

CHEMICAL CONTROL OF RATE AND ONSET TEMPERATURE  
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The chemistry of norbornenyl capped imide compounds (nadimides) is briefly reviewed with emphasis on the contribution of Diels-Alder reversion in controlling the rate and onset of the thermal polymerization reaction. Control of onset temperature of the cure exotherm by adjusting the concentration of maleimide is demonstrated using selected model compounds. The effects of nitrophenyl compounds as free radical retarders on nadimide reactivity are discussed. A simple copolymerization model is proposed for the overall nadimide cure reaction. An approximate numerical analysis is carried out to demonstrate the ability of the model to simulate the trends observed for both maleimide and nitrophenyl additions.

## INTRODUCTION

Norbornenyl-capped polyimide resins have been investigated as matrix resins since the early seventies (refs. 1 and 2). The application of composites employing matrix resins utilizing this addition chemistry has increased substantially in recent years (ref. 3). Engineering interest in these resin systems has outpaced the chemical understanding of the cross-link chemistry. Improved understanding would place the current technology on firmer chemical grounds, and would provide a basis for defining the potential for improvements in processability and thermo-oxidative stability. There have been several studies of nadimide thermal chemistry (refs. 4 to 6) since the initial mechanistic arguments of Jones, et al. (refs. 1 and 7), however, the reaction mechanism of the cross-link reaction has not been fully elucidated.

The principal purpose of this study was to evaluate chemical approaches for control of the onset temperature and rate of cure in nadimide resins. Two approaches are presented which provide such control. Another major aspect of this paper is the evaluation of a proposed copolymerization model for the mechanism of nadimide cure. The model is numerically evaluated to demonstrate that the major trends observed experimentally can be simulated by the model.

Experimental - The differential calorimeter scans (DSC) were run (typically) on approximately 2 mg of sample in aluminum pans (covered but not sealed) under 100 psi of nitrogen (static) at a heating rate of 10 °C/min.

Calculations - Calculations were performed on a microcomputer using a Basic language program (listing is available on request). The inherent limitations in speed, as well as the preliminary state of the model, prompted the utilization of a relatively coarse time interval (30 seconds) in the simulations.

## RESULTS AND DISCUSSION

### Background

Several thermal reactions of nadimide groups can be postulated. Figure 1 summarizes four processes which have been identified during nadimide thermal cures. It is not implied that this is the comprehensive set of reactions, but rather those which have been well documented.

The isomerization of nadic groups is well known, and the extent of this endo-to exo-rearrangement has recently been studied for nadimide oligomers (refs. 5, 8, and 9). The isomerization appears to occur rapidly even at moderate temperatures, and apparent equilibrium endo/exo mixtures can be attained in a few hours in the oligomeric and monomeric systems studied. It is not evident, however, that this activity contributes significantly to the overall cure chemistry for the usual high temperature conditions (relatively rapid rise to 316 °C), even though some differences in reactivity of the isomers has been postulated (ref. 5).

Diels-Alder reversion (reaction 2 of fig. 1) of the nadimide to form cyclopentadiene and maleimide is an element of nearly all mechanistic descriptions of nadimide thermal chemistry. Nondissociative mechanisms have been proposed to account for both polymerization and isomerization (ref. 8). However, even one of the proponents of nondissociative mechanisms for describing norbornenyl chemistry invokes reversion to account for the high-temperature reactions of nadimides (ref. 10). Cyclopentadiene has been monitored as a volatile by-product during thermal polymerization of nadimides (refs. 4 and 11), however, the amount of cyclopentadiene actually evolved is difficult to quantify and has not been fully documented. Consequently, the predominant evidence for reversion (mostly unreported in the literature) arises in materials engineering studies and in the fabrication of components where the odor of dicyclopentadiene can be detected in traps or inappropriately cured parts. The kinetics of the net cross-link reaction appear pseudo first order as determined calorimetrically (ref. 6). This observation and the magnitude of the rate constant are consistent with Diels-Alder reversion being the rate limiting step in the net reaction. It is this observation, and the chemical rationale discussed below that are the basis for the mechanistic model utilized in this paper.

