# Reactive Blending Approach to Modify Spin-Coated Epoxy Film: Part II. Crosslinking Kinetics

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**ABSTRACT:** Kinetics of the reactive blending of epoxy with a four-armed $\varepsilon$-caprolactone-based carboxylic acid end-functionalized oligomer was analyzed with a model-free approach. The employment of a dual catalyst system ensured high density of crosslinking in the blends and minimized phase separation even when comparatively high concentration of the oligomer was incorporated. The two reactions were examined separately before analysis of the dual-catalyzed system. The apparent activation energy of the single-catalyzed reactions could be seen to fall into three regimes. It is proposed that regime I is due to reaction control, the middle part (II) to mass transport, and the high conversion tail (III) to structural control. The results of a thermal analysis carried out on the crosslinked samples corresponded well with the findings of the kinetic analysis. The combined kinetic and thermal results can be used in optimization of the crosslinking process. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 3689–3696, 2006

**Key words:** activation energy; crosslinking; blends; differential scanning calorimetry (DSC); thermosets

## INTRODUCTION

Epoxy resin-derived materials are extensively used in manufacturing electronic goods. An unfortunate characteristic of epoxy resins, however, is the rigidity of the crosslinked network, which limits their applicability. As a means to overcome this problem, the modification of the mechanical properties of epoxies has been extensively investigated. Typically, reactive rubbers or thermoplastics are incorporated into the epoxy matrix. Depending on the degree of chemical interaction between the resin and the modifier polymer, reaction-induced phase separation may occur and alter the network structure significantly, with effect on the thermomechanical properties. The modified material can be studied by means such as dynamic mechanical analysis, differential scanning calorimetry (DSC), and scanning electron microscopy.[1–12] However, to understand the evolving network during crosslinking, the kinetics of the reaction need to be studied as well.

Both isothermal and nonisothermal methods have been used for the analysis of reaction kinetics. As well, relatively simple models have been employed to simulate reactions. Often the reactions are complex. For example, a number of chemical and physical changes occur during the crosslinking of a thermosetting resin, as the material is transformed from a viscous liquid to a highly crosslinked solid. These changes undergone in multistep reactions make the accurate calculation of activation energy a complex problem. Indeed, activation energies and pre-exponential factors can be determined only for simple systems. In addition to the probable changes in reaction mechanism during the crosslinking, the rate of solid-state reactions is affected by factors such as mass transport of the reactants and the vitrification of reacting species.[13–18]

The complexity of a reaction can be taken into account by using two-step models.[19] In general, however, the model-fitting approaches are not very effective in describing the crosslinking of epoxies.[20] Vyazovkin,[21] starting from the isoconversional methods introduced by Friedmann,[22] Ozawa,[21] and Flynn and Wall,[23] has proposed an alternative approach that allows the apparent activation energy to be determined as a function of the extent of conversion and/or temperature without assuming a particular form of the reaction model. Assuming a simple superposition of the individual reactions of a multistep mechanism, one obtains the conversion-dependent apparent activation energies. It is also assumed that all reactants have been converted into a product with full conversion ($\alpha = 1$) at the end of the reaction. In addition, the process must not involve simultaneously exothermic and endothermic reactions or competing reactions, and it should not be partially diffusion controlled. With these boundary conditions taken into account, the advantages of the model-free analysis, i.e., simplic-

ity and the avoidance of the erroneous choice of a kinetic model, can be put to work. Despite the evident advantages of the model-free analysis, there is an on-going debate about the theoretical justification.[24–29] Nevertheless, it is gaining acceptance as the thermal analysis community actively debates the best way to determine the reaction kinetics of complex systems.[14,15,24–29]

In the present study, we examine the reaction kinetics of a dual-catalyzed mixture of an epoxy and our previously synthesized[4] oligomer, utilizing the model-free kinetic approach.

