Rheological Cure Characterization of Phosphazene–Triazine Polymers

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ABSTRACT: Cyclomatrix phosphazene–triazine network polymers were synthesized by co-curing a blend of tris(2-allylphenoxy), triphenoxy cyclotriphosphazene (TAP), and tris(2-allylphenoxy) s-triazine (TAT) with bis(4-maleimido phenyl) methane (BMM). The co-curing of the three-component resin was investigated by dynamic mechanical analysis using rheometry. The cure kinetics of the Diels–Alder step was studied by examining the evolution of the rheological parameters, such as storage modulus (G'), loss modulus (G''), and complex viscosity (η^*), for resins of varying compositions at different temperatures. The curing conformed to an overall second-order phenomenological equation, taking into account a self-acceleration effect. The kinetic parameters were evaluated by multiple-regression analysis. The absence of a definite trend in the cure process with blend composition ratio was attributed to the occurrence of a multitude of competitive reactions whose relative rates depend on the reactant ratio and the concentration of the products formed from the initial phase of reaction. The cure was accelerated by temperature for a given composition, whereas the self-acceleration became less prominent at higher temperature. Gelation was accelerated by temperature. The gel conversion decreased with increase in maleimide concentration and, for a given composition, it was independent of the cure temperature. The activation energy for the initial reaction and the crosslinking process were estimated for a composition with a maleimide-to-allyl ratio of 2 : 1. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 908–914, 2003

**Key words:** polyphosphazenes; rheology; curing of polymers; kinetics (polym.)

INTRODUCTION

Cyclomatrix polyphosphazenes possess good thermal and flame resistance and improved atomic oxygen resistance. The general method for their synthesis is based on derivatization of cyclophosphazenes with reactive functional groups followed by curing.[1,2] Thus, curing of cyclomatrix phosphazene polymers via the thermal reaction of groups such as maleimide,[3,4] allyl-maleimide,[5] etc. have been reported. Triazine-based polymers are characterized by good thermal stability, enhanced toughness, and low moisture absorption. They are formed either by the thermal reaction of cyanate esters[6–8] or by reactions and chain extensions of triazine-based reactive intermediates.[9–11] A cyclomatrix polymer with both phosphazene and triazine rings in the network would be expected to possess these beneficial properties. Thus, in an earlier work, we reported the synthesis of a similar polymer formed from the thermal curing of cyanate-functional cyclotriphosphazenes.[12] The polymer possessed enhanced flame and thermal resistance, but was characterized by inferior shelf-life. With a view to develop a phosphazene–triazine cyclomatrix prepolymer with enhanced shelf-life, we explored the possibility of using the Alder-ene cure chemistry for designing a novel thermoset. The protocol was to affect the cure of a mixture of allylphenoxy triazine and allylphenoxy cyclotriphosphazenes using a bismaleimide. Tough thermoset polymers can be obtained by coreaction of maleimide and allyl groups, where the maleimide reacts with allyl phenols through the Alder-ene reaction sequence including an intermediate Wagner–Jauregg (W–J) reaction step.[13–15] The reaction mechanism and product profiles have been identified by studies on model compounds.[16] Some studies claim that copolymerization of maleimide and an allyl group is the major curing reaction.[17] In a previous work, we reported the curing of cyclomatrix phosphazene via the Alder-ene reaction.[5]

Alder-ene reactions of allyl phenyl derivatives, such as allylphenoxy triazine, with bismaleimides (BMIs) have been used to derive thermosetting formulations.[18] Recent studies claim the superiority of the such Alder-ene co-cured systems over the homopolymers, in terms of mechanical properties of neat resin and composites, without great sacrifice in thermal properties.[19,20]

The present paper examines the influence of reactant stoichiometry and temperature on the chemorheology and the curing behavior of a ternary reactive

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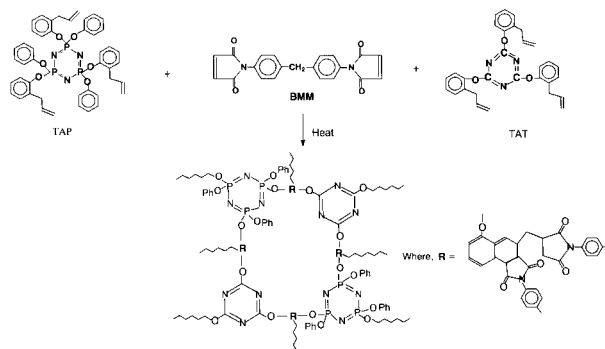
Scheme 1 Components of the blend and ideal structure of the phosphazene–triazine network.

blend of allylphenoxy phosphazene, allylphenoxy triazine, and a bismaleimide, studied by dynamic mechanical analyses.

