Macromolecules **2000,** *33,* 1671−1681

A Solid-State ^{13}C NMR Study of the Cure of ^{13}C-Labeled Phenylethynyl End-Capped Polyimides

Xiaomei Fang,[†] X.-Q. Xie,[†] Christopher D. Simone,[†] Malcolm P. Stevens,[‡] and Daniel A. Scola*,[†]

Polymer Science Program, Institute of Material Science, University of Connecticut, Storrs, Connecticut 06269-3136; and University of Hartford, West Hartford, CT 06117

Received July 21, 1999; Revised Manuscript Received December 6, 1999

ABSTRACT: The cure reactions of phenylethynyl end-capped polyimides were investigated using solid-state ^{13}C magic-angle spinning (MAS) nuclear magnetic resonance (NMR). A ^{13}C-labeled model compound (^{13}C-PEPA-3,4′-ODA) and an imide oligomer (^{13}C-PETI-5) were synthesized and characterized. The thermal cure process for ^{13}C-PEPA-3,4′-ODA was followed over the temperature range 318−380 °C and for ^{13}C-PETI-5 over the temperature range from 350 to 400 °C. Our NMR results showed that, for the model compound, as curing proceeded, the percentage of polymeric structures containing double-bonded and single-bonded carbon increased while the percentage of triple-bonded carbon gradually decreased and finally disappeared at the elevated temperatures. The PETI-5 cure process was very similar to the PEPA-3,4′-ODA cure process, and the percentage of double-bonded carbon structure of PETI-5 increased during the cure process as the percentage of triple-bonded carbon decreased. Moreover, for the PETI-5 resin system, a weak broad ^{13}C signal due to a single-bonded structure was observed after cure. The carbonyl groups remained relatively constant during the curing reactions for both the model compound and PETI-5 resin. The appearance of single-bonded structures in the cure of the model compound and PETI-5 can be derived from polyene structures by a further intra- or intermolecular Diels−Alder reaction to form cycloolefinic ring or branched structures. On the basis of the chemical shift data of several low molecular weight compounds with aromatic ring structures and polyene structures, we cannot exclude the formation of substituted aromatic ring structures from PEPA-3,4′-ODA or from PETI-5.

Introduction

The ethynyl group has become an important cure site for ethynyl end-capped polyimide systems[1−3] (Scheme 1) which have found applications in the electronics industry as low dielectric coatings.[4] The cure process of these end-capped polyimides has been widely investigated.[4,5] Studies by Swanson et al. by solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy have brought some insight into the cure mechanism of this resin system. In these studies, trisubstituted benzenes derived by cyclotrimerization, by thermal cyclization via Diels−Alder reactions, or from biradical polyene products and condensed polycyclic aromatic structures and alkenylaromatics have been proposed.

Pickard et al.[6] have investigated the kinetics and mechanism of bulk thermal polymerization of 3-phenoxyphenyl acetylene (Scheme 2). The soluble products generated in the polymerization reaction were analyzed. The authors revealed that the soluble material consists mostly of (1) polyene having a trans-cisoidal configuration (Scheme 3) and (2) lower molecular weight species such as 1,3,5-tris(3-phenoxyphenyl)benzene (Scheme 4) and 3-phenoxyphenyl acetylene dimer (Scheme 5).

A first-order reaction was determined for 20−60% conversion over the temperature range 127−327 °C by dynamic DSC, while by isothermal DSC, reaction orders from 2.3 to 2.9 over the temperature range 20−267 °C were determined for the first 50% of the reaction. More recently, a series of novel phenylethynyl end-capped imide oligomers have been introduced.[7−10] One NASA developed system, PETI-5 imide oligomer, has been investigated as a resin matrix in carbon composites for High-Speed Civil Transport (HSCT) applications. In this regard, the cure kinetics of two phenylethynyl materials have been investigated, a simple model compound, 3,4′-bis[4−phenylethynylphthalimido]diphenyl ether (PEPA-3,4′-ODA) (Scheme 6), and the NASA-developed imide oligomer, PETI-5 (Scheme 7).

In sharp contrast to the studies of Pickard et al.[6] on the simple 3-phenoxyphenylacetylene compound (Scheme 2), studies on a phenylethynyl end-capped model compound, PEPA-3,4′-ODA (Scheme 6), using infrared spectroscopy as the analytical tool in monitoring the disappearance of the ethynyl group at various temperatures isothermally, revealed first-order kinetics for the whole reaction period.[11] This reaction kinetics suggests that only a simple ethynyl to ethynyl addition reaction has occurred. However, as will be discussed below, carbon−carbon saturated bonds are also formed, ruling out first-order kinetics.

Although the triple bonds of simple terminated phenylethynyl imide molecules and more complex imide oligomers are expected to react by (1) an ethynyl to ethynyl addition chain reaction or (2) by an ethynyl to ethynyl chain extension reaction; more complex ethynyl to ethynyl trimerization or tetramerization reactions, ethynyl to vinyl and vinyl to vinyl cross-linking and branching reactions are also very viable possibilities. The cure mechanism of these systems is still poorly understood. The first study in the cure chemistry of a phenylethynyl model compound was carried out by Harrington et al. using high-pressure liquid chromatography (HPLC).[18] The model compound 4-phenoxy-4′-phenylethynylbenzophenone was cured at 375 °C from 0 to 60 min. The chromatogram of a sample quenched after 15 min at 375 °C revealed numerous

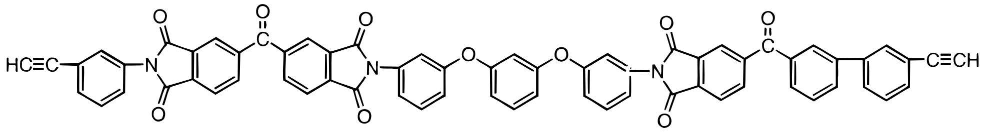
---

[†] University of Connecticut.

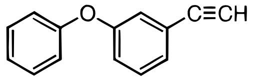
[‡] University of Hartford.

10.1021/ma991197m CCC: $19.00

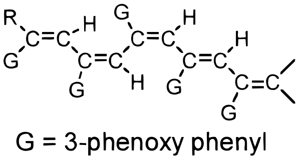
Scheme 1. Ethynylphenyl End-Capped Imide Oligomer



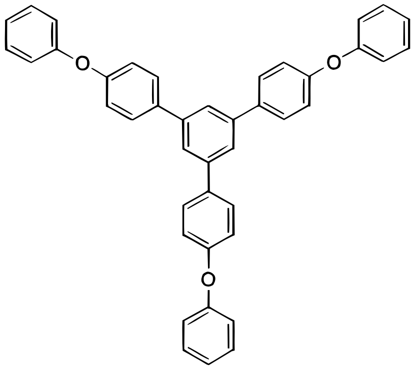
Scheme 2. 3-Phenoxyphenylacetylene



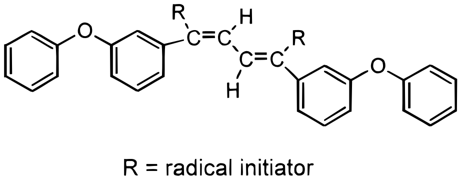
Scheme 3. Trans−Cis Polyene from Thermal Polymerization of 3-Phenoxyphenylacetylene



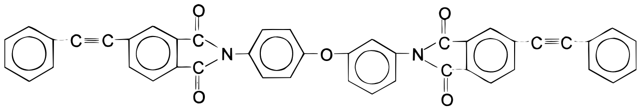
Scheme 4. 1,3,5-Tris(3-phenoxyphenyl)benzene



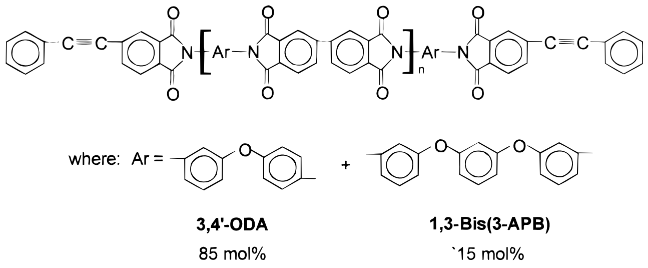
Scheme 5. 3-Phenoxyphenylacetylene Dimer