## METHODS

### Materials

The $\varepsilon$-caprolactone (CL)-based and carboxylic acid end-functionalized oligomer (PCL2-SA) that was synthesized earlier (in Part I)[4] was mixed with epoxy resin (SU8; Shell) in a grinding mortar. The ratio of oligomer to epoxy was 20:80 by weight. Imidazole (0.06 wt % of the solid content; Fluka) or triarylsulfonium hexafluoroantimonate (TH) (2.5 wt % of the epoxy content; Aldrich) or both together were added as catalyst. The TH was provided as a salt in polypropylene carbonate in ratio 50:50 by weight. Imidazole catalyzes the reaction between carboxylic acid and epoxy groups, and the TH salt acts as an acid–catalyst precursor that decomposes to cations upon UV light exposure, and catalyzes the ring-opening polymerization of residual epoxies.

### Characterization methods

DSC measurements were carried out on a Mettler Toledo Star DSC821 in the temperature range of 80–240°C used for the kinetic analysis, at heating rates of 2°C/min, 5°C/min, 10°C/min, and 20°C/min. The degree of crosslinking evaluated from the results of the kinetic study was compared with the results obtained by thermal analysis for the samples crosslinked according to a predefined baking program. The residual reactivity and the glass transition temperature ($T_g$) were determined from the first heating scan that was recorded in the temperature range of −50°C to 240°C at a heating rate of 10°C/min, during which complete conversion of the epoxy groups can be assumed.

### Model-free kinetic analysis

DSC was used to obtain information about the reaction rate. With very few exceptions the rate of a reaction increases with temperature. The relation between the rate constant, $k$, and temperature, $T$, was first proposed by Arrhenius:

$$k = Ae^{-E/RT} \tag{1}$$

The constant $A$ is called the pre-exponential factor, $E$ is the activation energy, and $R$ is the gas constant. Kinetic analysis of an epoxy crosslinking reaction, i.e., a cure, is usually based on the measurement of heat flow by DSC, which is proportional to both overall heat release and cure rate according to Eq. 2:[30]

$$\frac{dQ}{dt} = Q_{cure}\frac{d\alpha}{dt} = Q_{cure}k(T)f(\alpha) \tag{2}$$

where $dQ/dt$ is the heat flow, $t$ is the time, $Q_{cure}$ is the total heat released when an uncured sample is brought to complete cure, $d\alpha/dt$ is the cure rate, $\alpha$ is the extent of a monomer conversion to a crosslinked network, $k(T)$ is the Arrhenius rate constant, and $f(\alpha)$ is the reaction model. The extent of cure, $\alpha$, is determined by integrating the heat flow curve. The temperature dependence of the rate constant is introduced by replacing $k(T)$ with the Arrhenius equation, which gives

$$\frac{d\alpha}{dt} = Ae^{-E/RT}f(\alpha) \tag{3}$$

The pre-exponential factor, $A$, and the activation energy, $E$, are traditionally determined from isothermal experiments converting Eq. 3 to its logarithmic form, Eq. 4, to solve for $A$ and $E$:

$$\log_{10}k = \log_{10}A - \frac{E}{2.303RT} \tag{4}$$

The determination of activation energy is an important objective of any kinetic investigation. However, if the activation energy is determined according to the procedure presented here, the result is a single set of global Arrhenius parameters for the whole process. This makes the simulation of multistep reactions problematic. The model-free approach allows the apparent activation energy to be determined as a function of the extent of conversion and/or temperature without the assumption of a particular form of the reaction model. For nonisothermal conditions, when the temperature varies with time with a constant heating rate, $\beta = dT/dt$, Eq. 3 can be represented as:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}e^{-E/RT}f(\alpha) \tag{5}$$

Too often a single-step kinetic equation 5, taking $f(\alpha)$ in one of its various reported models,[31] is forced to fit the data. However, the use of an improper model can seriously impair the outcome of a kinetic evaluation.[32] For the epoxy cure, the reaction-order model $(1-\alpha)^n$

and the autocatalytic cure model $\alpha^m(1 - \alpha)^n$ are the most frequently used. It is generally accepted, however, that the epoxy cure is a multistep reaction that likely involves several reaction mechanisms and/or rate-limiting stages each with a different set of Arrhenius parameters.

