

# FT-IR STUDIES ON IMIDIZATION AND END GROUP REACTION BEHAVIORS OF A PHENYLETHYNYL TERMINATED IMIDE OLIGOMER

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**SUMMARY:** Most characteristic FT-IR absorption bands including the phenylethynyl end group occurring via imidization and cure during dynamic and isothermal heat treatments of LaRC™ PETI-5 were clearly resolved and assigned in the present study. The imidization and phenylethynyl end group reaction behavior of phenylethynyl terminated imide oligomers (LaRC™ PETI-5) with a number average molecular weight of 2500 g/mol has been extensively interpreted in terms of the disappearance and appearance of several characteristic absorption peaks. This study also measures the extent of imidization and the activation energy of cure reaction of this material. The results give some information on temperature- and time-dependency of the cure of LaRC™ PETI-5, which may be useful for determining the processing conditions necessary for use as a high temperature fiber sizing material.

**KEYWORDS:** Phenylethynyl terminated imide oligomer, LaRC™ PETI-5, imidization, end group reaction, activation energy, FT-IR.

## INTRODUCTION

Recently, a variety of phenylethynyl terminated imide oligomers for high temperature aerospace and aircraft applications, referred to as LaRC™ PETI, have been developed at the NASA Langley Research Center[1-3]. These materials have better processing windows and thermal oxidative stability than simple ethynyl terminated materials, and have many practical advantages as a potential material for coatings, adhesives, films and composite matrix resins[4,5]. Among the LaRC™ PETI series, a PETI-5 version of molecular weight 2500 g/mol has an excellent combination of processing, toughness, thermal, mechanical, physical and chemical performances at elevated temperature[6].

Phenylethynyl terminated polyimides require high temperature treatment to completely remove solvent and to convert the oligomeric precursor into cured polyimide. The LaRC™ PETI-5 amide acid oligomer is imidized via cyclodehydration between the amide and carboxylic acid groups to form the corresponding LaRC™ PETI-5 polyimide upon heating.

During thermal cure this material undergoes a complex reaction involving crosslinking and chain extension of phenylethynyl groups located at the imide polymer chain ends without releasing volatiles[5-7]. The neat LaRC™ PETI-5 resin is very viscous and may be applied onto the surface of various substrates as a sizing, coating, matrix prepreg or adhesive. Since processing requires the resin to be generally exposed to a prescheduled temperature and time cycle, it is necessary to understand the chemical changes that occur in LaRC™ PETI-5 during imidization, curing and consolidation in order to optimize resin processing and properties.

Fourier Transform infrared (FT-IR) spectroscopy is a powerful tool to monitor such chemical changes that occur during thermal treatment. The overall research objective of this work is ultimately to enhance fiber-matrix interfacial properties in high performance polymer matrix composites reinforced with carbon fibers or glass fibers by incorporating LaRC™ PETI-5 as a high temperature sizing material for better adhesion and toughness. To achieve this objective, an understanding of the chemical changes occurring during reaction of LaRC™ PETI-5 as a function of processing is needed. This publication reports on the changes in molecular structure during reaction through observation of temperature- and time-dependent intensity variations of the characteristic FT-IR absorption bands.

## EXPERIMENTAL

### Materials

The phenylethynyl terminated imide oligomer used in the present study was synthesized and supplied in the liquid form of an amide acid from Imitec, Inc. The ‘as-received’ LaRC™ PETI-5 is a random copolymer with a number average molecular weight of 2500 g/mol. The chemistry of LaRC™ PETI-5 has been described in Figure 1. The solids content in *N*-methyl-2-pyrrolidinone (NMP) as solvent is about 35 % by weight. The material was used ‘as-received’ throughout this work. The ‘as-received’ solution has been always stored in a refrigerator and only placed at ambient temperature for a couple of hours before use to prevent possible moisture absorption. FT-IR grade potassium bromide (KBr) powder was purchased from Aldrich Chemical Co.

