

Characterization, Properties, and Processing of LaRCTM PETI-5 as a High-Temperature Sizing Material. I. FTIR Studies on Imidization and Phenylethynyl End-Group Reaction Behavior

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ABSTRACT: The imidization and phenylethynyl end-group reaction behavior of phenylethynyl-terminated imide oligomers (LaRCTM 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. Most characteristic FTIR absorption bands including the phenylethynyl end group occurring via imidization and cure during dynamic and isothermal heat treatments of LaRCTM PETI-5 were clearly resolved and assigned in the present study. The results give some information on temperature- and time-dependency of the cure of LaRCTM PETI-5, which may be useful for determining the processing conditions necessary for use as a high-temperature fiber-sizing material. This study also measures the extent of imidization and the activation energy of cure reaction of this material. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 190–200, 2000

Key words: phenylethynyl-terminated imide oligomer; LaRCTM PETI-5; imidization; end-group reaction; activation energy; FTIR

INTRODUCTION

Advanced adhesives and composite matrix resins with high-temperature and processing performance are desirable for use in advanced aerospace and aircraft industries. Aromatic polyimides, especially acetylene or ethynyl-terminated polyimides, have been extensively studied as candidate resins for various applications over the past two decades due to their unique combination of properties.^{1–5} They exhibit superb thermal, me-

chanical, and chemical properties and low dielectric constants which are also useful for electronics applications. However, their use has been somewhat limited because of the difficulty in processing (i.e., high temperature and pressure and release of volatiles may cause deterioration of polyimide properties).⁶ The processibility of polyimides may be improved by terminating reactive end groups, controlling molecular weight and/or introducing some flexible molecules in the rigid polymer chain. Recently, a variety of phenylethynyl-terminated imide oligomers for high-temperature aerospace and aircraft applications, referred to as LaRCTM PETI, have been developed at the NASA Langley Research Center.^{7–11} These materials have better processing windows and thermal oxidative stability than simple ethynyl-terminated materials and have many practical advantages such as a potential material for coat-

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ings, adhesives, films, and composite matrix resins.^{12–13} 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.¹⁴

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 on 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.^{13–15} 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. Because 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 to optimize resin processing and properties.

Fourier transform infrared (FTIR) spectroscopy is a powerful tool used to monitor such chemical changes that occur during thermal treatment. The FTIR method has been also successfully used in many research areas to study cure,¹⁶ thermal aging,¹⁷ crosslinking reaction,¹⁸ semi-interpenetrating network,^{19–20} as well as structure identification^{21–22} of polyimides. 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 article reports on the changes in molecular structure during reaction through observation of temperature- and time-dependent intensity variations of the characteristic FTIR 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. (Schenectady, NY). The as-received LaRC™ PETI-5 is a random copolymer with a number-average molecular weight of 2500 g/mol, which is prepared from 3,4'-oxydianiline (ODA), 1,3-bis(3-aminophenoxy)benzene (APB), and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), endcapped with 4-phenylethynylphthalic anhydride (PEPA), as shown in Figure 1. The synthesis of LaRC™ PETI-5 has been described in detail elsewhere.^{7–8} 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 was always stored in a refrigerator and only placed at ambient temperature for a couple of hours before use to prevent possible moisture absorption. FTIR-grade potassium bromide (KBr) powder was purchased from Aldrich Chemical Co. (Milwaukee, WI).

Sample Preparation and FTIR Measurements

FTIR measurements were performed by using purging N₂ 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 FTIR measurements to avoid curing of the resin between the discs at high temperatures. The NaCl disc was subsequently heated to 100, 200, 250, 300, 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 FTIR measurement. FTIR 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, 300, 330, 350, and 370°C in an air-circulating oven. The clear KBr discs were molded from the powder and a pure KBr sample was used as the background. The discs were always kept in a desiccator prior to measurement. The resolution and the number of scans for the FTIR measurements were 4 and 50 cm⁻¹, respectively.

With increasing heat-treatment temperature, the color of the amide acid oligomer slowly changed from pale yellow at lower temperatures to dark brown at higher temperature.