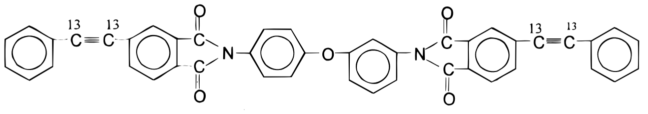
Scheme 6. 3,4′-Bis[(4-phenylethynyl)phthalimido)diphenyl Ether (PEPA-3,4′-ODA)



Scheme 7. Phenylethynyl-Terminated Imide Oligomer (PETI-5)



Scheme 8. ^{13}C-Labeled 3,4′-Bis[(4-phenylethynyl)phthalimido)diphenyl Ether (^{13}C-PEPA-3,4′-ODA)

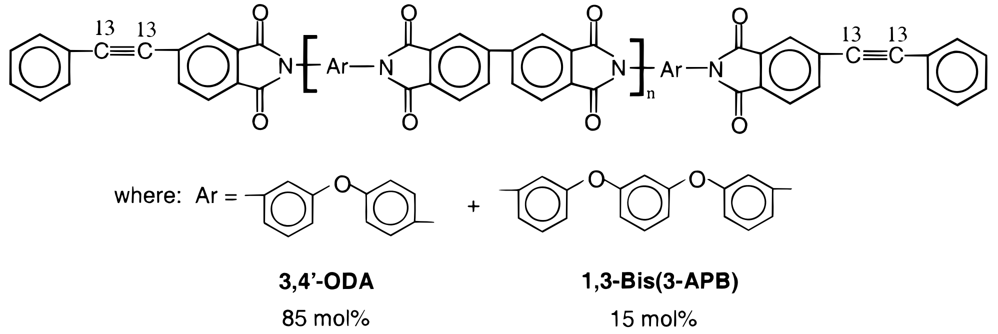


distinguishable peaks, but attempts to characterize the fractionated peaks by mass spectroscopy were unsuccessful because of the low concentrations. Solution ^{13}C NMR and ^{1}H NMR for this compound in the uncured and fully cured state were obtained. The ^{13}C NMR revealed several new peaks in the aromatic region but no assignments were made. DSC cure studies[18] of PETI-5 showed that the glass transition temperature remained essentially constant (~273 °C) after cure at 375 °C/30 min or 350 °C/90 min or 400 °C/12 min. A follow-up study was conducted by Wood et al.,[19] on the cure of 4-phenoxy-4′-phenylethynylbenzophenone at 325, 350, and 375 °C for various time periods to identify initial soluble cure products. Reverse-phase liquid chromatography (LC) in combination with mass spectroscopy (MS) was used to identify soluble components from the 350 °C/15 min cured sample run. This represented an average of only 18% of the cured products in this run. The remaining ~80% of insoluble product from this run was not analyzed. The combined LC/MS analysis data revealed that dimers, trimers and possible tetramers were formed in the initial cure of this material. Several pathways for dimer formation were discussed, namely (1) tail-to-tail product with phenyl ring migration, (2) ethynyl to phenoxy ether product with phenyl ring migration, and (3) ethynyl to ethynyl addition to form a labile cyclobutadiene dimer intermediate which on rearrangement formed a stable structure and diphenylacetylene having a combined mass of 748. The simple head to head or head to tail dimer product was discounted because the diradical dimer that could form is believed to be unstable at the 350 °C cure. It should be pointed out that, in the present study, the model compound is a bis(phenylethynyl) imide end-capped diphenyl ether, which is expected to have different reactivities based on its electronic nature and bulkiness relative to the monoethynyl end-capped ether model compound used in the referenced investigation. The expected steric and electronic effects of the bisphenylethynyl end-cappers relative to hydrogen in ethynyl end-capped oligomers and to monophenylethynyl compounds and the bulky nature of the oligomer repeat unit most likely contribute to the difficulties in elucidating the cure reaction mechanism of these phenylethynyl end-capped resin systems.

Therefore, in the present study, the simplest model of the PETI-5 oligomer was selected to develop an understanding of the cure process in the expectation that it could contribute to our understanding of the PETI-5 imide oligomer cure process.

Solid-state ^{13}C NMR with a magic-angle spinning has been able to provide high resolution spectra and utilized to determine the complicated chemical structure of solid polymers with great significance, especially for the insoluble and infusible thermosetting polymers. The cross-linked structures of acetylene-terminated and nadic end-capped polyimides studied by this technique

Scheme 9. ^{13}C-Labeled Phenylethynyl-Terminated Imide Oligomer (^{13}C-PETI-5)



have been elucidated.$^{4-5,12-13}$ In the present work, the cure process of the ^{13}C selectively labeled model compound PEPA-3,4′-ODA (Scheme 8) and PETI-5 imide oligomer (Scheme 9) was investigated by solid-state ^{13}C NMR techniques.

Experimental Section

General Information. 4-Bromophthalic anhydride (4-BrPAN) was obtained from Bromine Compounds Ltd., refluxed in acetic anhydride and recrystallized from boiling hexane, and dried in vacuo at 110 °C. Dichlorobis(triphenylphosphine)palladium(II) ($(Ph_3P)_2PdCl_2$) and chlorotris(triphenylphosphine)copper(I) ($(Ph_3P)CuCl$) were purchased from Aldrich and dried in vacuo at 110 °C. Unlabeled 4-phenylethynylphthalic anhydride (4-PEPA), 1,3-bis(3-aminophenoxyl) benzene (APB), and LaRC PETI-5 resin powder were provided by Imitec Inc. Phenylacetylene-1,2-$^{13}C_2$ (>99% atom ^{13}C) was purchased from Isotec Inc. 3,4′-Oxydianiline (3,4′-ODA) was obtained from Mitsui Petrochemical Industries, Inc. 3,3′4,4′-Biphenyltetracarboxylic dianhydride (BPDA) was purchased from Chriskev Co., Inc.

Synthesis of 1,2-^{13}C-Labeled 4-Phenylethynylphthalic Anhydride (^{13}C-PEPA). The procedure of Takekoshi and Terry was used.[14] Selectively ^{13}C-labeled 4-phenylethynylphthalic anhydride (^{13}C-PEPA) was prepared from 1,2-^{13}C-phenylacetylene and 4-BrPAN in triethylamine. In a nitrogen atmosphere, 4-BrPAN (2.247 g, 9.9 mmol), $(Ph_3P)CuCl$ (16.47 mg, 0.0186 mmol), $(Ph_3P)_2PdCl_2$ (10.80 mg, 0.0154 mmol), and triethylamine (9.2 mL) were added into a three-neck-round-bottom flask equipped with a magnetic stirring bar. The mixture was stirred at room temperature for 45 min. A mixture of ^{13}C-phenylacetylene (1.080 g, 10.4 mmol) and triethylamine (1.5 mL) was then pipetted into the reaction solution. The reaction mixture was heated to 100 °C to reflux for 10 min in an oil bath and then cooled to room temperature. Sodium hydroxide (22.6 mL of 1.0 N) was added, and the solution was stirred overnight. The basic solution was filtered, extracted with toluene (3 × 30 mL), and acidified with 6 N HCl to yield a light tan precipitate of crude 4-phenylethynylphthalic acid (^{13}C-PEPA diacid, 2.48 g, 93% yield). The ^{13}C-PEPA diacid was washed with water, dried at 65 °C in a vacuum overnight, and converted to ^{13}C-PEPA in acetic anhydride (4.0 mL) and at reflux temperature (150 °C) in 2 h. The crystals which formed on cooling at 4 °C overnight were filtered, washed with copious amounts of chilled hexane, and recrystallized from a 60:40 hexane−toluene solution. The recrystallized product was dried at 70 °C in a vacuum for 12 h to yield 1.74 g (70.0% yield) of light yellow powder.

DSC (at a heat rate of 20 °C/min under nitrogen): melting point peak at 155 °C (sharp). IR (KBr pellet): 2133 cm^{-1} ($^{13}C{\equiv}^{13}C$), 1844 and 1772 cm^{-1} (anhydride C=O). ^{1}H NMR in DMSO: 8.25 and 8.12 ppm of H’s in 3,5,6-position in phthalic anhydride; 7.67 and 7.51 ppm of H’s in aromatic ring. Anal. Calcd for $^{13}C_2C_{14}H_8O_3$: C, 77.6; H, 3.2; O, 19.2. Found: C, 77.2; H, 3.4; O, 19.3.