### Sample Preparation and FT-IR Measurements

FT-IR measurements were performed using purging N<sub>2</sub> gas at ambient temperature, with a Nicolet Model IR/42 Fourier Transform Infrared Spectrometer. A very small amount of neat LaRC™ PETI-5 resin containing NMP was placed between two sodium chloride (NaCl) crystal discs of 25 mm diameter. A thin film of the resin was formed on each disc surface by rubbing the discs together. Only one disc was used for FT-IR measurements to avoid curing of the resin between the discs at high temperatures. The NaCl disc was subsequently heated to 100°C, 200°C, 250°C, 300°C, and then 350°C for 1 h each in an air circulating oven, respectively. This procedure resulted in a sample that was cumulatively exposed to each given cure temperature prior to each FT-IR measurement. FT-IR spectra were collected from an identical spot of the sample in the disc. To examine the reaction behavior with time at fixed temperature, each 10 mm diameter KBr disc coated with the sample was isothermally cured at 200°C, 300°C, 330°C, 350°C, and 370°C in an air circulating oven.

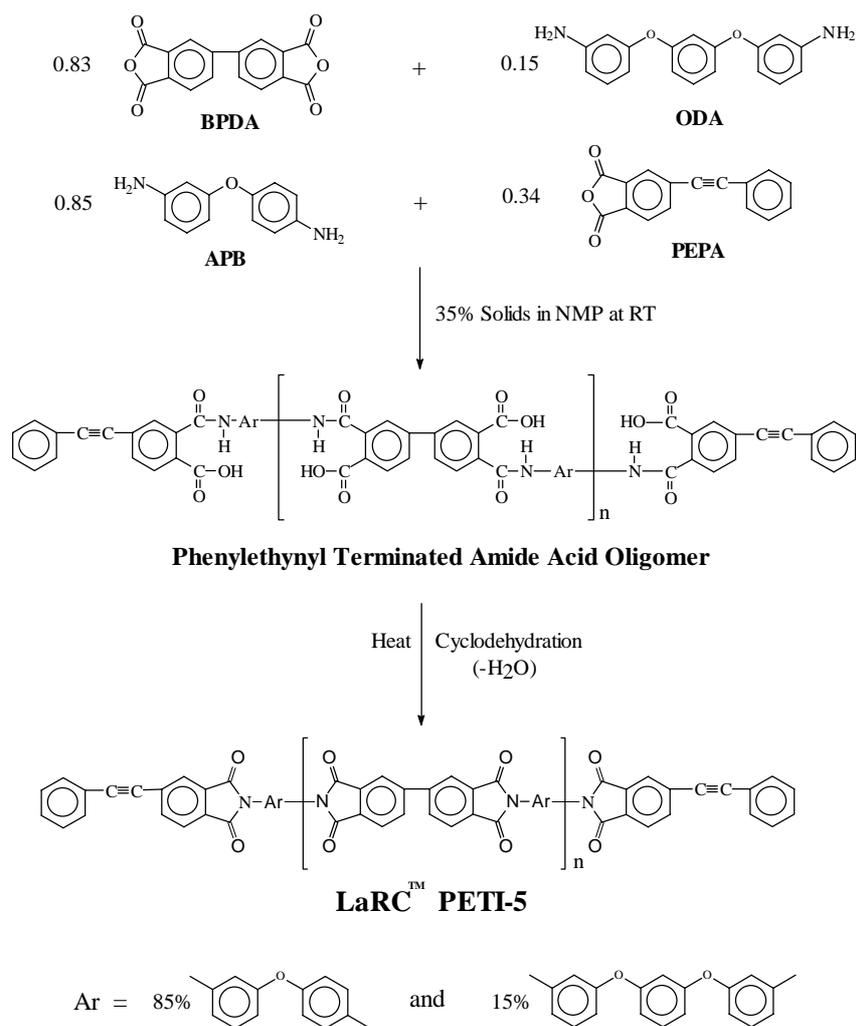


Fig. 1: Chemistry of LaRC™ PETI-5 amide acid oligomer ( $M_n=2500$  g/mol) and the polymer.