EXPERIMENTAL

Materials

Triphenoxy cyclotriphosphazene (TAP), containing a cyclotriphosphazene derivative with (on an average) three phenoxy and three allyl phenoxy groups, was synthesized by a reported procedure[5]. Tris allylphenoxy s-triazine (TAT) was synthesized by a modification of a reported procedure[18] and was characterized by elemental analysis and carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR). Bis(4-maleimido phenyl)methane (BMM) was synthesized from 4,4'-(diamino diphenyl methane) and maleic anhydride by a known procedure.[21] BMM was purified by filtration (i.e., passing a solution of it in chloroform through a basic alumina column) and then recrystallization .

Rheological analysis

Samples were prepared by melt mixing of weighed quantities of the three components at 130–140°C in an air oven for 30 min. The viscous resin so obtained was deaerated under vacuum while it was hot. Rheological characterization was done with a StressTech Reologica rheometer using a 20-mm parallel plate assembly in oscillation mode at a frequency of 4 Hz and a controlled stress of 100 Pa. The gap between the plates was maintained at 0.5 mm. The samples were loaded on to the plates at 150°C. The data analyses were done with the instrument software.

RESULTS AND DISCUSSION

The structures of the components of the reactive blend are shown in Scheme 1. A phosphazene–triazine network polymer with an idealized structure following

curing, as shown in Scheme 1, is expected. The crosslinking units would vary in structure for different compositions. Four compositions were analyzed for rheological behavior. In each case, the relative molar ratio of phosphazene-to-triazine was maintained as 1. The compositions in the equivalent ratio of allyl and maleimide groups were varied (i.e., 1 : 1.5, 1 : 2.0, 1 : 2.5, and 1 : 3.0). The Alder-ene reaction between the allyl phenyl group and maleimide could occur at different equivalent ratios of the two reactants, and the network structure and properties of the product depend on the composition and the cure temperature. Although ideal curing requires a ratio of 1 : 3.0, the polymer cured at a lower ratio possesses desirable mechanical characteristics.[29]

The nonisothermal rheogram of a resin with allyl/maleimide ratio of 1 : 1.5 is shown in Figure 1. There is a rapid increase in storage modulus at 230°C, and the reaction continues until 275°C. Although the initial ene and W–J reactions are reported to occur at temperatures from 160°C and higher, such reactions are not found to result in any substantial modulus buildup. The material strength is attained exclusively by the Diels–Alder (D–A) reaction that occurs at ~250°C. Under the dynamic conditions, gelation occurs at 235°C, as indicated by the crossing of the storage modulus (G') and loss modulus (G'') curves.

The isothermal rheograms of the four compositions, indicating the variation of G' with time at 230°C, are shown in Figure 2. The scattered data were smoothed (degree of smoothing 5). The cure completion is the point beyond which G' stagnates. The G' values beyond the cure completion point are not shown in Figure 2. Because the curing is done at a higher temperature, the evolution of G' is an indication of any progress of the D–A reaction and the homopolymerization of the BMI. The modulus generally increases with increase in maleimide content. The cure time does not show any systematic trend with composition possibly because the curing reactions are composition dependent. High maleimide content was expected to lead to a faster Alder-ene reaction. It is probable that the self-curing of BMI also occurs at higher BMI content. This reaction is known to be slow and could account for the slow build-up of G' at high maleimide loading.