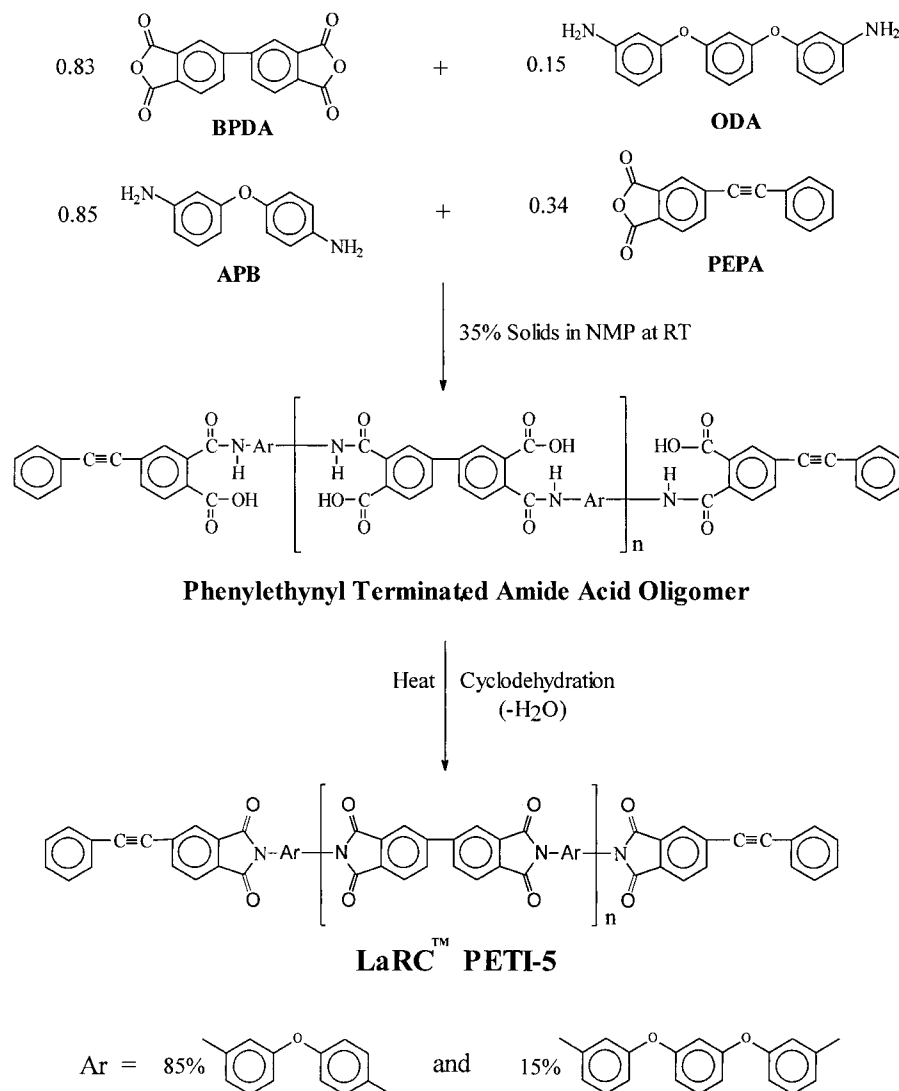


Figure 1 Preparation of LaRC™ PETI-5 amide acid oligomer ($M_n = 2500$ g/mol) and the polymer.

RESULTS AND DISCUSSION

Temperature Effect on Formation of the Polyimide Structure

The disappearance and appearance of most characteristic FTIR absorption bands during imidization and cure including the phenylethynyl end group were clearly resolved and assigned here. Figures 2 and 3 show the variations of the FTIR bands that occurred while LaRC™ PETI-5 was exposed to five different cure temperatures from 100 to 350°C for 1 h each in an air-circulating oven.

In the as-received sample, the absorption band from phenylethynyl-terminated amide acid oli-

gomer in the range of $\sim 3000\text{--}2800$ cm^{-1} is largely screened because of NMP solvent contained 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. The two peaks at 3254 and 3194 cm^{-1} in the as-received resin in Figure 2 are from the N—H stretching, strongly associated with hydrogen bonding in the amide acid oligomer. Typical C—H stretching bands from the solvent are shown between 3100 and 2800 cm^{-1} . This band also includes the O—H stretching of carboxylic acid group in the amide