## RESULTS AND DISCUSSION

### Temperature Effect on Formation of the Polyimide Structure

The disappearance and appearance of most characteristic FT-IR absorption bands during imidization and cure including the phenylethynyl end group were clearly resolved and assigned here. Figure 2 shows the variations of the FT-IR bands which occurred while LaRC™ PETI-5 was exposed to five different cure temperatures from 100°C to 350°C for 1 hour each in an air circulating oven.

The absorption band from phenylethynyl terminated amide acid oligomer in the ‘as-received’ sample is to some extent screened due to NMP solvent containing in the neat resin. The solvent is detected at a significant level at 100°C and at a lesser amount at 200°C. At 250°C, it is completely removed from the sample. It is likely that the resin begins to imidize below 200°C and completes its imidization reaction around 250°C. As seen in Figure 2, the band at 1660  $\text{cm}^{-1}$  is from the C=O stretching of amide bonds in the oligomer. This band almost

disappeared due to progressed imidization reaction after heating at 200°C for one hour. The absorption band resulting from the C-N bending of amide bonds is seen at 1545 cm<sup>-1</sup> below 200°C. This band also disappeared mostly at 200°C and completely at 250°C. This confirms that the phenylethynyl terminated amide acid oligomer is converted into the corresponding imide polymer through imidization reaction, which is started and activated below 200°C, and then proceeds with a slower rate above 200°C. The absorption band has a typical pattern of imide polymer in the range of 200–250°C.

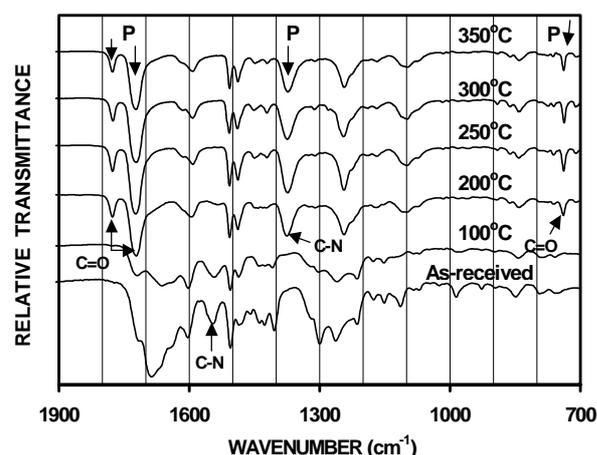


Fig. 2: Variations of FT-IR spectra of LaRC<sup>™</sup> PETI-5 heat-treated at different temperatures for 1 h each. P designates ‘imide polymer’.

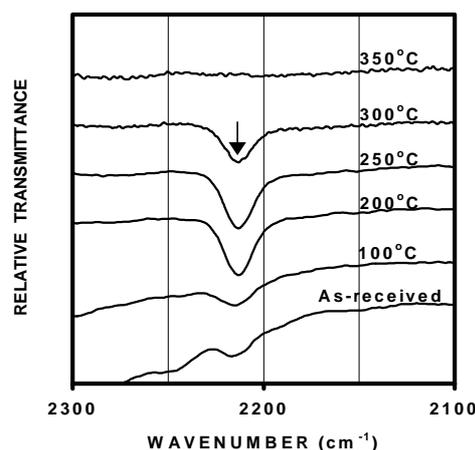


Fig. 3: Effect of cure temperature on the absorption peak change at 2213 cm<sup>-1</sup> due to the C≡C bond.