Double Diels-Alder adducts (reaction 3 of fig. 1) have been observed as by-products of the thermal reaction of selected nadimide monomers (ref. 5). This product provides a statistically favorable mode of consuming cyclopentadiene. It is not presumed to have a major effect on the cure reaction since its reactivity should be essentially equivalent to the parent nadimide.

The desired polymerization reaction is presumed to be free radical vinyl addition of all the species present at any instant as the system evolves as a function of time and temperature as noted above. It is presumed that the reaction is thermally initiated, and that the polymer composition and rate of polymerization are determined by the relative reactivities and concentrations of each component. For simplicity in the current model, it is presumed that all the cyclopentadiene is consumed in the double adduct noted earlier and that all the nadimide compounds have the same reactivity. These assumptions reduce the model to a classical binary copolymerization reaction of nadimide and maleimide with thermal initiation. The most unique aspect of the model is the Diels-Alder interrelation of the comonomers. This constraint requires that the concentration of the maleimide is defined by concentration of nadimide and the rate of Diels-Alder reversion at each time and temperature.

## Experimental Observations

Two chemical approaches have recently been observed (ref. 12) which can be employed to promote the onset of nadimide cure, as defined by the cross-link exotherm, at significantly lower temperatures than observed for the unmodified materials.

The first approach requires addition of maleimide oligomers to preimidized nadic oligomers or resins. The rationale for this chemical approach is based on the copolymerization model described above and is simply: an increase in the initial concentration of one of the principal coreactants should increase the rate of the net reaction. Figure 2 shows a series of differential calorimeter scans for mixtures of the bismaleimide and the bisnadimide of methylenedianiline. With increasing maleimide concentration, the cross-link exotherm progresses from a temperature characteristic of most nadimide oligomers (peak maximum near 360 °C) to lower temperatures, and, ultimately to that characteristic of the bismaleimide (peak maximum near 250 °C). Figure 3 shows the overall trend. The shape of this curve is not easily rationalized. In particular, the exotherm appears to exhibit significant sensitivity to quite low concentrations (near 0.1 mole fraction) of nadimide in maleimide. This chemical approach for decreasing cure temperature is most appealing since it permits continuous adjustment of the cure temperature over a range of about 100 °C as the composition changes from pure nadimide to pure maleimide. Unfortunately, the reactivity of the maleic double bond toward free amine (Michael addition) does not permit the utilization of this approach in monomeric precursor solutions for composite fabrication. The approach could be useful in applications currently using preimidized molding powders. However, it has not been fully evaluated.

The second approach requires addition of aromatic nitro compounds to a nadimide mixture. This approach evolved from a study of the reactivity of a large number of substituted phenyl nadimides (ref. 12) which showed the nitro-containing compounds to have exceptional low temperature reactivity. Figure 4 compares the cross-link exotherms for two nitro-containing systems with that for the bisnadimide of methylenedianiline. The principal observations for nadimide thermal cures in the presence of nitrophenyl additives were as follows: (1) Each nitro compound exhibits a unique cure temperature. (2) The cure temperature is related to (a) the number of nitro groups in the additive, and (b) the extent of electron withdrawal in the phenyl ring containing the nitro group. Table I summarizes the peak exotherm temperatures for several nadimide systems incorporating nitrophenyl groups. (3) The predominant cure exotherm shows little sensitivity to the concentration of the nitro additive. Even when the nitro groups are limited by concentration or mobility (in particular, nitrophenyl nadimides which will be restrained once the nadic moiety has been incorporated into the polymer), the systems exhibit initial exothermic activity at the temperature characteristic of the nitrophenyl additive and subsequently complete the cure at the temperature characteristic of unmodified nadimide.

The effect of nitrophenyl additives on the homopolymerization of maleimides was also examined. Nitrophenyl additives with bismaleimides retard the cure reaction in the classical sense (the cure exotherm moves to higher temperatures). The peak exotherm temperatures for mixtures of the bismaleimide of methylenedianiline with selected nitrophenyl additives are given in table II.

Overall, these nitrophenyl effects are rationalized on the basis of: (a) efficient retardation (i.e., inhibition) of the free radical reactions at low



where

$k_R$  reversion rate constant  
 $\Delta t$  time interval of the summation

and the subscripted terms are the concentrations after the previous iteration.