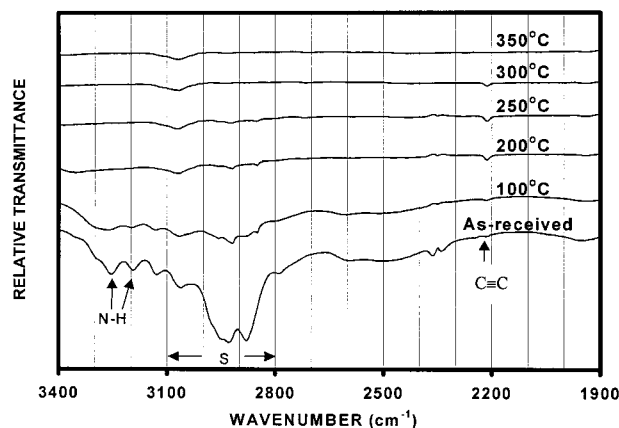


Figure 2 Variations of FTIR spectra between 3400 and 1900 cm^{-1} of LaRC™ PETI-5 heat-treated at different temperatures for 1 h each in air. S designates solvent, NMP.

acid oligomer. However, it is difficult to analyze because the band is interfered or hidden by the solvent. The O—H stretching of the carboxylic acid group in the oligomer can be also characterized by a broad band between 2650 and 2400 cm^{-1} . As seen in Figure 3, the band at 1660 cm^{-1} is from the C=O stretching of amide bonds in the oligomer. This band almost disappeared because of progressed imidization reaction after heating at 200°C for 1 h. The absorption band resulting from the C—N bending of amide bonds is seen at 1545 cm^{-1} 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.

There are several characteristic absorption bands representing the imide polymer in Figure 3. The strongest absorption occurred at 1723 cm^{-1} in this case. This resulted from C=O symmetrical stretching. However, the band overlaps with a strong band around 1700 cm^{-1} 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^{-1} from C=O asymmetrical stretching, at 1374 cm^{-1} from C—N stretching, and at 739 cm^{-1} from C=O bending from imide groups. The band at 1777 cm^{-1} is also slightly interfered by absorption of anhydrides occurring around 1780 cm^{-1} .

Table I summarizes characteristic absorption bands of particular interest that disappeared or appeared during imidization reaction of LaRC™ PETI-5, as described in Figures 2 and 3. 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^{-1} , Imide II at 1723 cm^{-1} , Imide III at 1374 cm^{-1} , and Imide IV at 739 cm^{-1} , respectively. It can be concluded that the heat treatment of LaRC™ PETI-5 above 200°C for 1 h is sufficient to virtually develop the structure of imide polymer, especially above 250°C for complete imidization in this work.

Identification of Reaction of Phenylethynyl End Group

More interestingly, the weak absorption band seen at 2213 cm^{-1} definitely results from stretching of alkyne (C≡C) groups, which are present in the reactive phenylethynyl group at the imide polymer chain ends of LaRC™ PETI-5. This peak is hardly observed in the presence of NMP solvent in the neat resin. The absorption band increasingly appears with diminishing amount of solvent remaining in the resin at higher temperatures. This band can be seen as a very weak absorption in Figure 2. A closer inspection of the band at 2213 cm^{-1} as featured in Figure 4 gives us more useful information on cure behavior of LaRC™

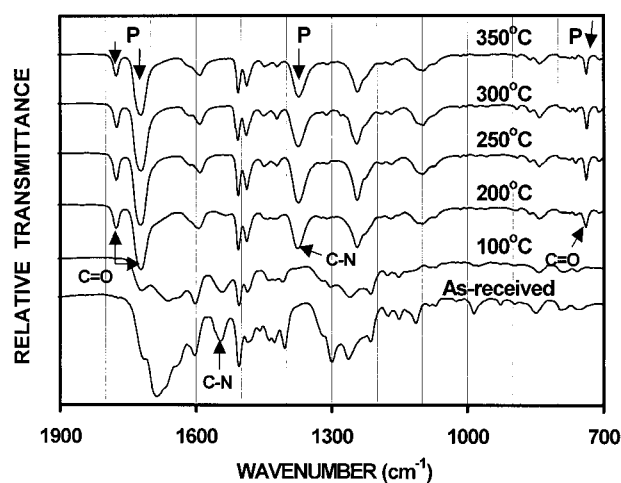


Figure 3 Variations of FTIR spectra between 1900 and 700 cm^{-1} of LaRC™ PETI-5 heat-treated at different temperatures for 1 h each in air. P designates imide polymer.