There are several characteristic absorption bands representing the imide polymer in Figure 2. The strongest absorption occurred at 1723 cm<sup>-1</sup> in this case. This is resulted from C=O symmetrical stretching. However, the band overlaps with a strong band around 1700 cm<sup>-1</sup> from carboxylic acid group in the amide acid oligomer. Therefore, the most useful bands for identification of the corresponding imide polymer are at 1777 cm<sup>-1</sup> from C=O asymmetrical stretching, at 1374 cm<sup>-1</sup> from C-N stretching, and at 739 cm<sup>-1</sup> from C=O bending from imide groups. The band at 1777 cm<sup>-1</sup> is also slightly interfered by absorption of anhydrides occurring around 1780 cm<sup>-1</sup>. Table 1 summarizes characteristic absorption bands of particular interest that disappeared or appeared during imidization reaction of LaRC<sup>™</sup> PETI-5. In this table Imides I to IV designate the most significant imide peaks serially numbered from the band in higher wavenumber to that in lower one. That is, Imide I indicates the band at 1777 cm<sup>-1</sup>, Imide II at 1723 cm<sup>-1</sup>, Imide III at 1374 cm<sup>-1</sup>, and Imide IV at 739 cm<sup>-1</sup>, respectively. It can be concluded that the heat treatment of LaRC<sup>™</sup> PETI-5 above 200°C for one hour is sufficient to virtually develop the structure of imide polymer, especially above 250°C for complete imidization in this work.

### Identification of Phenylethynyl End Group Reaction

More interestingly, the weak absorption band seen at 2213 cm<sup>-1</sup> is definitely resulted from stretching of alkyne (C≡C) groups, which are present in the reactive phenylethynyl group at the imide polymer chain ends of LaRC<sup>™</sup> PETI-5. This peak is hardly observed in the presence of NMP solvent in the neat resin. The absorption band increasingly appears with diminishing the amount of solvent remaining in the resin at higher temperatures. A closer

inspection of the band at  $2213\text{ cm}^{-1}$  as featured in Figure 3 gives us more useful information on cure behavior of LaRC™ PETI-5. The result represents the variation of absorption peak (indicated by the arrow) from the  $\text{C}\equiv\text{C}$  bonds in the phenylethynyl end group of the imide polymer chain at different cure temperatures. The band is largely screened by the presence of a significant amount of solvent below  $200^\circ\text{C}$  but it is apparently shown above the temperature because most of the solvent has been removed. The absorption peak slightly decreases with increasing temperature and at last it perfectly disappears at  $350^\circ\text{C}$ . It indicates that at  $350^\circ\text{C}$  the  $\text{C}\equiv\text{C}$  bonds are broken to be converted into  $\text{C}=\text{C}$  bonds that are ready to crosslink three-dimensionally with intermolecular chains in proximity. In fact, it has been found that the terminal phenylethynyl group is definitely responsible for the cure reaction of LaRC™ PETI-5. Accordingly, it can be concluded that a temperature above  $350^\circ\text{C}$  for one hour in air is needed to fully cure the LaRC™ PETI-5 resin through complete reaction of its phenylethynyl end groups.

*Table 1. Characteristic FT-IR absorption peaks that appear or disappear during imidization of LaRC™ PETI-5 in NMP.*

Functional Group	Frequency ( $\text{cm}^{-1}$ )	Band Characteristics
Amines	3254 & 3194 (weak)	N-H stretching
Carboxylic Acids	2400-2650 (broad)	O-H stretching
Alkynes	2213 (weak)	$\text{C}\equiv\text{C}$ stretching
Amides	1545 (medium)	C-N bending
Imide I*	1777 (strong)	C=O asym. stretching
Imide II**	1723 (very strong)	C=O sym. stretching
Imide III	1374 (strong)	C-N stretching
Imide IV	739 (strong)	C=O bending
* Anhydride peak (C=O stretching) in amide acid oligomer is included.		
** Carboxylic acid peak (C=O stretching) in amide acid oligomer is included.		