The effect of the retarder is introduced in a form suggested by Schultz and Strassberger (ref. 14):

$$\text{Rate}' = \text{Rate}/(1 + k_I [I])$$

where

$[I]$  concentration of retarder  
 $k_I$  rate constant for reaction with retarder

and the initiation rate becomes

$$RI' = RI + k_D [I\cdot]$$

where

$[I\cdot]$  concentration of reacted retarder  
 $k_D$  rate constant for regeneration of radicals

and the concentrations are modified as

$$[I] = [I]_0 - RI_0 \Delta t + k_D [I\cdot] \Delta t$$

$$[I\cdot] = [I\cdot]_0 + RI_0 \Delta t$$

to account for the variation with time and temperature.

#### Choice of Rate Constants

The Arrhenius activation energies and pre-exponential factors employed in the calculations are summarized in table III. The primary rationale for choosing these parameters was to utilize values typical of condensed phase, thermally-initiated vinyl polymerizations. Such data are limited; however, the well documented discussions of styrene and methylmethacrylate were chosen as guidelines. Specific rationale are noted below and summarized in table III. The Arrhenius parameters for the initiation rate constants were chosen to reflect literature values for thermally-initiated vinyl polymerization. The activation energies (25 kcal/mole) are considered to be reasonable estimates since they are typical of many vinyl monomers. The pre-exponential factor for maleimide ( $10^6 \text{ sec}^{-1}$ ) is analogous to that found for styrene and reflects a moderately reactive monomer. The factor for nadimide ( $10 \text{ sec}^{-1}$ ) reflects a very slowly reacting monomer similar to (but not as slow as) methylmethacrylate (ref. 15). The Arrhenius parameters for the propagation rate constants ( $A = 10^7 \text{ sec}^{-1}$  and  $E_a = 7 \text{ kcal/mole}$ ) are typical of most vinyl polymerizations. The termination rate parameters were again based on the reported data for styrene and methylmethacrylate. The activation energies (3 kcal/mole) are typical of many vinyl monomers. However, the pre-exponential factors are adjusted to reflect a termination frequency for maleimide ( $10^9 \text{ sec}^{-1}$ ) analogous to styrene, but increased efficiency for nadimide ( $2 \times 10^{11} \text{ sec}^{-1}$ ).

Overall, the rate constants defined by these parameters are considered to be conservative choices for this model. The accessible homopolymerization reaction, polymerization of bismaleimide, is well fit by the chosen parameters. The Diels-Alder reversion rate is defined by the Arrhenius parameters previously observed (ref. 5) for the net cross-link reaction ( $A = 4 \times 10^{13}$  and  $E_a = 44$  kcal/mole). These values appear consistent with published rate constants for such reactions (ref. 16). The choice of parameters for nadimide and the magnitude of the cross terms were strongly influenced by the necessity of simulating the elevated temperature exotherm of the bisnadimide. Within the scope of this model, the suppression of the nadimide cure exotherm to temperatures above 300 °C required both low reactivity of the nadimide (as defined above) and predominant cross termination. It should be noted that there are other kinetic factors (not included in this simple model) which may contribute to the late reaction exotherm of the nadimides. For example, chain transfer reactions could contribute to this effect.

The cross terms are, overall, rationalized by analogy of published data for maleic anhydride copolymerizations with norbornene or related vinyl monomers (ref. 17). The reactivity ratios were set equal and held constant ( $r_1 = r_2 = .01$ ). The cross initiation and cross termination terms were used as fitting factors in adjusting the calculated nadimide exotherm. A range of values was tested for the cross initiation factor ( $C = 1$  to 10) and a small value ( $C = 2$ ) appeared most useful. A large range of values was tested for the cross termination factor ( $O = 1$  to  $10^4$ ) and a large value ( $O = 10^3$ ) was found necessary, as discussed above, to simulate the nadimide data.

The additional parameters required for the model incorporating retardation were chosen using very simplistic assumptions. The rate constant,  $k_I$ , for reaction of retarder was presumed very large for all temperatures and simply set at unity. The dissociation or transfer rate constant was presumed to have classical vibrational activation and the pre-exponential was chosen accordingly ( $A = 4 \times 10^{13}$ ). A range of activation energies (30 to 40 kcal/mole) was evaluated. This energy range is consistent with the bond energy of inorganic esters of the type proposed above (ref. 13). This range of activation energies provided a reasonable simulation of the experimental trends as shown below.