Table I Characteristic FTIR Absorption Peaks that Appear or Disappear during Imidization of LaRC™ PETI-5 in NMP

Functional Group	Frequency (cm ⁻¹)	Band Characteristics
Amines	3254 & 3194 (weak)	N—H stretching
Carboxylic Acids	2400–2650 (broad)	O—H stretching
Alkynes	2213 (weak)	C≡C stretching
Amides	1545 (medium)	C—N bending
Imide I ^a	1777 (strong)	C=O asym. stretching
Imide II ^b	1723 (very strong)	C=O sym. stretching
Imide III	1374 (strong)	C—N stretching
Imide IV	739 (strong)	C=O bending

^a Anhydride peak (C=O stretching) in amide acid oligomer is included.

^b Carboxylic acid peak (C=O stretching) in amide acid oligomer is included.

PETI-5. The result represents the variation of absorption peak from the C≡C bonds in the phenylethynyl end group of the imide polymer chain at different cure temperatures. The band is

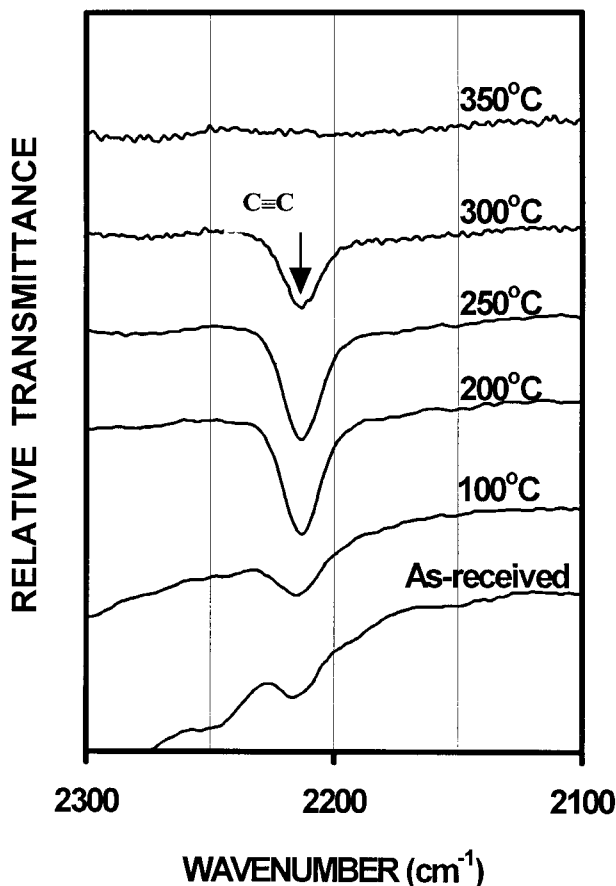


Figure 4 Effect of cure temperature on the change of the absorption peak at 2213 cm⁻¹ due to the C≡C bond in the phenylethynyl end group of LaRC™ PETI-5.

largely screened by the presence of a significant amount of solvent below 200°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°C. It indicates that at 350°C the C≡C bonds are broken to be converted into C=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°C for 1 h in air is needed to fully cure the LaRC™ PETI-5 resin through complete reaction of its phenylethynyl end groups.

Disappearance and Appearance of Characteristic Absorption Bands

The disappearance and appearance of most characteristic absorption bands discussed earlier can be quantitatively evaluated. Figures 5 and 6 represent the variation of representative amide acid and imide peaks observed via imidization on cure of LaRC™ PETI-5 at different temperatures. The values of ΔT (%) 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 that 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 cm⁻¹ was not used to evaluate the ΔT (%) due to its interference with the Imide II absorption band.

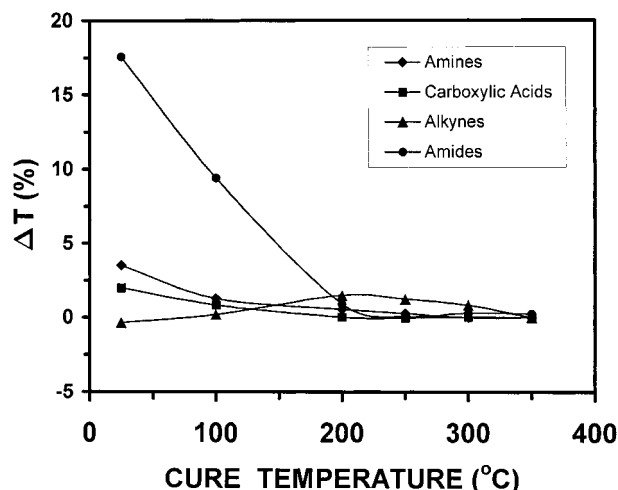


Figure 5 Variations of characteristic absorption peaks resulting from some chemical groups in phenylethynyl-terminated amide acid oligomer during cure at different temperatures.