## Disappearance and Appearance of Characteristic Absorption Bands

The disappearance and appearance of most characteristic absorption bands discussed earlier can be quantitatively evaluated. Figures 4 and 5 represent the variation of representative amide acid and imide peaks observed via imidization upon cure of LaRC™ PETI-5 at different temperatures. The values of  $\Delta T$  (%) in the x axis [designated as DT (%) in the figures] were calculated from the difference of the transmittance values between the absorption maximum and the minimum in close proximity to the peak. The absorption bands which overlapped with characteristic imide bands were not considered here to avoid any possible ambiguity. For example, the absorption band by carboxylic acid group in the amide acid oligomer around  $1700\text{ cm}^{-1}$  was not used to evaluate the  $\Delta T$  (%) due to its interference with the Imide II absorption band.

In Figure 4 the  $\Delta T$  values determined from amide, amine and carboxylic acid groups decrease with increasing temperature, and are constant above  $250^\circ\text{C}$ . All the values are close to zero at  $350^\circ\text{C}$ . This indicates that the conversion of phenylethynyl terminated amide acid oligomer into the corresponding imide polymer proceeds rapidly around  $200^\circ\text{C}$ , becomes less reactive with temperature, and is complete around  $250^\circ\text{C}$ . The reduction of the  $\Delta T$  value for the amide

group is remarkable and the value approaches close to zero around 220°C. The amide group in the oligomer is substantially consumed first during the imidization reaction.

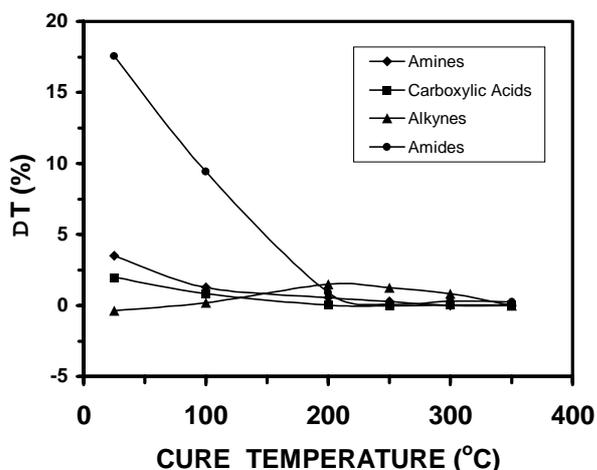


Fig. 4: Variations of characteristic absorption peaks resulting from some chemical groups in the amide acid oligomer during cure.

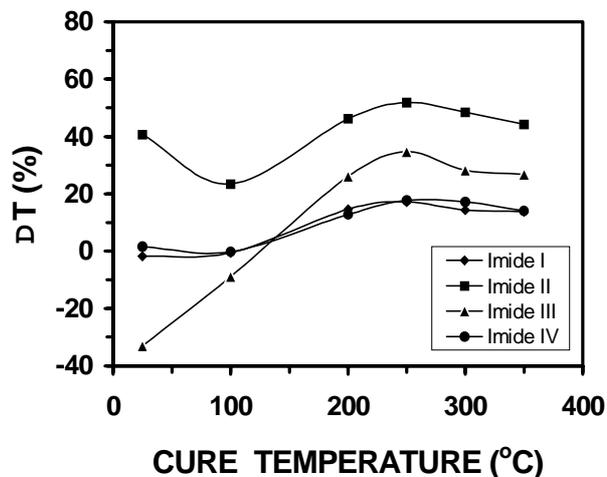


Fig. 5: Variations of characteristic absorption peaks resulting from typical imide bonds by imidization during cure.