Cure mechanism

Allyl phenyl compounds are known to react with maleimides, and the most accepted mechanism is the Alder-ene reaction.[16] Extending the same mechanism, a reaction sequence as shown in Scheme 2 is proposed for the blend. The network structure depends on the cure temperature and molar ratio of the reactants. At low cure temperature and low BMM concentration,
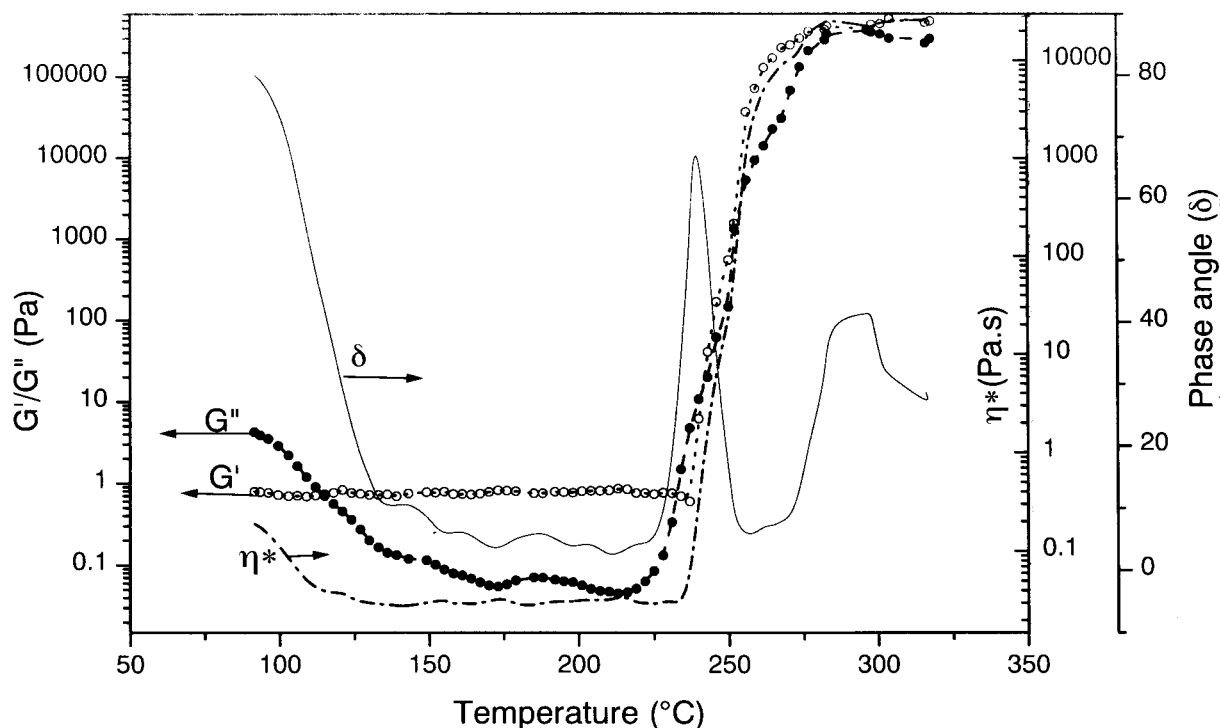
Figure 1 Nonisothermal dynamic mechanical analysis of PZTZ-15 (heating rate, 5°C/min;1 Hz).

structure 1 would dominate, and as the BMM content increases, there would be contribution from structure 2. The presence of structure 3 becomes important at a reactant stoichiometry (allyl/maleimide) of 1:3 and above and at high cure temperatures. Although curing occurs at different temperature zones, a significant build-up in mechanical properties occurs only at 230–270°C due to the D–A reaction, as is evident from a nonisothermal dynamic mechanical analysis (Figure 1). The change in complex viscosity (η^*) is negligible at the ene and W–J steps (160–190°C). The viscosity increase is sharp at the D–A stage.
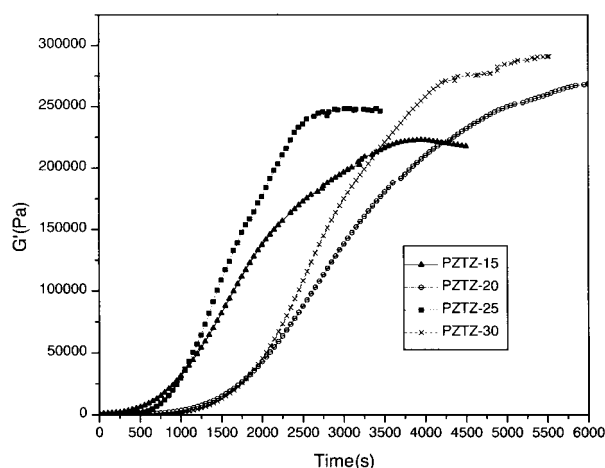
Rheokinetic analysis