Conventional isoconversional methods assume that the reaction rate at constant extent of conversion is only a function of temperature. This holds for single-step reactions providing that the heating rates are not extreme. For multistep reactions, activation energy can vary with the heating rate and the subsequent reaction path, thus leading to different extent of conversion. The differential method proposed by Friedmann[22] may result in erroneous values of activation energies because of poor resistance to experimental noise. The use of the integral methods[19,23] is therefore preferred.[20] However, the integral methods also require corrections.[33] To overcome the inaccuracies of the conventional approximation routines associated with the isoconversional methods,[19,22,23] Vyazovkin[21] developed a nonlinear approximation method for the temperature integral. Vyazovkin and Sbirrazzuoli[20] calculated, for a set of $n$ experiments carried out at different but constant heating rates, the minimum of the function

$$\sum_{i=1}^{n}\sum_{j\neq i}^{n}\left[\frac{I(E_\alpha,T_{\alpha,i})\beta_j}{I(E_\alpha,T_{\alpha,j})\beta_i}\right] \tag{6}$$

with

$$I(E_\alpha,T_\alpha) = \int_0^{T_\alpha} e^{-E_\alpha/RT}dT \tag{7}$$

which must be evaluated numerically. In Equation 6, the indexes $i$ and $j$ denote different heating rates, $n$ is the total number of heating rates, $\alpha$ is the conversion, and $I$ is the temperature integral. According to this empirical method, the activation energy can be evaluated at any given value of $\alpha$ for multi-step kinetics. Although the exact physical foundation of the aforementioned approach is still under debate, its application has produced viable results.

## RESULTS AND DISCUSSION

The crosslinking reaction under investigation involves two successive reactions: (1) imidazole-catalyzed reaction between PCL2-SA and the epoxy and (2) acid-catalyzed ring-opening etherification of the residual epoxy groups. The two reactions were examined separately before analysis of the dual-catalyzed mixture.

According to the DSC analysis, the imidazole-catalyzed reaction started near 100°C and the enthalpy of the reaction was 127.1 J/g. The acid-catalyzed reaction started at about 125°C and the reaction enthalpy was 176.5 J/g. The dual-catalyzed reaction started at about 80°C. It can be assumed that one of the catalysts has synergistic effect on the other but their exact role is not clear to us at the present moment. In other words, the information obtained from the separate crosslinking studies cannot be considered as simply additive. Moreover, the reaction enthalpies for the separate reactions cannot be determined from an analysis of the dual-catalyzed mixture because partial overlapping of the reactions exists with fast thermal scans. We note, too, that the total heat released in the reaction sequence is less than what one might expect from the data of the individual reactions. Thus, the activation energy value(s) provided by the model-free kinetic analysis were considered to be apparent rather than absolute. The kinetic information obtained from the model-free analysis is used as an approximation for the overall reaction sequence, which can be used, with caution, in determining the process conditions needed to obtain a "fully" cured coating. The kinetic study was performed with only one oligomer, PCL2-SA, and one PCL2-SA/epoxy blend (20:80 ratio by weight), which means that the information obtained must again be applied with caution in interpreting the kinetics of blends with the other oligomers (PCL0-SA and PCL5-SA) synthesized earlier (in Part I) and the kinetics of blends with different ratios of reactants.

The results of the model-free analyses are shown in Figure 1 for the acid-catalyzed crosslinking of the epoxy, in Figure 2 for the imidazole-catalyzed crosslinking of the PCL2-SA with epoxy, and in Figure 3 for the dual-catalyzed crosslinking of the mixture.