Synthesis of ^{13}C-Labeled 3,4′-Bis[(4-phenylethynyl)phthalimido]diphenyl Ether (^{13}C−PEPA-3,4′-ODA). The ^{13}C-labeled imide model compound (Figure 8) used in this study was ^{13}C-PEPA-3,4′-ODA prepared from ^{13}C-labeled 4-phenylethynylphthalic anhydride (^{13}C-PEPA) and 3,4′-oxydianiline (3,4′-ODA) in *N*,*N*′-dimethylformamide (DMF) solvent. ^{13}C-PEPA (0.45 g, 1.8 mmol) and 3,4′-oxydianiline (3,4′-ODA) (0.18 g, 0.9 mmol) were each dissolved in DMF (2.0 mL), respectively. Those two solutions were then mixed together and stirred for 12 h at room temperature. An excess of acetic anhydride was then added, the solution was refluxed for an hour cooled, and the product, which precipitated, was filtered and air-dried. The crude product was recrystallized from DMF, rinsed with methanol, and dried in vacuo at 200 °C for 6 h. The light yellow powder (0.484 g) was obtained in a yield of 80.5%.

DSC: melting point peak at 297 °C (sharp), at a heat rate of 20 °C/min under nitrogen. IR (KBr pellet): 2141 cm^{-1} ($^{13}C{\equiv}^{13}C$), 1778 and 1713 cm^{-1} (imide C=O). Anal. Calcd for $^{13}C_4C_{40}H_{24}N_2O_5$: C, 80.1; H, 3.6; N, 4.2. Found: C, 79.5; H, 3.8; N, 4.2.

Synthesis of ^{13}C-Labeled Phenylethynyl-Terminated Imide Oligomer (^{13}C−PETI-5). The ^{13}C-labeled imide oligomer (Scheme 9) used in this study was PETI-5 prepared from ^{13}C-PEPA, 3,3′4,4′-biphenyltetracarboxylic dianhydride (BPDA), 3,4′-oxydianiline (3,4′-ODA), and 1,3-bis(3-aminophenoxy) benzene (APB) in *N*-methyl-2-pyrrolidinone (NMP) solvent by the procedure of Bryant et al.[10] BPDA (2.672 g, 9.08 mmol) and a mixture of 3,4′-ODA (1.699 g, 8.50 mmol) and APB (0.439 g, 1.50 mmol) were each dissolved in NMP (7.0 mL), and then mixed and stirred for 1 h at room temperature. ^{13}C-PEPA (0.450 g, 1.80 mmol) was then added, and the solution was diluted with NMP to approximately 30% w/w and stirred for another 24 h under the nitrogen. Toluene (20 mL) and a small amount of NMP were then added, and the solution was heated to reflux using a Dean−Stark trap to remove water as an azeotrope. Toluene (20 mL) and a trace of water were collected in the first hour. The solution was refluxed for another 4 h and cooled. The solid which precipitated on addition of the solution to methanol (300 mL) was filtered and dried under a vacuum at 200 °C overnight to yield a yellow powder (4.65 g, 94.9%).

DSC (at a heat rate of 20 °C/min under nitrogen): glass transition temperature (T_g) at 224 °C and melting point peak at 351 °C. IR (KBr pellet): 2137 cm^{-1} ($^{13}C{\equiv}^{13}C$), 1778 and 1716 cm^{-1} (imide C=O). Anal. Calcd for PETI-5: C, 74.4; H, 3.2; O, 16.7. Found: C, 73.9; H, 3.4; O, 16.8.

Characterization. DSC. Differential scanning calorimetry (DSC) of imide model compounds, PEPA-3,4′-ODA and ^{13}C-PEPA-3,4′-ODA, and imide oligomers, PETI-5 and ^{13}C-PETI-5, was performed by a Perkin -Elmer DSC, 7 series analysis system at a heating rate of 20 °C/min under nitrogen atmosphere at a flow rate of 20 cm^3/min.

GPC. A Millipore model 150-C gel permeation chromatography (GPC) system was applied to determine the molecular weight of ^{13}C-labeled and unlabeled PETI-5 oligomer; NMP with 0.05 M LiBr was used as a solvent. The results were calibrated by standard poly(methyl methacrylate) (PMMA).

IR. Infrared spectra (IR) of the model compound and PETI-5 (KBr pellet) were taken by using a Nicolet Magna 560 FT-IR system.

Solution NMR. High-resolution solution nuclear magnetic resonance (NMR) spectra were acquired using a Bruker DMX500 NMR spectrometer. The solution NMR samples of ^{13}C-PEPA-3,4′-ODA and ^{13}C-PETI-5 were prepared from their NMP solution with additional deuterated dimethyl sulfoxide (DMSO-d_6). ^{13}C-PEPA-3,4′-ODA and ^{13}C-PETI-5 were dissolved in NMP solvent by heating to 200 °C for 5 s. The solution NMR samples of the low molecular weight compounds with various double-bonded structures were prepared from deuterated chloroform solution ($CDCl_3$). Chemical shifts were given with respect to tetramethylsilane (TMS)

Solid-State NMR Technique. Solid-state magic-angle spinning (MAS) ^{13}C NMR spectra were acquired by using single-pulse gated proton-decoupling experiments (1PDA) at 75 MHz using a Chemagnetics CMX300 NMR spectrometer with a commercial double-bearing 5 mm MAS probe. The magic angle was set using the ^{79}Br resonance of KBr. Samples (~100 mg) were packed in a Zirconia pencil rotor and spun at the magic angle at 5, 8, or 10 kHz as desired. The 90° pulse widths for ^{1}H and ^{13}C were 5 μs. A relaxation time of 75 s ($>5T_1$) was applied for single-pulse experiments to allow thermal equilibrium, and at least 16 scans were utilized to achieve a proper signal-to-noise ratio. For more accurate data, some spectra were collected after 128 and 700 scans. A 76 kHz proton decoupling field was used during the acquisition of the free induction decay. Chemical shifts were given with respect to tetramethylsilane (TMS) by using an external sample of solid glycine (176.03 ppm) for ^{13}C as the secondary reference.

Results and Discussion

Within the last five years, cross-linked structures of the cured PETI polyimides have been proposed based on the knowledge of acetylene cross-linked chemistry and the expected steric effects of phenyl groups on the ethynyl structures. The principal views on the cross-linked structures were focused on the polyene structures (Scheme 10a, reaction 1)[15] and cycloolefinic ring structures (Scheme 10b, reaction 6) derived from intra- or intermolecular reactions of the polyene.[11] All the possible ethynyl reactions are summarized in Scheme 10, which includes the hexaphenyl substituted aromatic ring structure (Scheme 10a, reaction 2). Synthetic ^{13}C-PEPA-3,4′-ODA and ^{13}C-PETI-5 gave IR spectra and DSC thermographs identical to the unlabeled model compound and LaRC PETI-5 oligomer (Figures 1 and 2). The NASA LaRC PETI-5 and synthetic ^{13}C-PETI-5 gave similar molecular weights as determined by GPC based on the PMMA calibration. A number-average molecular weight (M_n) of 8380 for NASA LaRC PETI-5 and of 8340 for synthesized ^{13}C-PETI-5 were obtained. A polydispersity of 1.7 for both samples was obtained. The GPC−differential viscometry (GPC/DV) technique[16] gave $M_n \sim 8050$. The stoichiometry of PETI-5 was adjusted to give a theoretical M_n of 5000, but the experimental data show that it is above 8000.

To identify the chemical structures of synthesized model compound and PETI-5 resin and to verify solid-state NMR spectra, ^{13}C solution NMR spectra of the starting materials, PEPA, PEPA-3,4′-ODA, and PETI-5 were recorded and are shown in Figure 3. The ^{13}C-enriched ethynyl carbons gave strong peaks in the region of 87−94 ppm, aromatic carbons in the region of 118−157 ppm, and an imide carbonyl group at 167 ppm. In addition, to help in the interpretation of the possible structure types generated during the cure process, solution ^{13}C NMR spectra of several model compounds were used to establish the ^{13}C chemical shift assignments for comparison with ^{13}C NMR spectra of the cured ^{13}C-PEPA-3,4′-ODA and ^{13}C-PETI-5 materials. The structural types and chemical shifts are listed in Table 1.