In Figure 5, the ΔT values determined from amide, amine, and carboxylic acid groups decrease with increasing temperature and are constant above 250°C. All the values are close to zero at 350°C. This indicates that the conversion of phenylethynyl-terminated amide acid oligomer into the corresponding imide polymer proceeds rapidly around 200°C, becomes less reactive with temperature, and is complete around 250°C. The reduction of the ΔT 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. Takekoshi²³ noted that the disappearance of the lower temperature peak in the infrared absorption spectrum indicates the consumption of amide acid, which occurs at about 225°C.

In Figure 6, the ΔT values of Imides I to IV gradually increase up to 250°C with the largest variation in the case of Imide III. All imide peaks show a maximum ΔT 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 FTIR absorption to the vibrational motion of chain segments.

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

The Extent of Imidization

FTIR analysis also provides useful information on the extent of conversion of poly(amide acid) into polyimide through imidization.^{24,25} The extent of imidization as a percentage in Figure 7 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 and 1777 cm^{-1} , respectively. The bands at 1723 and 739 cm^{-1} are not

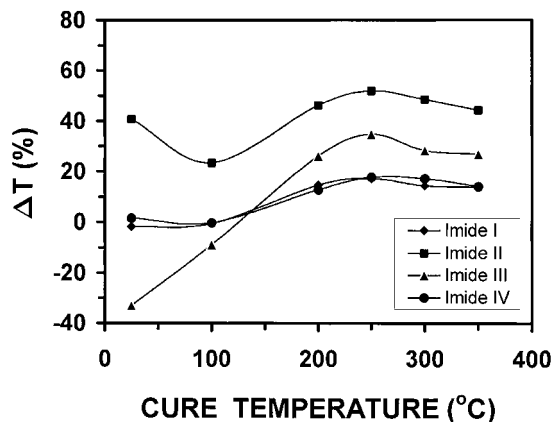


Figure 6 Variations of characteristic absorption peaks resulting from typical imide bonds by imidization of LaRC™ PETI-5 during cure at different temperatures.

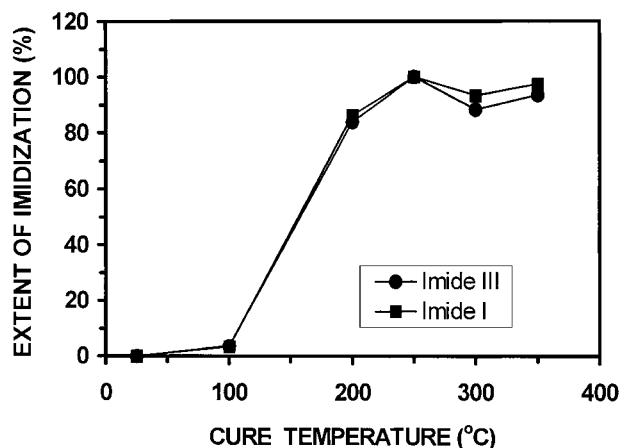


Figure 7 The extent of imidization as a function of cure temperature determined from the absorption peaks of Imides I and III.

considered in the calculation of the extent of imidization because the band at 1723 cm^{-1} overlaps with a carboxylic acid band in the amide acid oligomer and the one at 739 cm^{-1} overlaps with an anhydride absorption band. Although the band at 1777 cm^{-1} also overlaps with the anhydride absorption band, the overlap is not as much as at 739 cm^{-1} . To determine the extent of imidization for LaRC™ PETI-5, the following two assumptions are given. First, 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, the imidization process requires a higher temperature in the presence of NMP. Second, at 250°C the imidization reaction reaches completion (assumed to be 100%). Considering the results described in Figures 5 and 6, the assumptions are reasonable. In Figure 7, the imidization reaction initiates around 100°C , increases linearly up to about 200°C , and then proceeds slowly to 250°C . 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 .

The values of the extent of imidization determined for LaRC™ PETI-5 with a system of BPDA/(ODA + APB) endcapped with PEPA at various temperatures in the present study are

similar to a polyimide system of pyrometallic dianhydride (PMDA)/ODA studied by Ishida et al.²⁶ A small decrease in the extent of reaction after 250°C is probably due to a lack of sensitivity in detecting the vibrational segmental motion in the fully imidized molecular chains using FTIR, resulting from an increase in the local viscosity in the sample.