### Acid-catalyzed ring-opening polymerization of the epoxy

Results of the kinetic analysis of acid-catalyzed crosslinking of epoxy are shown in Figure 1. In the conversion range of about 0–5%, the crosslinking process is expected to be reaction controlled; in the region of 5–90% the mass transport becomes limiting. As the reaction proceeds and the molecular weight of the epoxy network increases, the viscosity of the material starts to increase resulting in gelation, vitrification, and the formation of highly crosslinked solid epoxy. This affects the apparent activation energy by decreasing it—a generally observed phenomenon.[34–36] The decrease in apparent activation energy does not mean that the reaction rate is increased because this is not an isothermal situation. The structural changes hinder the reacting species from contacting each other as the material deforms from liquid-like to vitrified gel and eventually to a solid. It is likely, therefore, that the
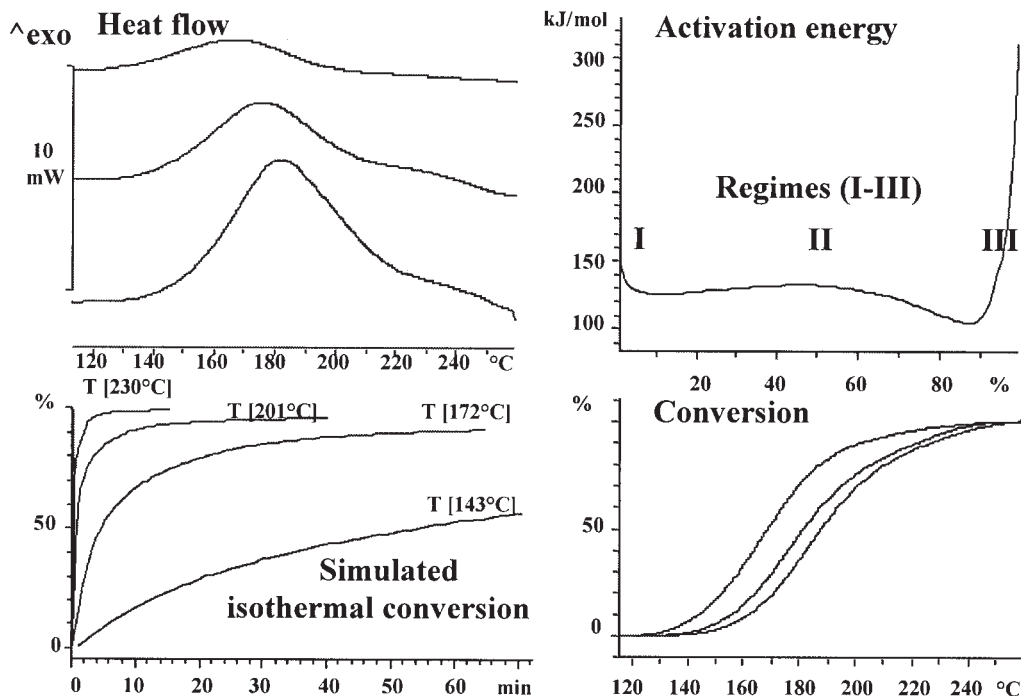
**Figure 1** Kinetics of the acid-catalyzed epoxy reaction.

reaction rate decreases as the structural control takes over. The structural effects grow stronger as the reactive fragments are both physically and chemically bound into the forming network, and the glass transition temperature of the evolving network increases. As long as the experimental temperature is higher than the glass transition temperature of the material under investigation there is no significant structural effect. This fact favors the use of a nonisothermal rather than an isothermal analysis in studying the curing kinetics. It is also reported that the heating rate in a nonisothermal analysis should be high rather than low to minimize the effects of structural change on the analysis.[37] However, for sequential reactions starting at different but nearby temperatures, it may be better to use lower heating rates to minimize the overlapping of reactions, as will be demonstrated later in the discussion of the dual-catalyzed reaction.

The activation energy was close to 125 kJ/mol before the structural control started. The structural control above 90% conversion causes uncertainty in the kinetic evaluation when the model-free approach is used.[37] However, the steep increase in apparent activation energy ($\alpha > 90\%$) is assumed to result from trapping of the growing epoxy macromolecules within the network and loss of mobility of their functional groups (epoxy rings). Note that the term apparent activation energy is used here because it is a function of the reaction mechanism itself and the structural changes. The fundamental reaction mechanism is assumed to remain the same (ring-opening polymeriza-

tion of the epoxy groups into covalent ether bonds) and the observed changes in the apparent activation energy are induced by the structural changes.