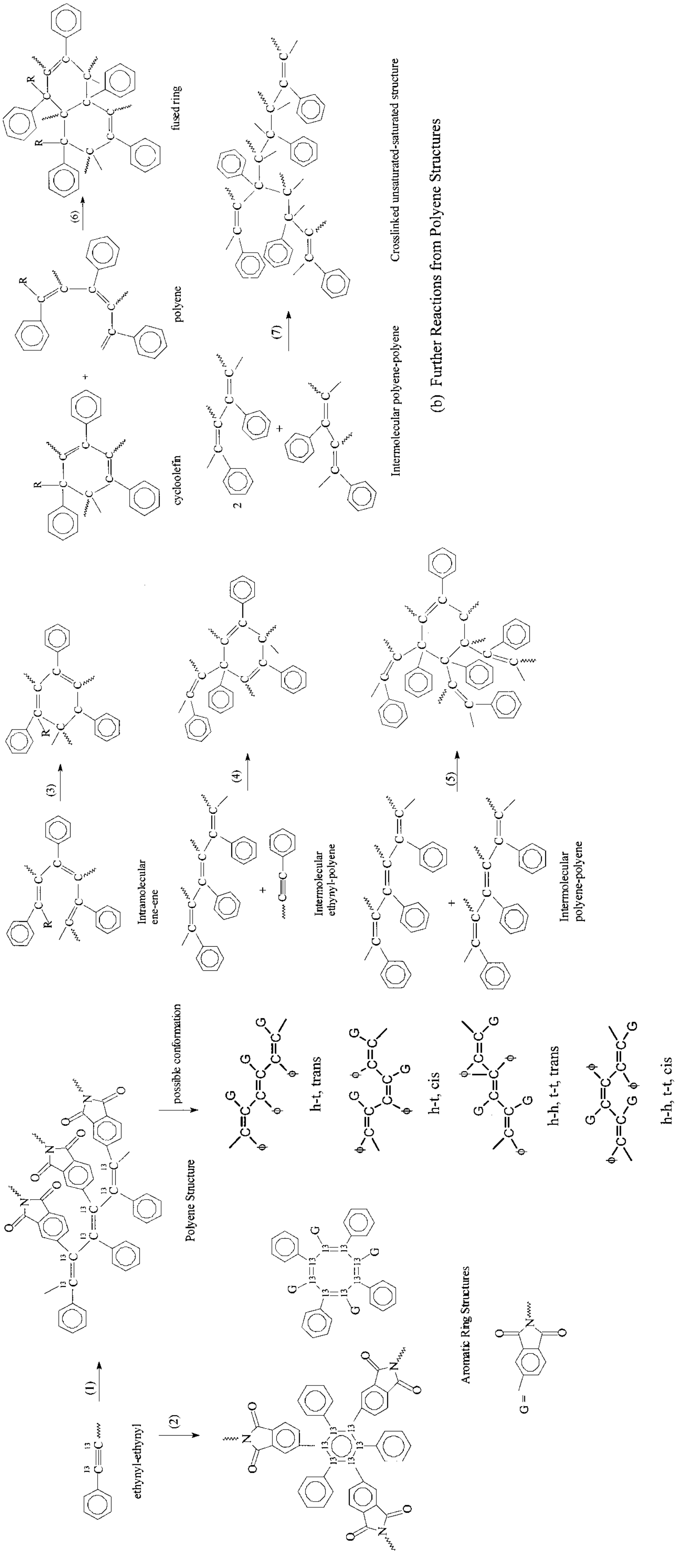
PEPA-3,4′-ODA Model Compound Studies. As an aid in the understanding of the cross-linking reaction and reaction products, a model compound, PEPA-3,4′-ODA, was used. This compound helped to resolve the signal overlaps generated by the PETI-5 oligomer during the cure process. Selectively ^{13}C-enriched material was used to probe the triple bond signal decreases and follow new bond formation during the curing process. The model compound was cumulatively cured in the solid-state according to the following schedule: 318 °C−80 min, 336 °C−80 min, 355 °C−30 min, 373 °C−30 min, 373 °C−60 min, and 380 °C−1 h. Stacked spectra of PEPA-3,4′-ODA, shown in Figure 4, were acquired by using gated ^{13}C single-pulse experiments as the curing temperature was increased from room temperature up to 380 °C. The chemical shift assignment was based on the chemical environment of each individual ^{13}C resonance. These values favorably compared with the published ^{13}C chemical assignment of similar compounds,[4−5,12] and were confirmed by our solution NMR studies (Figure 3).

To ensure that the utilized acquisition pulse delay of 75 s is sufficient (or longer than $5T_1$) for accurate ^{13}C peak integration, inversion recovery spin−lattice relaxation time (T_{1ir}) measurements were performed, and T_{1ir} values were calculated by using curve-fitting analysis of the variable recovery time. The results showed that a 75 s acquisition delay time is essential for both cured model compound ($T_1 = 9.5$ s for PEPA-3,4′-ODA cured at 380 °C) and cured imide oligomer ($T_1 = 10.3$ s for PETI-5 cured at 400 °C).

As shown in Figure 4, in the uncured state, the ^{13}C-labeled triple bond signals were observed in a range 85−92 ppm, whereas almost no other signals appeared except the spinning sidebands (SSB) of the ^{13}C-enriched triple bond carbons. After curing at 318 °C for 80 min, two groups of new peaks emerged at 125−145 and 50−65 ppm, attributed to the newly formed $^{13}C{=}^{13}C$ double bonds and saturated $^{13}C{-}^{13}C$ single bonds, respectively. As the temperature increased, we observed that triple-bond signals gradually decreased whereas signals arising from the double bonds and single bonds increased. After 373 °C for 1 h no signal due to $C{\equiv}C$ was observed. This was confirmed by measuring the polymer after cure at 380 °C under a high spinning rate of 10 kHz and after 128 repetitive scans (Figure 5). The ethynyl to ethynyl addition reaction can generate four possible complex geometric structures, as well as cyclic structures indicated in Scheme 10.

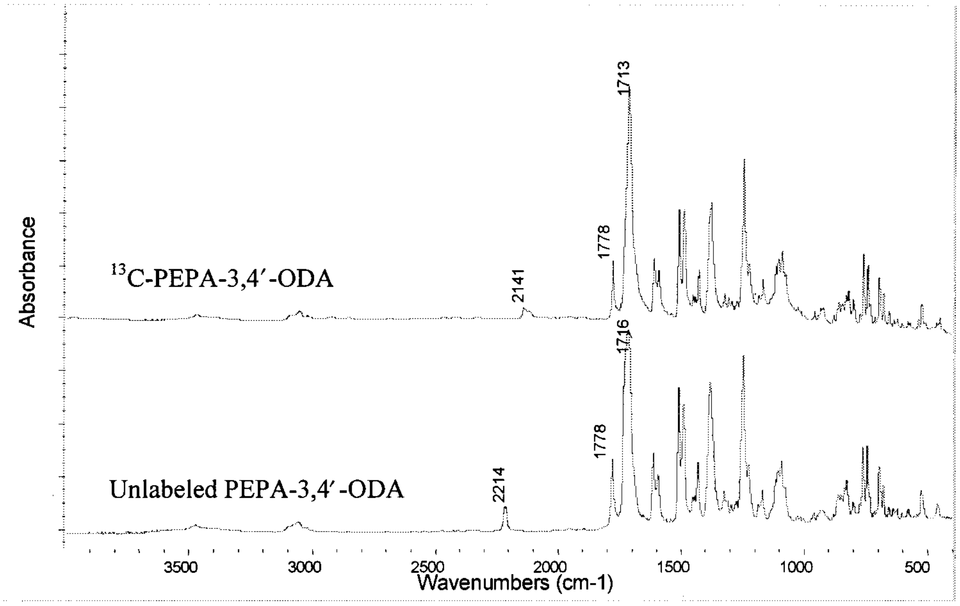
Quantitative analyses of the NMR data acquired at a spinning rate of 5 kHz and 16 scans for ^{13}C-PEPA-3,4′-ODA were performed by calculating the relative percentage of ^{13}C peak integration as shown in Table 2. This was done by calculating the percentage of each bond type by integration of the assigned absorption for each. The overlapped spinning sidebands of the ^{13}C-enriched ethynyl groups were subtracted for this calculation. The subtraction spectrum of cured unlabeled PEPA-3,4′-ODA from cured ^{13}C-PEPA-3,4′-ODA (Figure 7) shows broad absorption peaks over the ranges 110−155 and 50−75 ppm. The subtraction analysis was performed based on the assumption that the carbonyl group does not change. The absorption peaks between 50 and 75 ppm fall in the range for saturated C−C single bonds, while the broad absorption in the range