It is emphasized that these rate parameters were used without change for all the calculations described below. The only variables explored in the calculated results were the activation energy for dissociation of the retarding intermediate (discussed above) and the initial concentrations: nadimide ( $[NI] = 0$  to 5 mole/liter), maleimide ( $[MI] = 0$  to 5 mole/liter), and retarder ( $[I] = 0$  to 5 mole/liter).

#### Calculated Results

It should be kept in mind that these are intended to be "order of magnitude" approximations of the reaction scheme. The principal desire is to demonstrate that the observed trends in the experimental data can be reproduced with this simple model.

Figure 5 shows the calculated concentration dependence of the temperature of maximum rate of polymerization for the mixed bismaleimide/bisnadimide systems. The general shape of the curve compares favorably with the experimental data (fig. 3). Although some of the initial parameters of the numerical model might be debated, it should be noted that all the rate parameters are the same in each calculation and hence the only variable reflected in this curve is the relative concentrations of

bismaleimide and bisnadimide. It is of particular interest that the sensitivity at low nadimide concentrations appears to be reproduced in this simple model. It seems that, for this model, the cross termination term predominates for even small concentrations of nadimide. Recall that the large cross termination factor was introduced to reproduce the high temperature cure of the nadimide system; thus, it is implied that the nadimide (or the cyclopentadiene evolved) has a net retarding effect on the free radical reactions of the cure.

The calculated effect of retarder on the rate of polymerization of nadimide is demonstrated in figures 6 and 7. Figure 6 shows, for  $E_a(I) = 33$  kcal/mole and a 1 mole/liter concentration of the retarder, a peak reaction rate near 250 °C rather than approximately 325 °C calculated for the unmodified nadimide system. Varying the concentration,  $[I]$ , from 1 to 5 mole/liter in the calculation changed the peak temperature less than 20 °C, which simulates the observed small concentration dependence moderately well. The effect of increasing the activation energy for dissociation of the retarded intermediate,  $E_a(I)$ , from 30 to 38 kcal/mole at constant concentration is shown in figure 7. This range of activation energies covers the desired range noted above, and produces a span of peak polymerization temperatures which is consistent with the experimental data. Calculated data for bismaleimide with retarder is shown in figure 8 and, again the general trend can be reproduced. These calculations require activation energies slightly higher than for the nadimides, however, and the calculations, overall, appear to be more sensitive to the nitrophenyl parameters for the retardation effect and possibly reflects limitations in the simple model.

#### CONCLUDING REMARKS

Two chemical approaches were described which provide control of the onset and rate of polymerization of nadimides:

- (1) Addition of bismaleimide to nadimides. This approach provides a continuous range of cure temperatures between the two extremes of the monomers.
- (2) Addition of nitrophenyl compounds. This approach provides specific onset temperatures characteristic of the additive chosen.

A simple copolymerization model was chosen to describe the net polymerization of nadimides and to account for the trends in thermal reactivity observed with the two concepts described above. An approximate numerical analysis was carried out which successfully reproduced the major experimental trends.

From this analysis it was concluded that the rate of polymerization of nadimide was dominated by (1) the inherent low reactivity of nadimide toward homopolymerization, (2) the Diels-Alder reversion to form maleimide (the comonomer), and (3) a large cross termination rate.

From this analysis it was concluded that nitrophenyl additives affect nadimide cures in two ways: (1) as a free radical retarder at low temperatures (<200 °C), and (2) as free radical generators at temperatures where the retarded intermediates dissociate.

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TABLE I - PEAK EXOTHERM TEMPERATURE OF BISNADIMIDE OF METHYLENEDIANILINE WITH SELECTED NITRO PHENYL ADDITIVES

Additive	Concentration (mole fraction)	Exotherm maximum (C°)
nil	--	350
3, 5-NO <sub>2</sub> Benzonitrile	.15	233, 330 (minor)
	.38	233
	.51	233
3, 4-NO <sub>2</sub> Toluene	.17	255, 335 (minor)
	.27	255
	.42	255
3-NO <sub>2</sub> Phenylnadimide	.20	287, 360 (minor)
	1.0	287, 360 (minor)

TABLE II - CORRELATION OF MAXIMUM CURE EXOTHERM TEMPERATURES FOR VINYL MONOMERS WITH NITRO PHENYL ADDITIVES

Additive	Temperature of maximum exotherm (C°) for	
	Bisnadimide <sup>a</sup>	Bismaleimide <sup>a</sup>
nil	350	250
3, 5-NO <sub>2</sub> Benzonitrile	233	235
3, 4-NO <sub>2</sub> Toluene	255	305
4-NO <sub>2</sub> Chlorobenzene	297	265

<sup>a</sup>Bisimides of methylenedianiline.