Dunne et al.[38] proposed that the residuals of the photoinitiator they employed in their study decompose into acids that catalyze the reaction at temperatures above 180°C. This results in a second enthalpy release from the continuing reaction of the epoxy rings. For a sample that was not exposed to ultraviolet light, we also noticed a reaction at around 190°C, which is assumed to start because of thermal decomposition of the remains of triarylsulfonium hexafluoroantimonate catalyst precursor. This would explain the appearance of a shoulder on the heat flow curve during the epoxy cure (see Fig. 1).

### Imidazole-catalyzed PCL2-SA reaction with epoxy

Regime I in imidazole-catalyzed reaction is broader than regime I in acid-catalyzed reaction. This is as expected, since the reaction rate is much faster (compare the simulated isothermal curves in Figs. 1 and 2), and higher conversions are therefore achieved within a narrower temperature interval. The $T_g$ for the imidazole-catalyzed blend was evaluated to be 124°C, and most of the crosslinking reaction took place above that temperature during the nonisothermal analysis. Regimes II and III are clearly seen for the reaction. However, the transition from regime I to II is not as sharp. There is an indication of structural effects around the final degree of conversion above 95%.
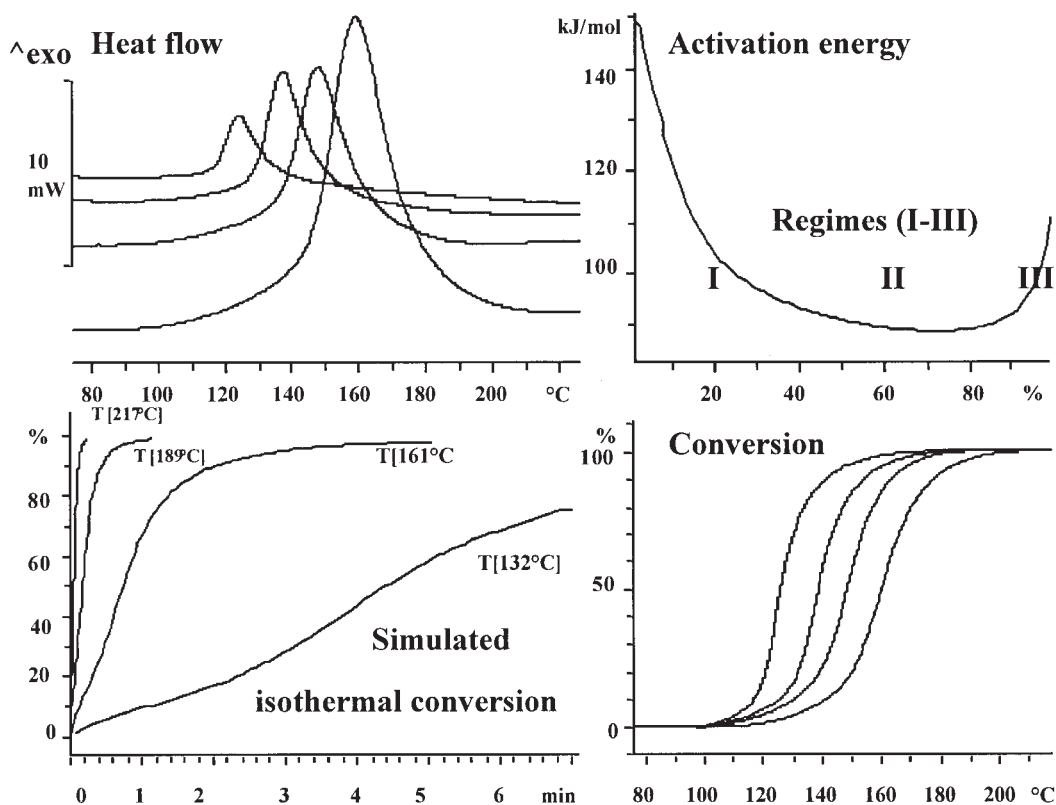
**Figure 2**  Kinetics of the imide-catalyzed PCL2-SA/epoxy reaction.

