA, 4 – TGA curve of neat DGEBA, 5 – TGA curve of neat 4-NPDA.

From DSC curve of DGEBA/4-NPDA system, two well separated exothermic peaks are observed at about 170 °C and 270 °C. From TGA curve of this system, it is seen that below 220 °C there is no mass loss. A significant mass loss starts at about 235 °C and is apparently associated with decomposition. Comparing TGA curve with DSC curve, we can see that decomposition is related to the second peak in DSC curve. The DSC trace of neat DGEBA shows deviation from a base-line above ≈100 °C. Because there is no significant mass loss from 100 °C to ≈220 °C in curve 4, the deviation is likely associated with self-curing [4]. TGA curve of neat 4-NPDA shows that there is no significant mass loss below the first DSC peak temperature (168 °C) at the heating rate of 2 °C min^{-1}. A significant mass loss occurs only when the curing process associated with first DSC peak comes into decelerating stage. It is seen that up to 250 °C DGEBA/4-NPDA system demonstrates a very small (≈2%) mass loss in curve 3 and up to 290 °C neat DGEBA shows the same mass loss in curve 4. This information provides a clue about a possible identity of the second peak in the DSC curve of DGEBA/4-NPDA system. Although this peak is mostly associated with degradation of cured material, it is not impossible that some self-curing may also occur. Since the material of interest obviously destroyed at this stage, further studies of the respective processes lie outside our purpose, which is to investigate the formation and properties of this material.

Fig. 2 shows DSC curves of DGEBP/4-NPDA and DGEBA/4-NPDA systems. Solid line represents the DGEBA/4-NPDA system and dash line represents DGEBP/4-NPDA system. Because the latter is a mixture of two solids, DSC curve

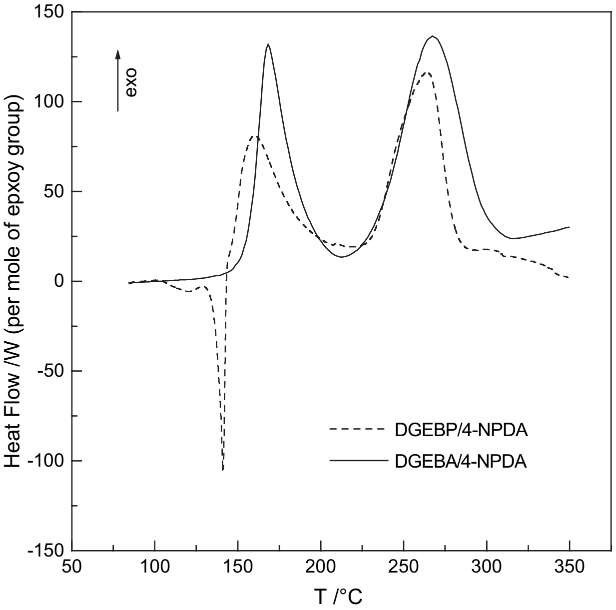

Fig. 2. Comparison of DSC curves of DGEBA/4-NPDA and DGEBP/4-NPDA systems at 2 °C min^{-1}.

of DGEBP/4-NPDA demonstrates two endothermic peaks (≈120 °C and 140 °C) related to the melting of DGEBP and 4-NPDA. These peaks are followed by two exothermic peaks at 160 °C and 260 °C. Since the DGEBA system is liquid, the DSC curve of DGEBA/4-NPDA system shows only two exothermic peaks at 170 °C and 270 °C. The different molecular weights of DGEBP and DGEBA result in different amounts of epoxy in the mixture even though the mass of samples is same. Therefore, the reaction heat, Q per gram of sample cannot be used to compare the two systems. In order to compare the reaction heat for these two systems and with the literature values, the DSC data have been converted to W per mole of epoxy group. The values 100–120 kJ mol^{-1} are typical for epoxy-aromatic amine reaction and reported most frequently as the heat of reaction per mole of epoxy group of curing [5–9]. Our data show that ΔH is 109 kJ mol^{-1} for DGEBA/4-NPDA system and 98 kJ mol^{-1} for DGEBP/4-NPDA system so that the values are quite close to each other and consistent with the literature values.