TABLE III - ASSUMED ARRHENIUS PARAMETERS

Rate constant	A (1/sec)	E <sub>a</sub> (kcal)	Rationale
Initiation: k <sub>I11</sub>	10	25	Slow; similar to MMA
k <sub>I22</sub>	10 <sup>6</sup>	25	
Propagation: k <sub>p11</sub>	10 <sup>7</sup>	7	Moderate; similar to styrene
	k <sub>p22</sub>	10 <sup>7</sup>	
Termination: k <sub>T11</sub>	2x10 <sup>11</sup>	3	Typical for vinyl
	k <sub>T22</sub>	10 <sup>9</sup>	
Thermal: k <sub>R</sub>	4x10 <sup>13</sup>	44	~Efficient for vinyl
	k <sub>D</sub>	4x10 <sup>13</sup>	
Reasonable bond energies			
Cross terms: r <sub>1</sub> = r <sub>2</sub> = .01, φ = 1000, c = 2			

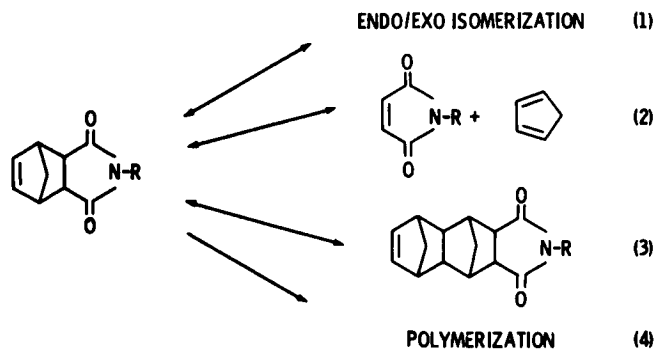


Figure 1. - Four possible thermal reactions of nadimides.

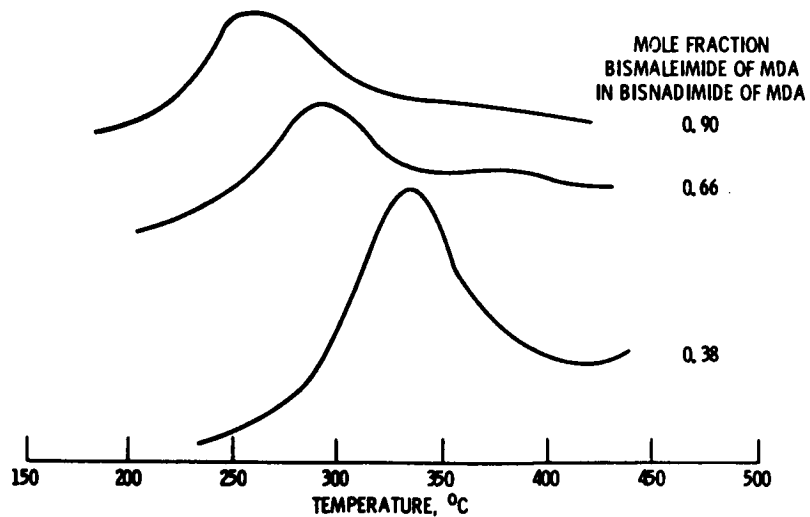


Figure 2. - The effect of bismaleimide concentration variations on the cure exotherm of bisnadimide.