In Figure 5 the  $\Delta T$  values of Imides I to IV gradually increase up to 250°C with a largest variation in case of Imide III. All imide peaks show a maximum  $\Delta T$  around 250°C. The values obtained from the alkyne band slowly increase up to 200°C with a maximum and then gradually decrease with temperature, as explained earlier. This demonstrates that the imidization of LaRC™ PETI-5 can be accomplished around 250°C. This result also supports quantitatively the fact that a typical absorption band of imide polymer appears at 200°C and is clearly seen at 250°C. The reason for a slight decrease above 250°C is that with an increase of the degree of imidization, the glass transition temperature and chain stiffness of the imide polymer also increase and the local mobility of chain segments is largely restricted while being consolidated. When the glass transition temperature reaches the reaction temperature, the imidization proceeds more slowly. Consequently such molecular behavior may cause less sensitivity of FT-IR absorption to the vibrational motion of chain segments.

In the case of Imide II, a decrease of the  $\Delta T$  value between 25°C and 100°C is because carboxylic acid in the amide acid oligomer is slowly consumed with increasing temperature and the band peak at 1720  $\text{cm}^{-1}$  somewhat overlapped with the Imide II band decreases. The value of  $\Delta T$  lower than zero in the low temperature region of the Imide III is ascribed to a strong absorption peak from NMP solvent at 1404  $\text{cm}^{-1}$ , which may interfere with the imide peak at 1374  $\text{cm}^{-1}$ . The peak at 739  $\text{cm}^{-1}$  for Imide IV can be influenced by absorption (at 720  $\text{cm}^{-1}$ ) from the C=O bond of the anhydride group present in the oligomer.

### The Extent of Imidization

FT-IR analysis also provides useful information on the extent of conversion of poly(amide acid) into polyimide through imidization[8]. The extent of imidization has been determined from the heights of the absorption bands for Imides I and III normalized to the height of the absorption band for as-received LaRC™ PETI-5 at 1374  $\text{cm}^{-1}$  and 1777  $\text{cm}^{-1}$ , respectively. For the ‘as-received’ resin, the extent of imidization is zero at ambient temperature prior to any further heat treatment. In fact, amide acid can be easily stabilized with favorable conformation in NMP at ambient temperature. Therefore, imidization process requires a

higher temperature in the presence of NMP. The imidization reaction initiates around 100°C, increases linearly up to about 200°C, and then proceeds slowly to 250°C. At 250°C the resin reaches complete imidization reaction (assumed to be 100 %). This can be explained by the fact that below 200°C the solvent in the neat resin does not play an important role in the reaction, but still contributes to stabilizing the conformation of amide acid. With increasing temperature, the cyclodehydration reaction between the carboxylic acid and the amide group becomes pronounced producing an unfavorable ring conformation which slows down above 200°C.

### Isothermal Effects

Although the spectra observed after isothermal treatments for 20 min and 30 min exhibit some characteristic bands indicating the progress of imidization reaction, it can be seen that a large portion of the amide acid oligomer is still participating in the reaction. The reaction also competitively takes place with an evaporation of NMP. It can be said that the spectral shape may change into a typical pattern of imide polymer after an isothermal treatment for about 40 min. That is, Imides I to IV bands as noted earlier increase after 40 min. The disappearance of characteristic amide acid bands also occurs simultaneously. Therefore, it can be expected that there may be an active cyclodehydration between carboxylic acid and amide groups with a generation of a very small amount of H<sub>2</sub>O as a result of imidization during an isothermal heating between 30 and 40 minutes at 200°C.

It has been reported that the compounds with disubstituted acetylene end groups undergo crosslinking reaction at temperatures between 300°C and 350°C[9]. The peak due to the C≡C bond has completely disappeared at 350°C in the present work. Since these C≡C bonds in the reactive phenylethynyl group located at the imide polymer chain ends are responsible for cure reaction involving crosslinking and chain extension, a determination of the reaction conditions for optimal cure is critical for better properties and performance. Therefore, it is worth examining the effect of isothermal cure on the spectral response of the absorption due to the C≡C bond as a function of time and temperature. The absorption peak due to the C≡C bond at 2213 cm<sup>-1</sup> decreases to some extent but has not disappeared completely even after curing for 4 hours at 300°C. This means that many of the bonds are not involved in the cure reaction.