From Fig. 2 the first exothermic peak of DGEBP/4-NPDA system is at a lower temperature and develops faster than that of DGEBA/4-NPDA system. It demonstrates that the DGEBP/4-NPDA system reacts faster at lower temperature than DGEBA/4-NPDA system. It means that the former is a more reactive epoxy monomer than the latter. The difference in reactivity may result from stereochemical structure and effect of conjugation. Details will be discussed in Section 3.3. Although DGEBP is more reactive at higher temperatures, it is by far less reactive than DGEBA below 150 °C (m.p. of DGEBP). The reason for that is that below this temperature DGEBP is a solid material as well as most of amines are used for curing. Therefore, DGEBP–amine mixtures can be safely stored for long periods of time, whereas DGEBA–amine liquid mixtures have rather limited pot-life even at room temperature.

3.2. Glass transition temperature analysis

The glass transition temperature, T_g of the cured material was measured under four kinds of conditions. Firstly we cured the system from 25 °C to 210 °C at 2 °C min^{-1}, then cooled it immediately down to room temperature and measured T_g. The measured value was ≈125 °C (Fig. 3). It is worthy of note that the DSC runs on this sample did not show a release of any residual heat that would typically occur on heating of an incompletely cured sample above its T_g. However, annealing of these samples at 165 °C, 175 °C and 190 °C for a period of up to 55 h demonstrated a noticeable increase in T_g. For each of the conditions, we measured T_g in three repetitive heat–cool scans. Fig. 3 shows the DSC curves of DGEBA/4-NPDA system after various annealing times at 190 °C. As seen, the glass transition step shifted continuously from ≈125 °C to ≈165 °C with the increasing annealing time. A similar tendency was observed at other annealing temperatures (Fig. 4). It appears that the average limiting value of T_g lies in the region around 160 °C. The glass transition signifies the onset of long range molecular motion in the polymer chain that involves some 10–50 chain atoms [10]. Therefore, an increase in T_g (Fig. 4) indicates that molecular motion becomes increasingly hindered on annealing. An obvious explanation to this effect is an increase in the degree of crosslinking that results from continuing curing process. Apparently this process is very slow so that DSC could not detect any significant heat release while scanning the not annealed sample (Fig. 3).

Note that most of the observed DSC curves (Fig. 3) of the cured material showed a small enthalpy overshoot, although heating was performed at the same rate as cooling. Similar effect was observed for other polymers such as poly(vinyl pyrrolidone) and poly(ethylene 2,6-naphthalate), whereas the

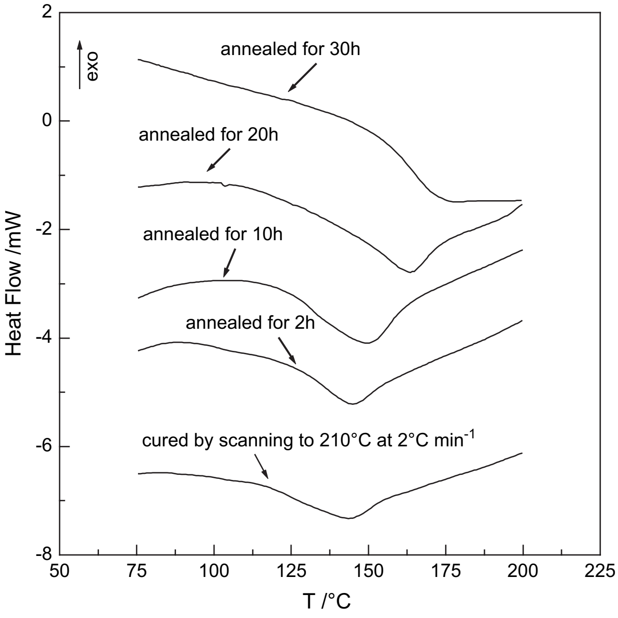

Fig. 3. DSC curves of DGEBA/4-NPDA system cured by scanning to 210 °C at 2 °C min^{-1} and then annealed for various time at 190 °C at the heating rate of 20 °C min^{-1}.

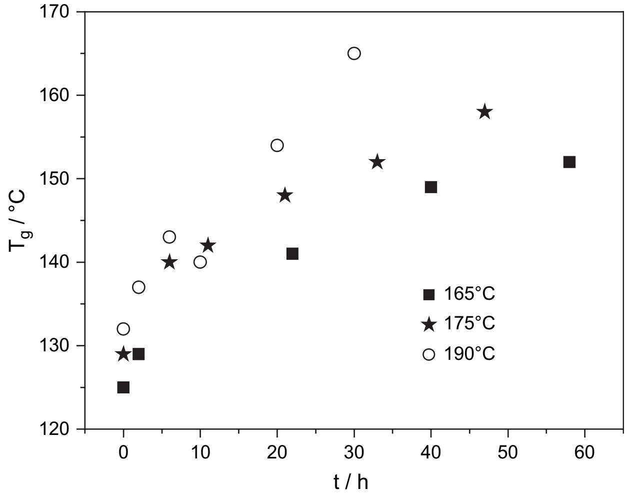

Fig. 4. Glass transition temperatures (T_g) of DGEBA/4-NPDA as a function of annealing time at various annealing temperatures.