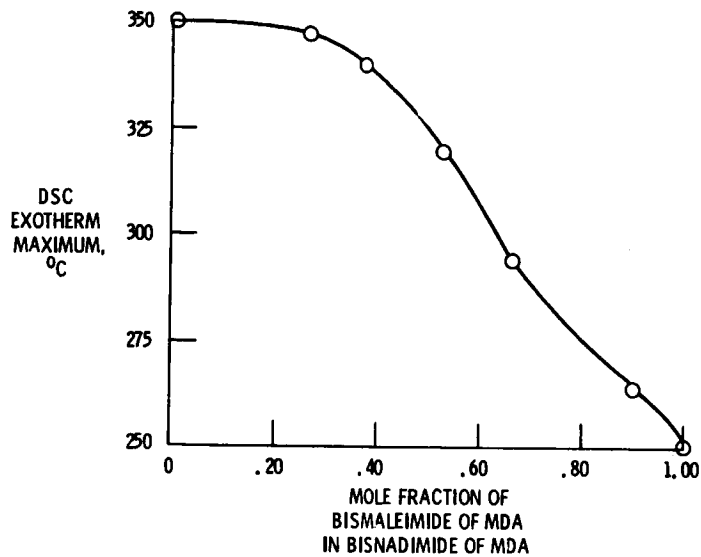


Figure 3. - Variation of cure exotherm maximum with concentration of bismaleimide in nadimide.

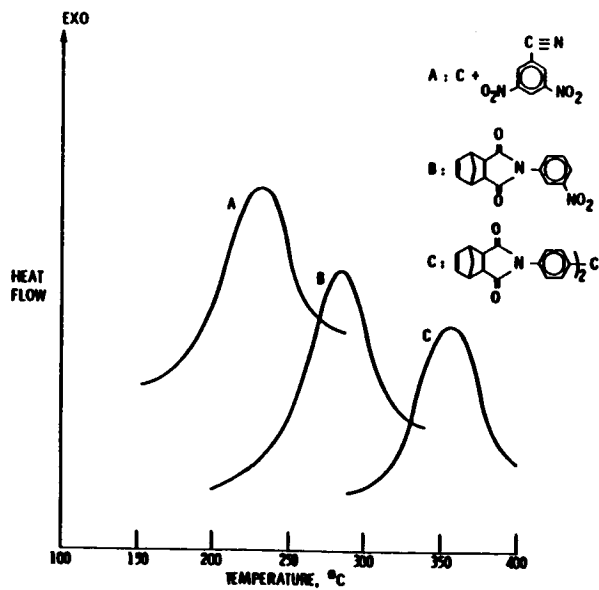


Figure 4. - Decrease in temperature of cure exotherm for nadimide in the presence of nitro phenyl groups.

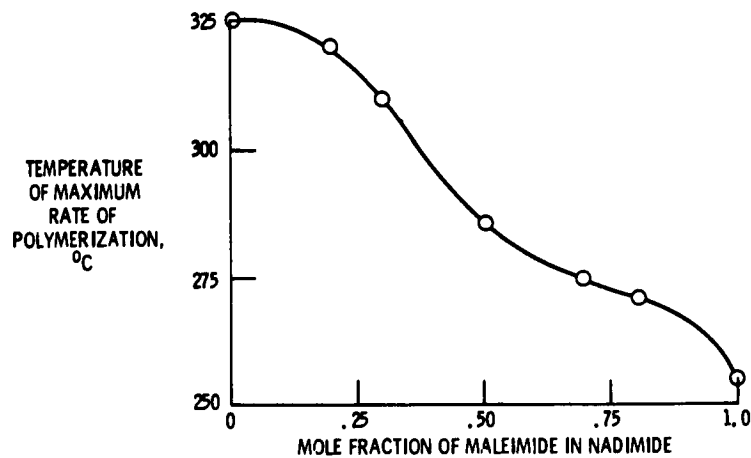


Figure 5. - Calculated dependence of maximum polymerization rate on concentration of maleimide in nadimide.