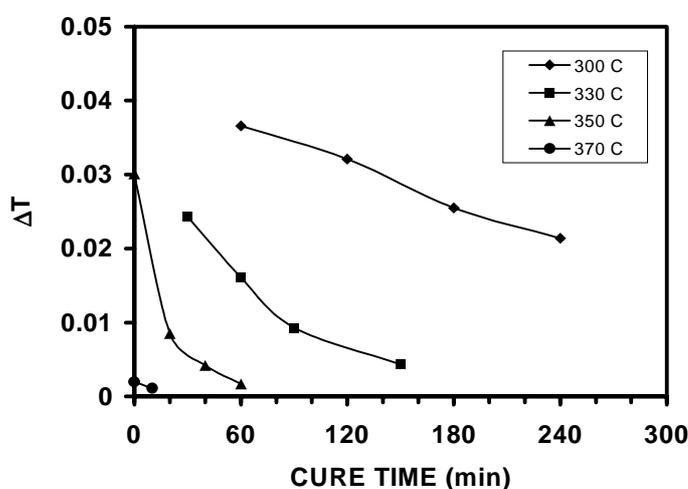


Fig. 6: Effect of isothermal cure temperature on the disappearance of the C≡C absorption peak from the phenylethynyl end group, quantified by  $\Delta T$  at 2213 cm<sup>-1</sup>.

Figure 6 represents the effect of isothermal cure of LaRC™ PETI-5 on the disappearance of the absorption peak at 2213 cm<sup>-1</sup> from the phenylethynyl end group. The value of  $\Delta T$  in the figure has been calculated from the difference of the transmittance values between 2213 and 2250 cm<sup>-1</sup>. The transmittance at 2250 cm<sup>-1</sup> is slightly greater than at 2213 cm<sup>-1</sup> even after a complete disappearance of the absorption band by the C≡C bond. This is why the minimum values of  $\Delta T$  at 350°C and 370°C are slightly higher than zero. Here, the decrease of  $\Delta T$  at 2213 cm<sup>-1</sup> as a function of time reflects the rate of disappearance of the absorption peak by the C≡C bond during cure. The rate of disappearance rapidly increases with increasing temperature. At 300°C, the value of  $\Delta T$  shows an almost linear decrease with cure time. With increasing temperature a higher order dependency is shown in the earlier stage of cure.

### **The Activation Energy of Cure Reaction**

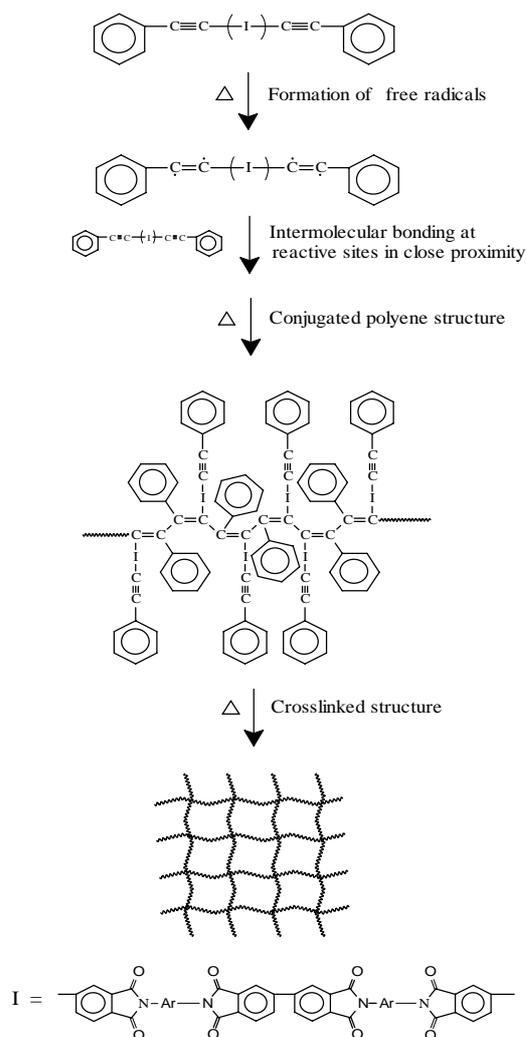
An evaluation of the activation energy of thermoset cure reaction may give useful information on reaction barriers and mechanisms. In reaction kinetics, a rate equation is generally related to the rate of consumption of the reactants or the extent of conversion through a rate constant. Here, the rate of disappearance of a specific absorption peak at a fixed time interval, i.e., the transmittance difference over the time difference [ $\delta(\Delta T)/\delta t$ ] may be correspondingly considered as a reaction rate through an Arrhenius relationship.