Scheme 10. Proposed Cure Reactions of Phenylethynyl End-Capped Group

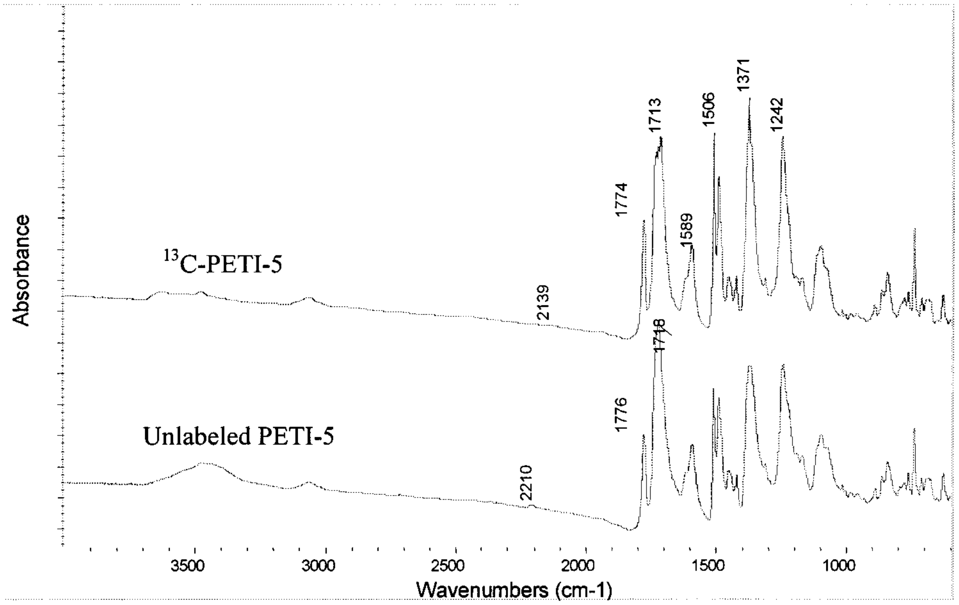


(b) Further Reactions from Polyene Structures

(a) Polyene and aromatic ring structures from phenylethynyl group reactions



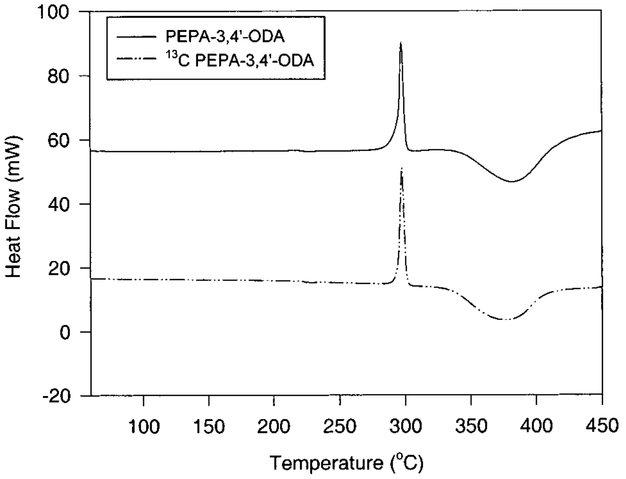
(a) PEPA-3,4′-ODA



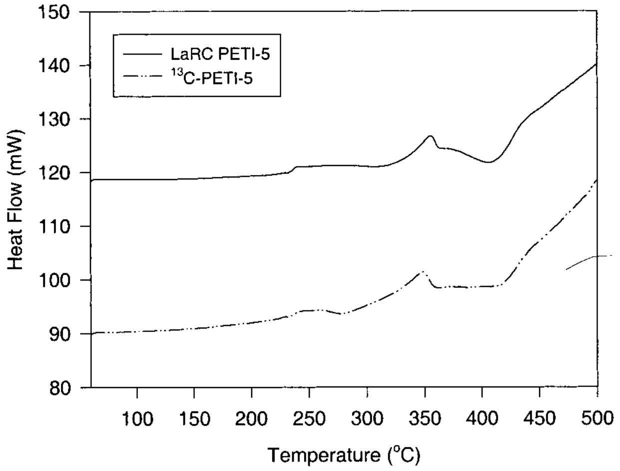
(b) PETI-5

Figure 1. IR spectra of ^{13}C-labeled and unlabeled PEPA-3,4′-ODA and PETI-5.

110−150 ppm falls in the range for various types of double bonds, conjugated double bonds, and aromatic ring structures. Clearly the weak signals which appear at 126 ppm due to the aromatic peaks of cured unlabeled material are excluded in the subtraction spectrum. This indicates that the double bonds formed directly from the ^{13}C-labeled phenylethynyl triple bonds are essentially different from the double bonds in the aromatic ring structures of the starting material. The chemical shifts in the range 126−155 ppm with a strong shift at 136 ppm in the subtraction spectrum of cured ^{13}C-PEPA-3,4′-ODA fall in the range for unsaturated double-bonded structures and aromatic and fused ring systems. Chemical shifts for various types of aromatic fused ring, olefins and polyenes, and partially saturated aromatics are listed in Table 1. The chemical shift range for the aromatic carbons falls between 120.6 and 143.5 ppm and for conjugated olefins in the range 124.6−146.8 ppm, while that for the aliphatic saturated carbons falls between 22.4 and 39.4 ppm. Since the polymeric material is insoluble, it is not possible to separate the components of cured PEPA-3,4′-ODA for identification. However, the chemical shifts of the products of the polymerization reaction are closely related to the chemical shifts of these compound types, and therefore, a general scheme for potential product types can be assigned as indicated in Scheme 10. The evidence for the formation of polyene structures and C−C single-bonded structures is strong based on chemical shift data, but detailed structural features remain unclear. The formation of new aromatic structures resulting from a trimerization or tetramerization reaction to form



(a) PEPA-3,4′-ODA



(b) PETI-5

Figure 2. DSC thermograms of ^{13}C-labeled and unlabeled PEPA-3,4′-ODA and PETI-5.

hexasubstituted benzenes or octasubstituted cyclooctatetraenes cannot be verified or discounted from the ^{13}C NMR data. The presence of stable aromatic structures should result in a more thermooxidatively stable material than a polyene structure. This has not been investigated systematically for comparison with high-temperature aromatic thermoplastic polyimides.