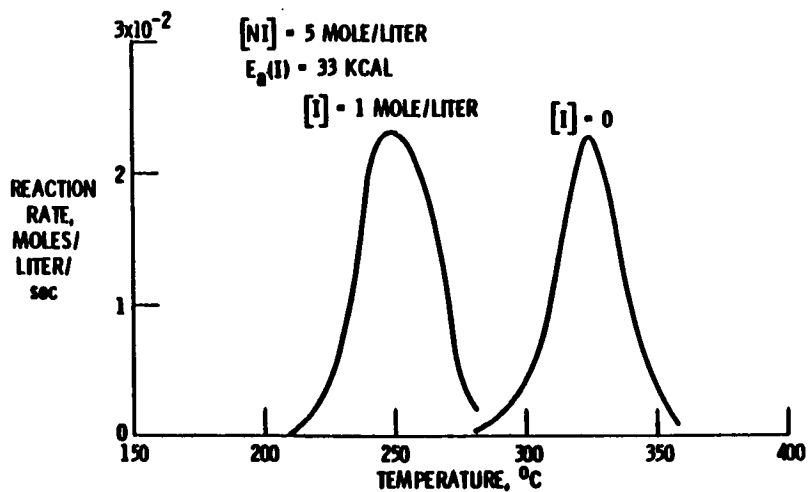


Figure 6. - Calculated effect of retarder on nadimide reaction rate.

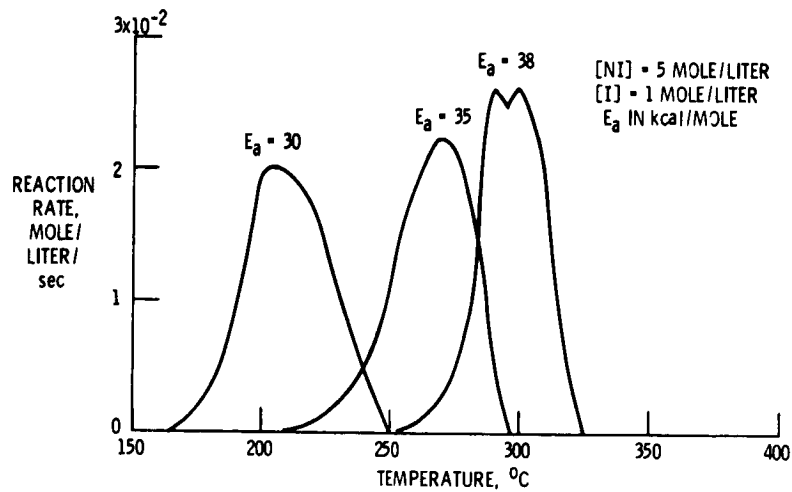


Figure 7. - Calculated effect of activation energy,  $E_a$ , for regeneration of retarder on nadimide reaction rate.

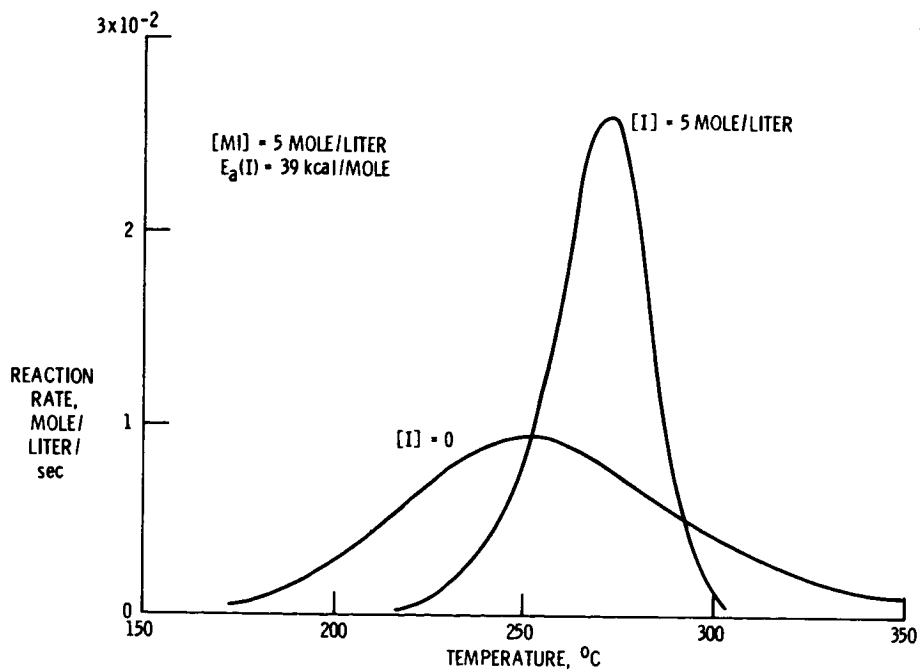


Figure 8. - Calculated effect of retardation on rate of polymerization of bismaleimide.