overshoot did not occur in poly(vinyl chloride) (PVC) and poly(butyl methacrylate) [11]. The size of the effect is likely to be larger in materials with the larger width (i.e., ''non-exponentiality'') of the relaxation time distribution. In our cured samples, the effect may be additionally enhanced by slight aging that may occur during cooling the material from T_g down to 25 °C and reheating it back to T_g.

The obtained data on an increase in T_g with the annealing time (Fig. 4) demonstrate an important difference with a similar data obtained earlier [2] for DGEBP/4-NPDA system. In that system, after annealing for 5 h at 165 °C, T_g increased to 149 °C that appeared to be the ultimate degree of curing. For DGEBA/4-NPDA system, after annealing at 165 °C for 5 h, T_g increased to only 134 °C, whereas T_g of 149 °C was reached after ≈40 h at 165 °C. It suggests that the crosslinking kinetics is significantly slower in the DGEBA system than in DGEBP.

3.3. Kinetic analysis

Kinetic analysis of epoxy cures carried out under non-isothermal conditions can be performed by a number of various methods that include single as well as multiple heating rates [12]. It has, however, been demonstrated [12] that the single heating rate methods are not capable of producing reliable values of the kinetic parameters that would be consistent with the values obtained for isothermal cures. It should be noted that the flawed nature of the single heating rate kinetic methods was stressed in discussions [13,14] of the results of the ICTAC Kinetics Project [15]. The general recommendation of the Project was that for reliable kinetic evaluations one should use the methods that employ kinetic curves obtained at multiple heating rates. Isoconversional methods provide a good example of multiple heating rate methods. As shown previously for epoxy cures [12], isoconversional methods allow one to produce reliable kinetic parameters as well as to accomplish agreement with isothermal data. Without assuming a particular form of the reaction model, these methods allow for evaluating an effective activation energy (E_α) as a function of the extent of reaction (α). If changes in the cure mechanism are associated with changes in the activation energy, they can be detected by these methods [16–19]. In particular, it has been demonstrated in earlier work by Sbirrazzuoli and Vyazovkin [19–21] that for curing systems a change from a kinetic to diffusion regime that occurs on approaching vitrification causes a significant decrease in the E_α values.

In this paper we perform kinetic analysis of the DSC data by using an advanced isoconversional method developed by Vyazovkin [22,23].

For a series of n experiments carried out under different temperature programs, $T_i(t)$, the activation energy is determined at any particular value of α by finding E_α, which minimizes the function:

$$\Phi(E_\alpha) = \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \tag{1}$$

where,

$$J[E_\alpha, T_i(t_\alpha)] \equiv \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left[\frac{-E_\alpha}{RT_i(t)}\right] dt \tag{2}$$

In Eq. (2), α varies from $\Delta\alpha$ to $1-\Delta\alpha$ with a step $\Delta\alpha$ ($\Delta\alpha = m^{-1}$, where m is the number of intervals chosen for analysis). Because m is usually set as 50, $\Delta\alpha$ equals to 0.02. The integral, J, in Eq. (2) is evaluated numerically by using the trapezoid rule. The minimization procedure is repeated for each value of α to find the dependence of the activation energy on the extent of conversion.

The variation of effective activation energy with conversion (α) and that of conversion with temperature are shown in Fig. 5. The scatter plot represents the dependence of effective activation energy on extent of conversion for the cure process (first DSC peak in Fig. 1). The line plots represent the dependence of conversion on temperature. For DGEBA/4-NPDA system, the cure process is characterized by a quick decrease in activation energy from ≈120 to the value of ≈65 kJ mol^{-1} when $\alpha = 0$–0.4, then remains practically constant. For DGEBP/4-NPDA system, the activation energy of the cure process is practically constant, 50–55 kJ mol^{-1}. The values 50–70 kJ mol^{-1} are typical for epoxy-amine reaction and reported most frequently as the activation energy of curing [24]. Because the constancy of activation energy indicates a single limiting process, the cure of DGEBA with 4-NPDA represents more complex kinetics. When $\alpha > 0.5$, the difference between these two systems is not very large, but it may be worthy of note that DGEBP curing shows somewhat lower activation energy that may be associated with stereochemical structure of epoxy monomer and the effect of conjugation. From the curve of extent of conversion versus temperature, we can see that the extent of conversion in the DGEBP/4-NPDA system is higher than that in DGEBA/4-NPDA system at the