As the curing reaction proceeded from 318 to 373 °C, the peak integration values for the triple-bond signals decreased from 91.5% to 3.1% and finally disappeared, while the integration values for unsaturated double bonds increased from 8.5% to 87.2% and then decreased to 81.9% after continued cure at 380 °C for 2 h, and the aliphatic single bonds increased from zero to 10.8%–15.5%. The carbon percentage for the carbonyl signal remained relatively constant during the whole curing period, as expected. The percentage differences of peak integration for the double bonds and single bonds suggested that the major reaction of ^{13}C≡^{13}C is the formation of new ^{13}C=^{13}C double bonds, and a small fraction of the ^{13}C=^{13}C bonds reacted further to form ^{13}C–^{13}C single bonds at a low temperature relative to the final cure temperature of 380 °C. Of special significance is the appearance of 1.8% aliphatic ^{13}C–^{13}C single bonds after cure at 318 °C for 80 min, which increases to a concentration of 12.6% after 336 °C for 80 min. Clearly, this shows that the double bond ^{13}C=^{13}C formed from ^{13}C≡^{13}C continues to react intermolecularly or intramolecularly to form ^{13}C–^{13}C single bonds. The possible structures that can form single bonds are shown in reactions 3–7 in Scheme 10b. Analysis of these structures in terms of the concentration of carbon–carbon single bonds and carbon–carbon double bonds and on the complexity of the reaction clearly suggests that molecules with structural features shown in reactions 3, 4, and 7 are more likely than molecules with structural features shown in reactions 5 and 6. If the structures in reactions 3 and 4 represented 100% of the carbon–carbon single-bonded reaction products, the percentage of double bonds and single bonds would be 66.5% and 33.5%, respectively. Since only about 10.0% single carbon–carbon bonds are present, then it can be assumed that molecules with these structural features represent a small fraction of the ^{13}C present. Therefore, the percentage difference of carbon peak integration for the double bonds and single bonds (Table 2) suggests that the major reaction of ^{13}C≡^{13}C is the formation of new ^{13}C=^{13}C double bonds with only a small fraction of ^{13}C=^{13}C reacting further to form ^{13}C–^{13}C single bonds.

For more quantitative data, to fully suppress the spinning sidebands, single-pulse ^{13}C NMR spectra were acquired at a spinning rate of 10 kHz, on cured and uncured samples (Table 3). Theoretically, based on the chemical structure of uncured ^{13}C-labeled PEPA-3,4′-ODA, the calculated ^{13}C percentages of C≡C, C=C, and C=O are 90.8%, 8.3%, and 0.8% respectively, which are in agreement with the values derived from integration of these peaks. Therefore, the data in Table 3 more nearly represent the ^{13}C levels due to newly formed double (~88%) and single (~10%) bonds. The increase in the ^{13}C levels in carbonyl (3.8% vs 1%) merely reflects the error in the measurements, and not to carbonyl formation. It has been noted that for both the 5 and 10 kHz spinning rates, the integration error may increase as the peaks become broader and overlapped due to increases in the high molecular weights. The long chain chemical structures cause long relaxation times, resulting in weak signal absorption.

PETI-5 Studies. Solid-state NMR experiments were also applied to study the curing process of the imide oligomer PETI-5 by using a similar approach as described for the PEPA-3,4′-ODA study. The following cure processes for PETI-5 were carried out in this study: 350 °C–15 min, 360 °C–20 min, 370 °C–30 min, 370 °C–h, 380 °C–1 h, 390 °C–2 h, 400 °C–3 h. Three separate samples were used for the first three schedules. One sample was used for the study commencing at 370 °C–1 h to a final cumulative cure at 400 °C–3 h. The relatively high molecular weight for uncured PETI-5 brought more difficulty in NMR integration due to the severe line broadening and overlapping of NMR peaks. Analyses of these spectra were again based on the calculation of the peak integration percentages of each interested component. The results obtained at spinning rates of 8 and 10 kHz are summarized in Tables 4 and 5. The stacked ^{13}C NMR spectra of PETI-5 oligomer at a spinning rate of 10 kHz before cure and after cure at 400 °C are shown in Figure 6. The uncured material gave signals for the C≡C triple bond at 85–92 ppm, the C=C double bond at 108–154 ppm and the C=O carbonyl carbon around 165 ppm. For ^{13}C-labeled PETI-5 with a number-average weight of 8340 (before curing), the calculated ^{13}C percentages of C≡C, C=C, and C=O are 43.7%, 48.7%, and 7.6%, respectively,

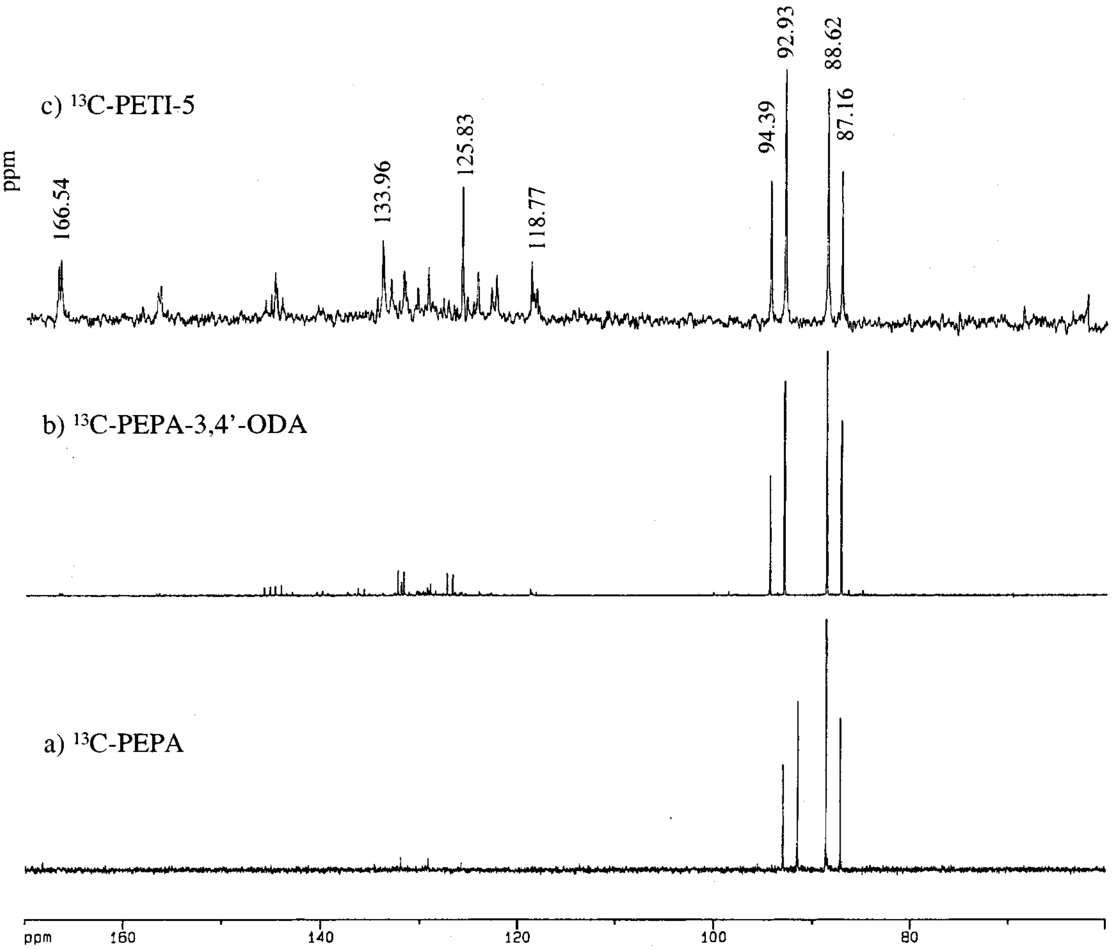


Figure 3. Solution NMR spectra of ^{13}C-labeled (a) PEPA (in DMSO-d_6), (b) PEPA-3,4′-ODA (in NMP + DMSO-d_6), and (c) PETI-5 (in NMP + DMSO-d_6).

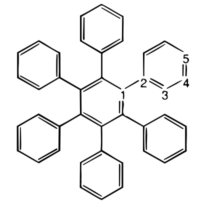
which are very close to the NMR integration values as shown in Table 5.

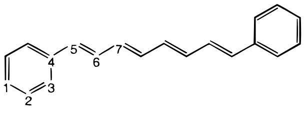
The observed cure mechanism of PETI-5 was similar to the model compound as the cure process proceeds over this temperature range. As given in Table 4, the phenylethynyl triple bond decreased with the increase of cure extent, and was completely consumed after cure at 370 °C for 1 h. The ethynyl group reacted to produce unsaturated double bonds as predicted. A weak broad signal for the C−C-single bonded product is shown in Figure 6, but the low concentration of ^{13}C triple bonds initially prevents integration of this weak signal.