Isothermal Effects

Figure 8 shows the effect of isothermal heating at 200°C on the variation of the FTIR absorption bands of LaRC™ PETI-5. Although the spectra observed after isothermal treatments for 20 and 30 min exhibit some characteristic bands indicating the progress of the 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 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, bands of Imides I to IV 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_2O as a result of imidization during an isothermal heating between 30 and 40 min at 200°C . In addition, it is likely that the peak due to the $\text{C}\equiv\text{C}$ bond in the phenylethynyl group at 2213 cm^{-1} increases with increasing isothermal time. The $\text{C}\equiv\text{C}$ band is not sensitive or reactive under such thermal conditions given here, as described earlier (Fig. 4). The

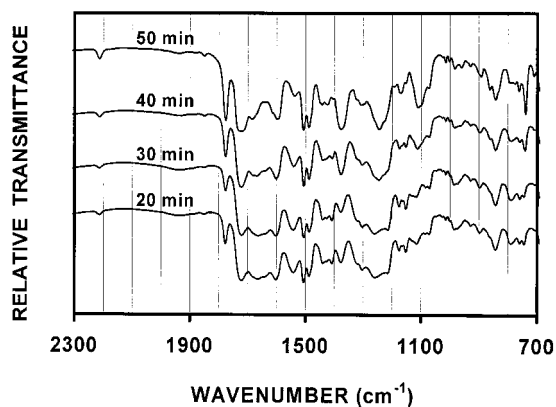


Figure 8 Effect of isothermal heating at 200°C on the variations of the FTIR spectra of LaRC™ PETI-5.

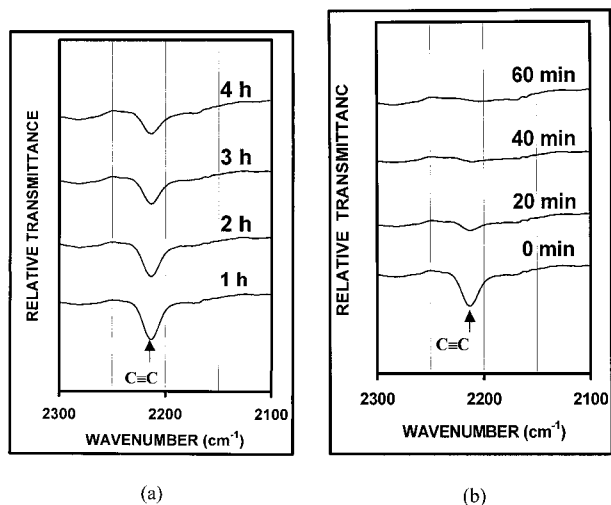


Figure 9 Effect of isothermal cures at 300°C (a) and 350°C (b) on the spectral change at 2213 cm^{-1} due to the $\text{C}\equiv\text{C}$ bond in the phenylethynyl end group of LaRC™ PETI-5.

increase is therefore because the peak is increasingly revealed as the solvent blocking the peak is gradually removed with increasing time.

It has been reported that the compounds with disubstituted-acetylene end groups undergo crosslinking reaction at temperatures between 300 and 350°C.^{27,28} The peak due to the $\text{C}\equiv\text{C}$ bond has completely disappeared at 350°C in the present work. Since these $\text{C}\equiv\text{C}$ 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 $\text{C}\equiv\text{C}$ bond as a function of time and temperature. The results are represented in Figures 9 and 10. As seen in Figure 9(a), the absorption peak due to the $\text{C}\equiv\text{C}$ bond at 2213 cm^{-1} decreases to some extent but has not disappeared completely even after curing for 4 h at 300°C. This means that many of the bonds are not involved in the cure reaction. In Figure 9(b), it can be seen that the absorption due to $\text{C}\equiv\text{C}$ has disappeared more rapidly at 350°C than at 300°C. The spectral trace at 2213 cm^{-1} has mostly disappeared after an isothermal treatment for 40 min at 350°C and completely disappeared after 60 min at 350°C.