Rheokinetic models based on the evolution of storage modulus, which is generally proportional to the density of the networks formed, can follow the cure process. For thermosetting resins, Malkin and Kulichikhin[22,23] proposed the following self-accelerating rheokinetic model that was used for cure analysis of phenol-formaldehyde resins:

$$d\alpha \ / \ dt = k(1 + c\alpha)(1 - \alpha)^n \qquad (1)$$

Figure 2 Storage modulus–time plot for resins with varying BMI content at 230°C.
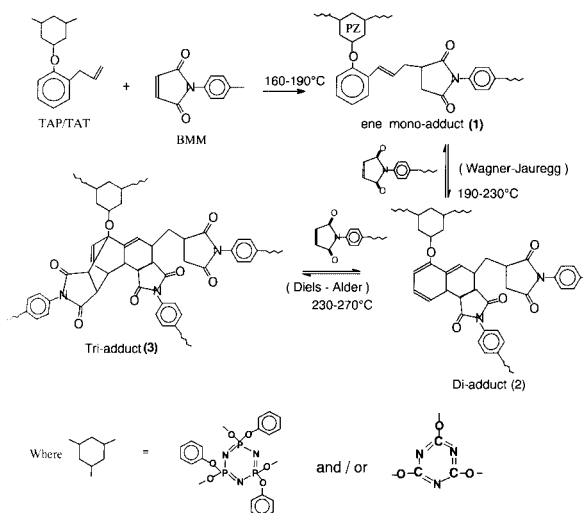
Scheme 2 Expected reaction sequences and structures at different reactant stoichiometries and cure temperatures.

TABLE I
Kinetic Constants for Various Compositions Cured at 230°C

Resin reference	Allyl : maleimide	t_{gel} (s)	Gel conversion (%)	$k_1 \times 10^5$ (s^{-1})	$k_2 \times 10^3$ (s^{-1})	m	n
PZTZ-15	1:1.5	350	1.2	2.1	1.62	1.02	0.73
PZTZ-20	1:2.0	850	0.7	3.2	1.22	1.07	0.78
PZTZ-25	1:2.5	372	0.6	6.0	2.41	1.00	0.84
PZTZ-30	1:3.0	625	0.6	4.4	1.69	0.83	0.83

where α is the rheological conversion at time t, k is the rate constant, and c is the self-accelerating term. This kind of phenomenological equation has been used for analyzing various thermosets, such as epoxy,[24] silicone,[25] unsaturated polyesters,[26] etc. Such models become particularly valid when the products of an initial reaction participate in further reaction with the original reactants, as in the present case. Marcovic et al.[27] used a third-order form of this equation to analyze the cure of novolac resin by rheometry.

In the present case, as with self-accelerating reaction models generally used for cure analysis by differential scanning calorimetry (DSC),[28] we used a more generalized equation:

$$d\alpha/dt = k_1(1 - \alpha)^m + k_2\alpha^n(1 - \alpha)^m \qquad (2)$$

where k_1 and k_2 are the general and self-accelerated rate constant terms, respectively, and m and n are the corresponding reaction orders.

In the present case, the rheological conversion, α, was calculated from the storage modulus values at any time t (G'_t) and the final stagnating modulus (G'_s) as follows:
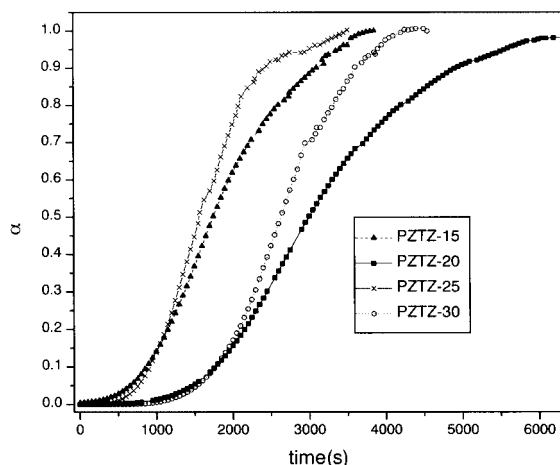
$$\alpha = G'_t/G'_s \qquad (3)$$