Between 40% and 90% conversion, the apparent activation energy remains close to 90 kJ/mol, which is attributed to mass transport control. The decrease in the apparent activation energy in the low-conversion zone is also reported by other workers.[39] Despite the uncertainties in the results presented earlier, they are of value in choosing appropriate process conditions.

**Dual-catalyzed reaction**

We report here the results of the dual-catalyzed reaction of the PCL2-SA and epoxy, but emphasize that the reactions were not entirely successive but exhibited some overlapping, as shown in Figure 3. To minimize the effect of the overlapping, only the information obtained from the slowest heating rates was used in the kinetic analysis. As was noted above, the successive reactions can be assumed to influence each other, preventing the overall reaction from reaching full conversion. By this, we mean that the PCL2-SA may not be entirely incorporated into the network through chemical bonding but rather physically entrapped. In fact, the apparent activation energy for the imidazole-catalyzed reaction was found to be negative, which indicates that increase in temperature decreases the reaction rate at the expense of the rate of the acid-catalyzed reaction. We concluded that proper crosslinking of the reaction mixture must occur during

the imidazole-catalyzed reaction to ensure covalent incorporation of PCL2-SA within the polymer network before the epoxy reaction. This means that, in the real process, the reaction needs to be carried out in two distinct steps. When the reaction mixture is not acid-catalyzed before the first baking step, i.e., if the reaction mixture is not exposed to ultraviolet light at the outset, the imidazole-catalyzed reaction can be carried out at elevated temperatures, which need to be above the $T_g$ of the crosslinked sample to prevent the diffusion effect. The $T_g$ for the sample was determined to be 64°C. According to the results, it was concluded that the first step of the baking process should be carried out at 90°C for 90 min.

Obtaining an improved physical meaning for the kinetic analysis would require that slower heating rates (<2°C/min) be used for enhanced separation of the successive reactions. The model-free isoconversional approach helped us to control the complex reactions of the blend cure, but the reactions are too complex for a complete kinetic understanding by this approach.

**Discussion on activation energy**

Even though there are some characteristic differences between the systems, three activation energy regimes for the reactions can be extracted. The dual-catalyzed
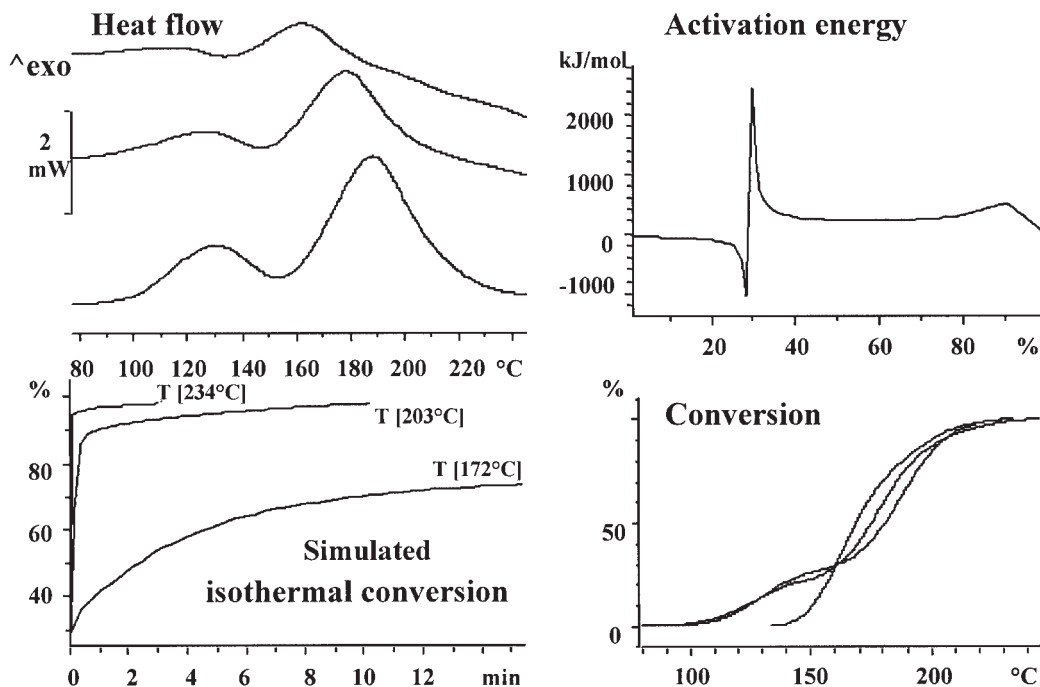
**Figure 3** Kinetics of the dual-catalyzed PCL2SA10/epoxy reaction.