The absorption band at 2213 cm^{-1} has been monitored with varying cure temperature and

time. Figure 10 represents the effect of isothermal cure of LaRC™ PETI-5 on the disappearance of the absorption peak from the phenylethynyl end group. The value of ΔT in the figure has been calculated from the difference of the transmittance values between 2213 and 2250 cm^{-1} . The transmittance at 2250 cm^{-1} is slightly greater than at 2213 cm^{-1} even after a complete disappearance of the absorption band by the $\text{C}\equiv\text{C}$ bond. This is why the minimum values of ΔT at 350 and 370°C are slightly higher than zero. Here, the decrease of ΔT at 2213 cm^{-1} as a function of time reflects the rate of disappearance of the absorption peak by the $\text{C}\equiv\text{C}$ bond during cure. The rate of disappearance rapidly increases with increasing temperature. At 300°C, the value of ΔT shows an almost linear decrease with cure time. With increasing temperature, a higher order dependency is shown in the earlier stage of cure.

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 $\text{C}\equiv\text{C}$ bond in the end group during cure, as seen in Figures 4, 9, and 10. These end groups react predominantly and rapidly through a free-radical mechanism during thermal cure.^{1,7} Free radicals at the ends of an imide polymer

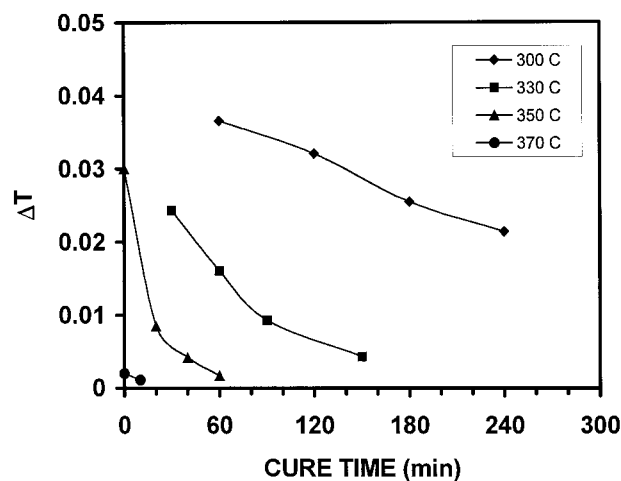


Figure 10 Effect of isothermal cure temperature on the disappearance of the $\text{C}\equiv\text{C}$ absorption peak from the phenylethynyl end group, quantified by ΔT at 2213 cm^{-1} .

chain can form intermolecular bonds with reactive sites of another chain in close proximity. It is known that a conjugated polyene structure can be made at this stage.^{1,7} 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, because the exact mechanism and structure of this material have not been reported, a proposed crosslinking reaction scheme of LaRC™ PETI-5 is illustrated in Figure 11.

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.²⁹ Although several simultaneous reactions take place during the cure process, some simple models have been developed, assuming that only one reaction may represent the entire cure process. This can be described with an Arrhenius relationship given by

$$k = Ae^{-(E_a/RT)}$$

where E_a is the activation energy, k is the rate constant obeying an Arrhenius temperature dependency, A is the preexponential factor, R is the gas constant, and T is the absolute temperature. 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.

Accordingly, 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 FTIR spectroscopy. The Arrhenius plot for the kinetic result of the cure reaction is shown in Figure 12. The rate constant has been determined from the change of the ΔT 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