Effect of composition

Four different compositions, as detailed in Table I, were analyzed for their rheological behavior at 230°C. The conversion rate ($d\alpha/dt$) was obtained from the differential of α versus time plots that are shown in Figure 3. Conversion rate as a function of conversion is depicted in Figure 4 for a typical case. The self-acceleration is evident from the evolution of the curve. The rate constant k_1 was obtained from the data on the conversion rate tending to zero conversion. Using this value of k_1, the graphs in Figure 4 were fitted with eq. 2 by a computerized multiple-regression analysis, furnishing the various kinetic constants that are tabulated in Table I. Reasonably good fit was obtained for all cases.

The initial rate constant (k_1) has a tendency to increase with increase in maleimide content. The maximum self-acceleration term is attained with the ratio 1:2.5. The reaction order converges to unity for the initial step and to 0.8 for the accelerated one, and is independent of the composition. The overall order is 1.8, and the nearest whole number is two. The gel time (t_{gel}) was obtained from the cross point of G' and G'', as shown in Figure 5 for a representative case. The phase angle (δ) tends to 45° at this point. Although the gel time varied irregularly with composition, the conversion at gel point decreased with enhanced maleimide content, implying the role of maleimide in enhancing the crosslink density. The gel conversions were very low, which can be attributed to the fact that the
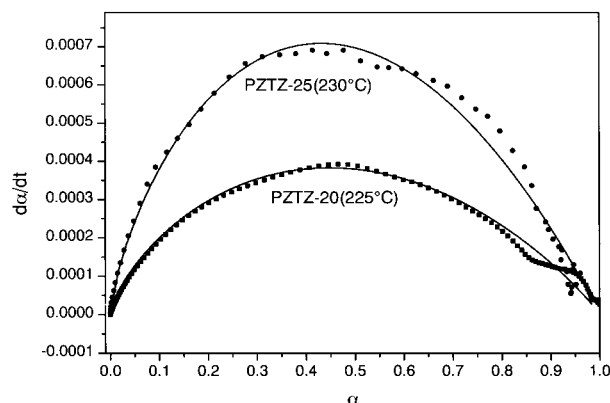

Figure 3 Conversion–time plot for resins with varying BMI content at 230°C.

Figure 4 Dependency of conversions rate on conversion, and the multiple regression fit.
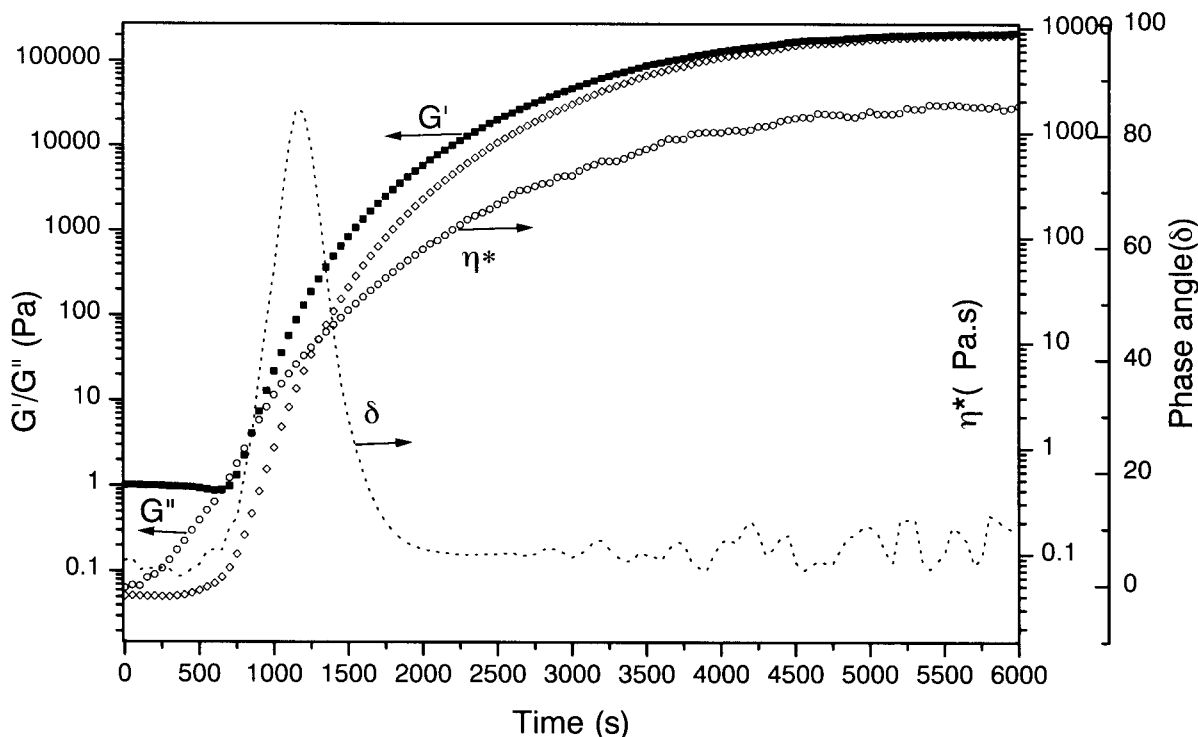
Figure 5 Determination of gel point for PZTZ-20 at 230°C.