In the present work the activation energy of the cure reaction based on the phenylethynyl end group in LaRC™ PETI-5 imide oligomer has been determined from isothermal experiments using FT-IR spectroscopy. The Arrhenius plot for the kinetic result of the cure reaction is shown in Figure 11. The rate constant has been determined from the change of the  $\Delta T$  value obtained for the same interval of cure time (i.e., 20 min in this case) at a given temperature. The slope of the plot gives the activation energy for the cure reaction to be about 36.9 kcal/mol. This result is quite consistent with results published by others[10,11].

### **Proposed Crosslinking Scheme**

The reactive site for curing a phenylethynyl terminated imide oligomer is definitely a phenylethynyl end group. This has been demonstrated in this work by monitoring the disappearance of the absorption band due to the change of chemical state of the C≡C bond in the end group during cure. These end groups react predominantly and rapidly through a free radical mechanism during thermal cure[1,10]. Free radicals at the ends of an imide polymer chain can form intermolecular bonds with reactive sites of another chain in close proximity. It has been known that a conjugated polyene structure can be made at this stage[1,12].

However, due to the steric hindrance effect of the bulky phenyl group, reaction between the polyenes is in general difficult. Therefore, a high processing temperature above 350°C is necessary to effectively activate the crosslinking reaction among the reactive sites in the polyene and phenylethynyl group. However, since the exact mechanism and structure of this material have not reported, a proposed crosslinking reaction scheme of LaRC™ PETI-5 is illustrated in Figure 7.



*Fig. 7: A proposed crosslinking scheme of LaRC™ PETI-5 through the reactive phenylethynyl end group. The letter I designates the central part of an imide oligomer structure.*

## CONCLUSIONS

It has been found that some characteristic absorption bands including alkynes in the phenylethynyl end group are obscured significantly in the presence of NMP solvent in the neat LaRC™ PETI-5 but they begin to appear as the amount of solvent remaining in the resin decreases at higher temperature.

Heat treatment of LaRC™ PETI-5 above 200°C for one hour is sufficient to develop the structure of the imide polymer, and heat treatment above 250°C results in complete imidization.

FT-IR analysis provides useful information on the extent of conversion of phenylethynyl terminated imide oligomers into the corresponding imide polymer via imidization as well as on the activation energy of cure reaction of LaRC™ PETI-5. The cure reaction involving crosslinking and chain extension by a reaction of phenylethynyl end groups is completed as LaRC™ PETI-5 resin is heated at 350°C for 60 min or at 370°C for 10 min in air.

The isothermal decrease at  $2213\text{ cm}^{-1}$  as a function of time reflects the rate of disappearance of the absorption peak from the  $\text{C}\equiv\text{C}$  bond in the phenylethynyl end group during cure. The rate of disappearance of the  $\text{C}\equiv\text{C}$  bond increases with increasing temperature from  $300^\circ\text{C}$  to  $370^\circ\text{C}$  but it does not completely disappear even after curing for 4 hours at  $300^\circ\text{C}$ . At temperatures less than  $300^\circ\text{C}$ , a portion of the phenylethynyl end groups may remain unreacted or require much longer period of reaction time to be fully cured.

## ACKNOWLEDGEMENTS

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