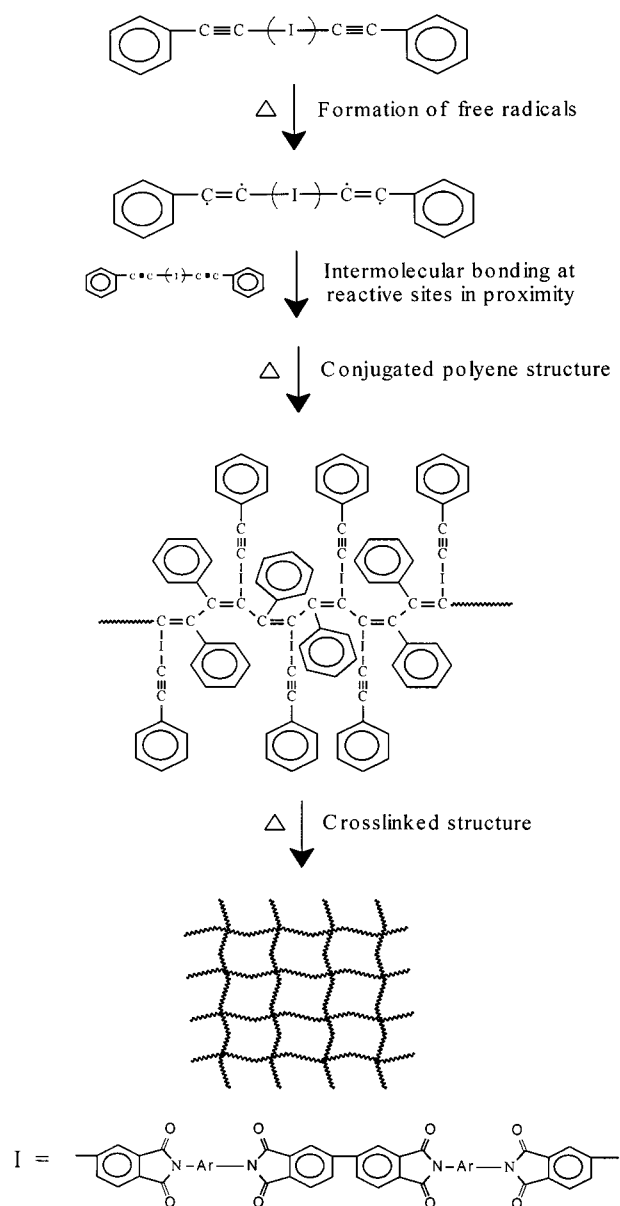


Figure 11 A proposed crosslinking scheme of LaRC™ PETI-5 through the reactive phenylethynyl end group. The letter I designates the central part of an imide oligomer structure.

the cure reaction to be about 36.9 kcal/mol. This result is quite consistent with results published by others. There have been some kinetic studies^{4,30,31} to obtain the activation energy on the reaction of acetylene-terminated polyimides, using a differential scanning calorimeter (DSC). Hinkley³⁰ reported that the temperature dependence of a phenylethynyl-terminated imide oligomer with a number-average molecular weight of 5000 g/mol obeys an Arrhenius relationship

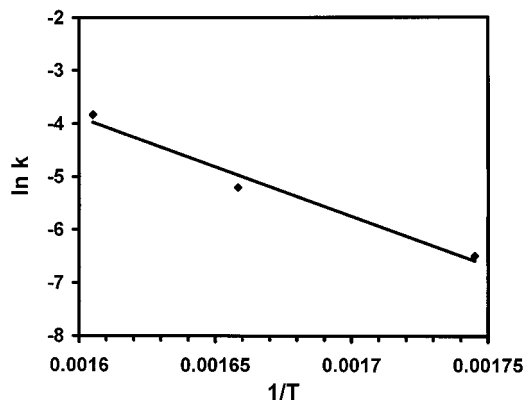


Figure 12 An Arrhenius plot based on the isothermal cure reaction of the phenylethynyl end group in LaRC™ PETI-5 determined from FTIR measurements.

having the activation energy of 33 kcal/mol. Takekoshi and Terry³¹ published that two phenylethynyl-terminated model compounds, *N*-(3-phenylethynyl)phthalimide and *N*-(4-phenylethynyl)phthalimide have activation energies of 31.6 and 36.5 kcal/mol, respectively. They described that the latter model compound, which closely resembles the structure of the compound studied here, followed first-order kinetics for the disappearance of the ethynyl group using isothermal data obtained by DSC measurements. In addition, Sastri et al.⁴ found that various arylacetylene-terminated resins showed a range of activation energy of ~29.9–39.7 kcal/mol, depending on the molecular structure.

CONCLUSION

It was found that some characteristic absorption bands including alkynes in the phenylethynyl end group are significantly obscured 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 1 h is sufficient to develop the structure of the imide polymer, and heat treatment above 250°C results in complete imidization.

FTIR 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 imidization reaction becomes active

around 100°C; the rate increases linearly up to about 200°C, and then proceeds more slowly to 250°C. The activation energy of cure reaction based on the phenylethynyl end group in LaRC™ PETI-5 determined using FTIR data is about 36.9 kcal/mol, which is quite consistent with other results determined using a DSC. 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 cm⁻¹ as a function of time reflects the rate of disappearance of the absorption peak from the C≡C bond in the phenylethynyl end group during cure. The rate of disappearance of the C≡C bond increases with increasing temperature from 300 to 370°C but does not completely disappear even after curing for 4 h at 300°C. At temperatures < 300°C, a portion of the phenylethynyl end groups may remain unreacted or require a much longer period of reaction time to be fully cured.

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