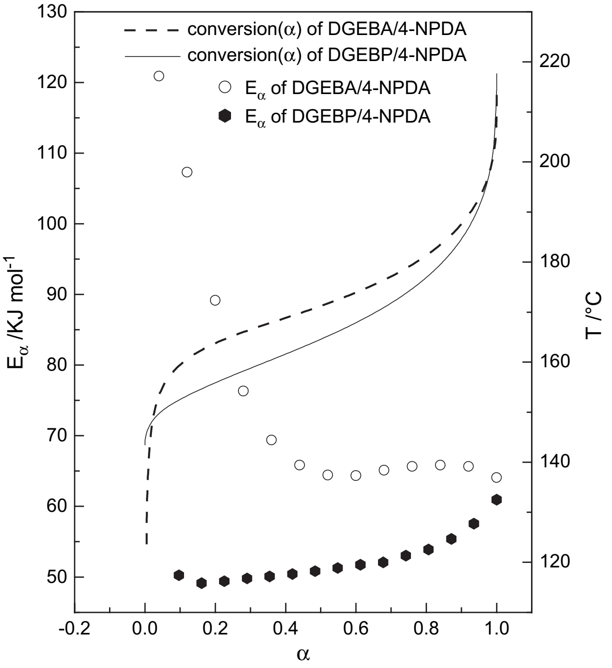

Fig. 5. Variation of effective activation energy (E_α) on the extent of conversion and the dependence of the extent of conversion on temperature at the heating rate of 8 °C min^{-1} for DGEBA/4-NPDA and DGEBP/4-NPDA systems.

same temperature. This is consistent with the difference in the activation energy and therefore suggests that the difference maybe due to the difference in the energy barriers for epoxy-amine reactions. Note that neither of the systems has demonstrated a decrease in E_α at later stages of curing that would be indicative of vitrification [19–21]. Apparently the systems vitrify on cooling of the cured materials.

The decrease (from ≈120 to the value of ≈65 kJ mol^{-1} in Fig. 5) in the effective activation energy of epoxy curing is sometimes observed at the early stages and is likely associated with the rate dependence on viscosity [18]. Specifically, the rate of a chemical reaction generally depends on the physical properties of the reaction medium. So the viscous properties of the liquid epoxy may impose diffusion limiting on the curing rate. This also suggests the effective activation energy as a function of viscosity as well as temperature which is a factor affecting viscosity. When $\alpha > 0.5$, the difference in activation energy of these two systems can be explained by stereochemical structure of monomer and the effect of conjugation. DGEBP is a practically linear molecule and the two epoxy groups are at both ends. For DGEBA, the center of the monomer is a tertiary Bu^t-C, and the tetrahedral carbon makes the monomer not linear. Because the symmetric structures on both sides of the tetrahedral carbon exist at an angle, two epoxy groups are closer than that of DGEBP. With the proceeding of polymerization and crosslinking, the steric hindrance increases, which leads to higher activation energy of DGEBA–amine system. Another reason may be the effect of conjugated structure that forms among two benzene rings and two oxygens in DGEBP. In DGEBA the two benzene rings are separated by a tertiary Bu^t-C, which destroys the conjugation.

4. Conclusions

Our study shows that the reaction of DGEBA and 4-NPDA occurs in two steps, which are represented by two peaks in a DSC curve. Based on the results of DSC, TGA and advanced isoconversional kinetic analysis, the first process (first peak in DSC curve) is assigned to the cure of DGEBA with 4-NPDA. The second process (second peak in DSC curve) is associated with the decomposition of the material. After completion of the first exothermic process the material is partially cured. By comparing DGEBA/4-NPDA with DGEBP/4-NPDA system, the former shows lower reactivity. The difference in reactivity of these two epoxy monomers is likely due to the stereochemical structure of monomer and the effect of conjugation. Comparison of activation energies of these two systems suggests that the lower reactivity of DGEBA correlates with the higher activation energy of DGEBA/4-NPDA cure reaction.

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