rheological analysis refers to the D–A step of the complex cure sequences. The preceding, ene and W–J reactions (at lower temperature) produce multifunctional polymer adducts. Therefore, even minor reaction at the D–A step results in gelling rendering the gel conversions extremely small.

Effect of temperature

The effect of temperature on the rheokinetics was examined for the resin PZTZ-20, which was analyzed

for cure behavior at 215, 225, and 230°C. The storage modulus–time and conversion–time plots are shown in Figures 6 and 7, respectively. These results indicate that the absolute modulus is marginally enhanced at a higher cure temperature. The conversion–time (Figure 7) and conversion rate–time plots (Figure 8) show that the reaction is facilitated with an increase in temperature. The dependency of conversion rate on conversion, manifesting the temperature effect on cure rate is shown in Figure 9. The kinetic parameters obtained by the curve fitting are given in Table II. Typical curve
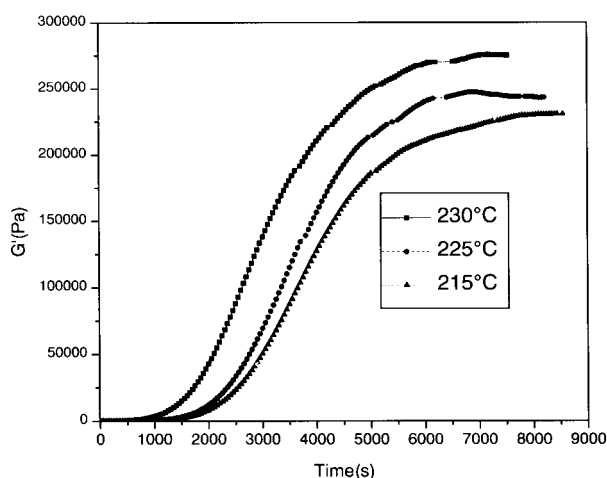

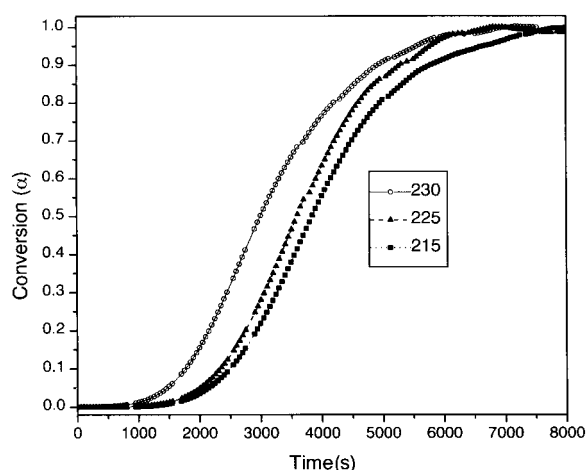**Figure 6** Plot of G'–time for PZTZ-20 at various temperatures.