system seems to be an exception as was discussed here. The regimes are assumed to represent a change in the physical limiting factor of the reaction, while the actual reaction mechanism remains the same. It is proposed that the regime of low conversion (I) is due to the reaction control, the middle part (II) to the transport of matter, and the high conversion tail (III) that shoots up to the structural control. In regime I, the activation energy declines steeply (in particular in the imidazole-catalyzed reaction), as would be expected because the conversion is temperature dependent. The apparent activation energy at increasing conversion thus corresponds to increasing temperature and more thermal activation is brought to enhance the motion of the reactive species. In regime II, there is enough thermal activation for the reaction and the mass transport controls the reaction. In regime III, no thermal activation is sufficient for the reaction to proceed in the network because the reactive species are structurally bound.

### Verification of crosslinking conditions

To determine whether the results of the kinetic analysis were in agreement with the thermal properties of the crosslinked samples, a thermal analysis of the networks was carried out by DSC. Glass transition temperatures and the existence of residual reactivity were examined. The most important thermal properties are presented in Table I along with the swelling results. Lack of residual reactivity and increased $T_g$

did not ensure solvent resistance as was shown with some of the coatings. We note that a given reaction can reach its full conversion, i.e., the full degree of crosslinking, in the blends of different stoichiometric amounts of the reactants, but the density of the crosslinking may be insufficient so that the loosely incorporated chains do not prevent solvent penetration into the network. The density of crosslinking of the networks was evaluated earlier (Part I)[4] and to the appropriate extent the results are shown in Table I. The crosslinking density is directly related to the swelling behavior of the networks. The more loosely tied networks swelled significantly in acetone and became easily removable from the substrate, while samples with high crosslinking density did not show swelling.

In the absence of the catalysts, the reaction mixture did not show any reaction judging from the intactness of the $T_g$ and the lack of any released heat of reaction. In the presence of imidazole catalyst, the PCL2-SA oligomer reacted with epoxy and reached full conversion in a single-step crosslinking bake carried out at 180°C for 60 min. This was also demonstrated by the model-free kinetic analysis, as shown in the simulated isothermal conversion curves (Fig. 2). The prebake condition (90°C for 30 min), in contrast, resulted in two residual reaction enthalpies. Either way, in the presence of only the imidazole catalyst the PCL2-SA/epoxy mixture did not provide adequate density of networking because the cured film swelled in acetone.

### TABLE I
### DSC and Swelling Results for the Crosslinked PCL2-SA/Epoxy Coatings

| Polymer system[a,b] | Amine | Photoinitiator | $T_{g1}$ (°C) | $T_{g2}$ (°C) | Residual reactivity | $\bar{M}_n^{cc}$ (g mol) | Swelling[d] |
|---|---|---|---|---|---|---|---|
| Epoxy resin | No | No | 38 | – | No | – | Yes |
| Epoxy/PCL2–SA10 | No | No | 39 | – | No | – | Yes |
| Epoxy/PCL2–SA10 | Yes | No | 124 | – | No | 70,000 | Yes |
| Epoxy/PCL2–SA10 | Yes | Yes | 162 | 59 | Minor (180–220°C) | 300 | No |
| Epoxy/PCL0–SA10 | Yes | Yes | 131 | 66 | No | 30 | No |
| Epoxy/PCL5–SA10 | Yes | Yes | 57 | – | No | 100 | No |
| Epoxy[e] | No | Yes | 131 | – | Significant (140–220°C) | – | No |
| Epoxy[f] | No | Yes | 180 | – | No | 50 | No |

$T_{g1}$ and $T_{g2}$ refer to the glass transition temperatures of the crosslinked mixture that were detected during the heating scan ($-50$ to $220$°C).