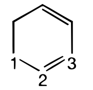
To quantify the double bonds formed and to identify the nature of the double bond formed from the phenylethynyl triple bond, the spectra of cured unlabeled materials were subtracted from the spectra of ^{13}C-labeled cured materials for both PEPA-3,4′-ODA and PETI-5, as shown in Figures 7 and 8, respectively. For the model compound, NMR peak integration showed that 90.8% of carbons in ^{13}C-labeled triple bond were due to the 99% ^{13}C-enriched labeled carbons, whereas only 9.1% of carbons were due to an unlabeled triple bond. Therefore, the double bond appearance in the NMR spectrum from unlabeled sample should be mainly attributed to the aromatic benzenes (9.1%) in the starting compound, while a majority of double bonds in the cured ^{13}C-enriched sample should be derived from the phenylethynyl triple bond only. It is of interest to note that the main double bond peak of cured unlabeled model compound appears as a peak at 126 ppm and that of the cured labeled one appears as a peak at 136 ppm, as shown in Figure 7c. This indicates that the unsaturated double bonds formed directly from the phenylethynyl triple bonds are essentially different from the double bonds in the aromatic ring structures of the starting material and therefore could be attributed to a cyclotrimerization or cylcotetramerization reaction to form hexasubstituted benzenes or octasubstituted cyclooctatetrenes.

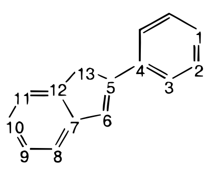
The subtraction spectrum for ^{13}C-PETI-5 resin system (Figure 8c) is not as clearly defined as for ^{13}C-PEPA-3,4′-ODA because of the low concentration of ^{13}C≡^{13}C triple bonds in this high molecular weight ^{13}C-PETI-5, even though the spectra were taken after 700 repetitive scans. The subtraction spectrum (Figure 8c) was scaled up to give better observation. Carbon−carbon single-bond formation was observed by the weak broad absorption in the region 45−70 ppm. The weak single-bond signals prevent a quantitative integration most likely due to a low concentration of the ^{13}C−^{13}C species. The broad absorption in the range between 100 and 150 ppm is indicative of a broad range of unsaturated double bonded structures. The signal peak at 136 ppm increased to a shoulder in the NMR spectrum of the cured labeled sample. The increase of peak intensity at 136 ppm is much weaker due to the low concentration of the triple bond in the PETI-5 oligomer. However, this is an indication that a trimerization or tetramerization reaction to form substituted aromatic ring structures occurs in the PETI-5 system. A quantitative or even

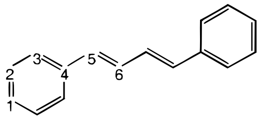
Table 1. Chemical Shifts of the Known Small Compounds in $CDCl_3$ Solution

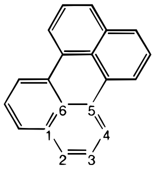
Sample	^{13}C	NMR Peak
	1	140.8
	2	140.4
	3	126.7
	4	131.5
	5	125.3

	1	129.6
	2	133.1
	3	127.9
	4	137.8
	5	129.1
	6	126.8
	7	133.9

	1	22.4
	2	126.6
	3	124.6

	1	127.0
	2	129.1
	3	126.0
	4	136.4
	5	146.8
	6	126.9
	7	145.8
	8	121.4
	9	127.9
	10	125.1
	11	124.1
	12	143.5
	13	39.4

	1	129.6
	2	133.2
	3	127.9
	4	137.7
	5	129.0
	6	126.8

	1	131.7
	2	128.3
	3	126.9
	4	120.6
	5	135.2
	6	129.2
	----------	

semiquantitative determination cannot be made from the ^{13}C NMR data. The arguments for the structure types formed during the cure of the PEPA-3,4′-ODA model compound clearly apply to the PETI-5 cure products based on the ^{13}C chemical shift data in Figure 8 and a comparison of chemical shift data of compounds in Table 1.

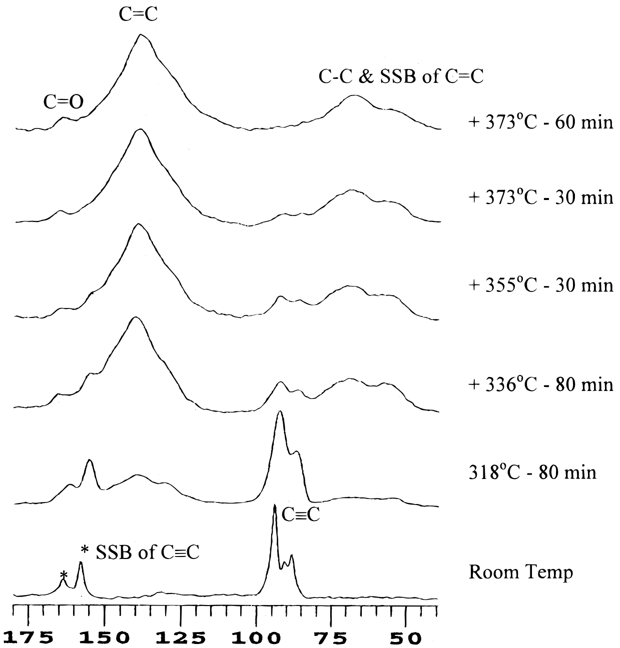


Figure 4. Solid-state ^{13}C NMR spectra of ^{13}C-labeled PEPA-3,4′-ODA (a) before and (b) after curing (at a spinning rate of 5 kHz). SSB = spinning side band.

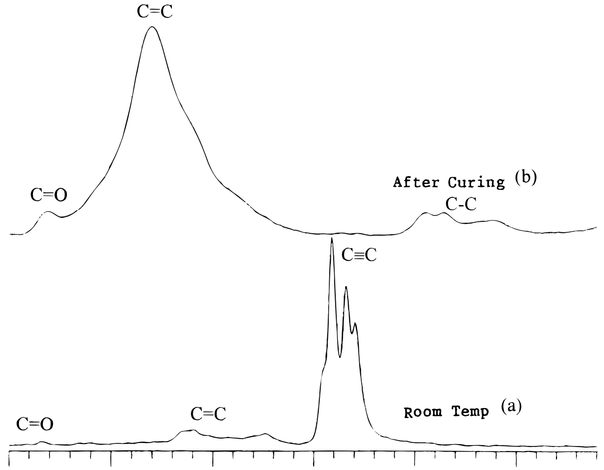


Figure 5. Solid-state ^{13}C NMR spectra of ^{13}C-labeled PEPA-3,4′-ODA (a) before and (b) after curing (at a spinning rate of 10 kHz).

Table 2. NMR Integration Results of ^{13}C-Labeled PEPA-3,4′-ODA at a Spinning Rate of 5 KHz

	^{13}C carbon percentage from integration			
sample	C≡C	C=C	C=O	C−C
room temp	91.5	8.5		
318 °C−80 min	56.2	42.0		1.8
+336 °C−80 min	11.6	72.3	3.5	12.6
+355 °C−30 min	10.5	74.1	2.5	12.9
+373 °C−30 min	3.1	83.7	2.4	10.8
+373 °C−60 min		87.2	1.9	10.9
+380 °C		81.9	2.6	15.5

From our earlier studies,[11] the kinetics of the thermal cure of PEPA-3,4′-ODA was investigated by following the disappearance of the ethynyl group over the temperature range from 318 to 373 °C, and the reaction followed first-order kinetics determined by infrared spectroscopy. However, the solid-state ^{13}C NMR results demonstrated that not only do the ethynyl triple bonds react to form carbon−carbon double bonds but also some of the newly formed double bonds further react to form carbon−carbon $^{13}C-^{13}C$ single bonds at the low temperatures of 318 and 336 °C. This strongly suggests that the earlier kinetic results by the IR technique do not reflect the whole cure reaction mechanism but only the first step reaction from ethynyl triple bond to double bond. The first-order kinetic data from IR study were based on starting materials, and the concentration of the triple bonds. Therefore, if we consider the whole cure reaction of PEPA-3,4′-ODA, including the single-bond formation, the reaction order should be > 1. The kinetics of the thermal cure of PETI-5, based on the increase of glass transition temperature[11] or the decrease of exothermic peak of cure reaction[17] by DSC, gave 1.5-order kinetics for the overall reaction. Those DSC kinetic data were derived from the final chemical structures of the materials after curing, and therefore, reflected the whole

Table 3. NMR Integration Results of ^{13}C-Labeled PEPA-3,4′-ODA at a Spinning Rate of 10 kHz