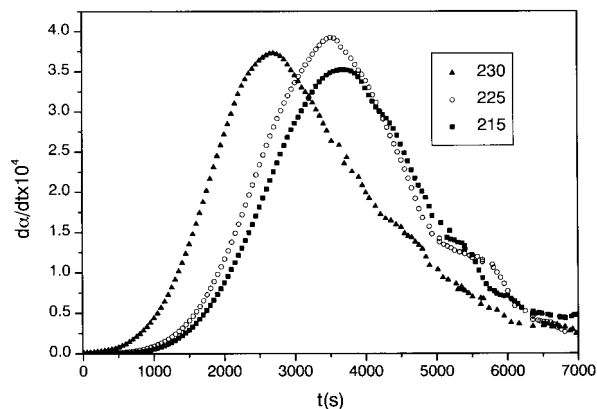**Figure 7** Conversion–time plot for PZTZ-20 at various temperatures.

Figure 8 Conversion rate–time plot for PZTZ-20 at various temperatures.

TABLE II
Rheokinetic Parameters for PZTZ-20 at Different Temperatures

Temperature (°C)	t_{gel} (s)	Gel conversion (%)	$k \times 10$ (s^{-1})	$k_2 \times 10^3$ (s^{-1})	m	n
215	1400	0.60	0.5	1.31	1.13	0.82
225	1135	0.80	2.1	1.26	0.95	0.82
230	850	0.70	3.2	1.22	1.07	0.78

fitting is demonstrated in Figure 4. The data conformed well to the kinetic model as described by eq. 2. The reaction orders are in the same range for the varying compositions and are unaffected by temperature. The initial rate constant increases with a rise in temperature, whereas the self-acceleration constant decreases. The latter behavior is contrary to general auto-acceleration kinetics observed by DSC kinetic analysis. This difference may possibly be ascribed to the phenomenological approach in defining the conversion from G'. A similar decreasing trend for the self-acceleration constant has been observed by Djonlagic et al.[27] for the cure of novolac resin. The activation energy for the initial cure reaction, obtained from the Arrhenius relationship of k_1, is 258 kJ/mol. The t_{gel} values included in Table II show that the gel time decreases with a rise in temperature. Gelation is an important phenomenon in a crosslinking reaction. The activation energy for this process, obtained from the plot of $\ln(t_{gel})$ versus $1/T$, is 93 kJ/mol. The conversion at gel point is quite independent of the temperature, implying that it is mostly a function of the extent of reaction for a given composition.
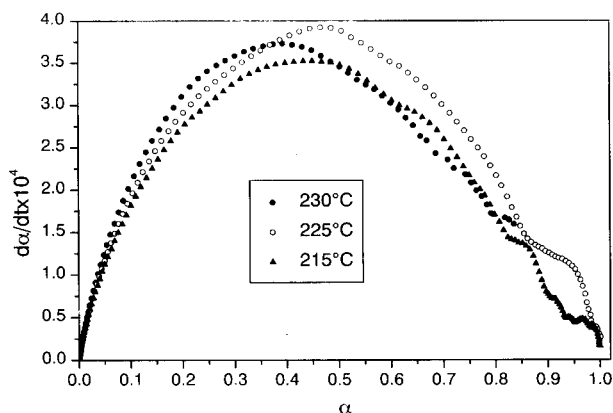
CONCLUSIONS

The kinetics of the curing reaction of a ternary blend of allylphenoxy phosphazene, allylphenoxy triazine, and a bismaleimide can be described by a second-order self-accelerated phenomenological equation. The overall reaction order is independent of the allyl/BMI ratio or the cure temperature. The storage modulus tends to increase with enhanced BMI content and temperature. The absence of a definite trend in the reaction parameters with blend composition may be attributed to the complexity of the various competing reactions. The curing is facilitated by temperature, as reflected in a decreased gel time and enhanced initial rate constant. The substantially diminished gel conversions at the D–A step implies formation of multifunctional reactive intermediates in the preceding reaction steps. However, the auto-acceleration effect is less pronounced at higher temperature. The calculated activation parameters for cure initiation and crosslinking and the kinetic parameters are useful for predicting the cure profiles at a given temperature. The physical and thermal properties of the cured polymers will be described in an ensuing publication.

Figure 9 Dependency of conversion rate on conversion for PZTZ-20 at various temperatures.

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