[a] The number after PCL refers to the number of theoretical CL units per branch of the polymer, SA refers to the succinic acid functional end–group and 10 refers to the weight percent of modified polymer in the epoxy.

[b] Crosslinking was carried out at 180°C for 60 min.

[c] Ref. [4].

[d] The crosslinked coatings were immersed in acetone for 30 min and scratched with a wooden spatula. If the coating was removed or deformed by the spatula "Yes" was entered to indicate poor chemical resistance.

[e] Crosslinked at 90°C for 30 min.

[f] Crosslinked at 180°C for 60 min.

According to the simulation (see Fig. 1), the acid-catalyzed epoxy reaches almost full conversion during a 60-min bake at 180°C. DSC analysis of a sample baked in this way showed that the epoxy did indeed react to the full conversion, since no residual reactivity was detected. The total heat of reaction for the epoxy crosslinking when no oligomer was incorporated was 176.5 J/g. With use of the dual-catalyst system without exposure of the blend to ultraviolet light, only the reaction enthalpy for the reaction between PCL2-SA and epoxy was detected. From this we inferred that the acid catalyst remained inactive until the exposure and effected only the reaction of epoxy groups.

Combination of the imidazole-catalyzed pre-crosslinking with the cationic ring-opening reaction of the residual epoxies in the dual-catalyzed two-step baking process resulted in the formation of solvent resistant coatings. The blends showed some residual reactivity, however. The reaction enthalpy was attributed to the continuing reaction of residual epoxies and the conversion of the overall reaction was determined to be 96% (6.5 J/g/176.5 J/g) assuming that the first reaction had reached full conversion. The simulated isothermal conversion curves were in agreement in suggesting that a one-step bake for 60 min at 180°C is not sufficient to provide the full conversion. On the basis of the DSC analysis of the PCL2-SA/epoxy that showed only minor residual reactivity after crosslinking in the two-step baking process, and on the basis of the kinetic analysis, it is inferred that full conversion could be achieved with prolonged baking for 90 min.

We note that with incomplete reaction between the oligomer and epoxy during dual-catalyzed crosslinking there is a strong tendency for a reaction-induced phase separation. This is because the molecular weight of the network increases rapidly when the prebake is followed by UV light activation of the cationic ring-opening catalyst and the second polymerization of the residual epoxy groups at elevated temperature. Indeed, the existence of double $T_g$ for some samples in DSC analyses suggested a phase separation. However, where a second $T_g$ was detected, it was weak and broad, which indicated a fairly strong chemical interaction between the phases and thus negligible phase separation.

## CONCLUSIONS

The reaction kinetics of the dual-catalyzed reactive blending of brittle epoxy with flexible four-armed oligomer was analyzed by a model-free kinetic method. The results obtained from separate investigations of the two reactions helped in determining the proper conditions for crosslinking. Understanding of the crosslinking process enabled minimization of the reaction-induced phase separation while maximizing the amount of incorporated oligomer. The reaction was complex, however, and the reaction mechanism as well as the physical controlling factor changed during the dual-catalyzed reaction. The apparent activation energy of the reaction was observed to fall into three regimes as a function of conversion. It is pro-

posed that regime I represents reaction control, the middle part (the regime II) the mass transport, and the high conversion tail (the regime III) the structural control. The results of thermal analysis of the crosslinked samples were in agreement with the results of the kinetic analysis and on the basis of the results the overall crosslinking process could be optimized to realize good-quality films.

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