	^{13}C carbon percentage from integration			
sample	C≡C	C=C	C=O	C−C
room temp	actual: 90.9	8.3	0.8	
	theory: 90.8	8.3	0.9	
380 °C−120 min		88.2	3.8	8.0

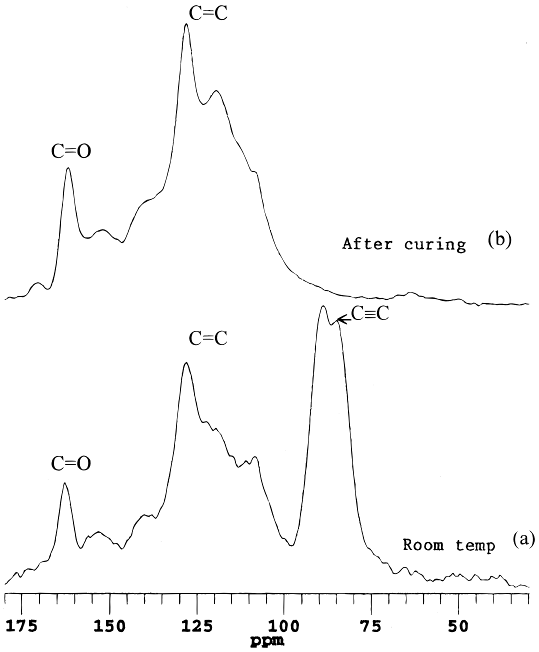


Figure 6. Solid-state ^{13}C NMR spectra of ^{13}C-labeled PETI-5 (a) before and (b) after curing (at a spinning rate of 10 kHz).

Table 4. NMR Integration Results of ^{13}C-Labeled PETI-5 at a Spinning Rate of 8 KHz

	^{13}C carbon percentage from integration		
sample	C≡C	C=C	C=O
room temp	44.7	50.5	4.8
350 °C−15 min	42.2	52.3	5.5
360 °C−20 min	22.5	65.0	12.5
370 °C−30 min	3.1	85.4	11.5
370 °C−60 min		86.0	14.0
+380 °C−1 h		85.9	14.1
+390 °C−2 h		85.9	14.1
+400 °C−3 h		89.3	10.7

Table 5. NMR Integration Results of ^{13}C-Labeled PETI-5 at a Spinning Rate of 10 KHz

	^{13}C carbon percentage from integration			
sample	C≡C	C=C	C=C	C=O
room temp	actual: 42.2	42.2	51.0	6.8
theory: 43.7	43.7	48.7	7.6	
400 °C−3 h			85.1	14.9

cure reaction mechanism. The complicated 1.5-order kinetics suggests there is more than one reaction step involved in the cure reaction, even though solid-state ^{13}C NMR data cannot provide sufficient evidence to differentiate between ene and aromatic structures or differentiate between ring or chain ^{13}C−^{13}C single-bonded structures of cured PETI-5 resin, which could help in the interpretation of the kinetic studies. It becomes clear from this study, that a limitation exists in following the total cure reaction by the disappearance of the triple bond and in determining structural features by solid-state ^{13}C NMR.

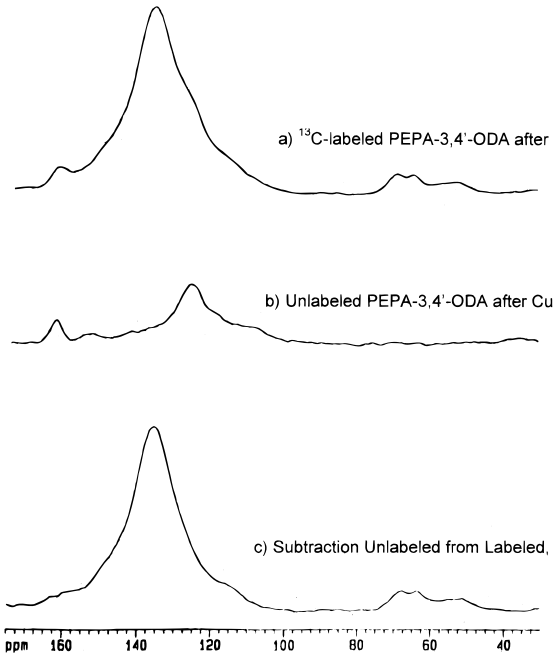


Figure 7. Comparison of solid-state ^{13}C NMR spectra of ^{13}C-labeled and unlabeled PEPA-3,4′-ODA after curing (at a spinning rate of 10 kHz).

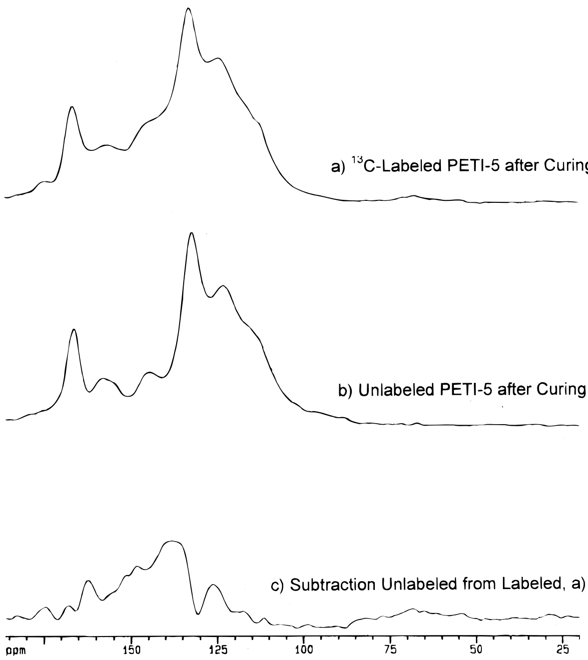


Figure 8. Comparison of solid-state ^{13}C NMR spectra of ^{13}C-labeled and unlabeled PETI-5 after curing (at a spinning rate of 10 kHz).

Conclusion

Solid-state ^{13}C magic-angle spinning nuclear magnetic resonance (NMR) was performed to determine the cross-linked structures of phenylethynyl end-capped polyimides. The cure reactions of model compound, PEPA-3,4′-ODA, and imide oligomer, PETI-5, with ^{13}C-enriched phenylethynyl end-capped groups were investigated in this study. For PEPA-3,4′-ODA, the major reaction was the ethynyl to ethynyl reaction to form double bonds, and a minor reaction of double bond to double bond or ethynyl to conjugated double bond to further form single bonds was also observed. In the cured sample, the percentages of double-bond carbon increased from 8.3%

to 88.2% and single-bond carbon increased from zero to 8.0% according to data from a spinning rate of 10 kHz. In the PETI-5 study, equivocal evidence for formation of the single-bonded structures was also observed as a result of the cure reaction. The double-bond carbon percentage increased from 51.0% at the beginning up to 85.1% after curing as determined from the data collected at a spinning rate of 10 kHz. The major curing reaction for the phenylethynyl end-capped PETI-5 oligomer is ethynyl to ethynyl to produce chain extension or polyene structures. The formation of hexasubstituted or tetrasubstituted aromatic ring structures from PEPA-3,4′-ODA model compound or PETI-5 could be rationalized based on chemical shift data, but the broad absorption peaks prevented their identity and integration for quantitative evaluation.

References and Notes

(1) Landis, A. L.; Bilow, N.; Boschan, R. H.; Lawrence, R. E.; Aponyi, T. J. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1974**, *15*, 533−537.

(2) Bilow, N.; Landis, A. L.; Milles, L. J., **1975,** US Patent 3,879,349.

(3) The family of acetylene end-capped oligomer is sold commercially as thermids by Natural Starch and Chemical Corp.

(4) Swanson, S. A.; Fleming, W. W.; Hofer, D. C. *Macromolecules* **1992**, *25*, 582−588.

(5) Sefcik, M. D.; Stejskal, E. O.; McKay, R. A.; Schaefer, J. *Macromolecules* **1979,** *12*, 423−425.

(6) Pickard, J. M.; Jones, E. G.; Goldfarb, I. J. *Macromolecules* **1979**, *12*, 895−902.

(7) Bryant, R. G.; Jensen, B. J.; Hergenrother, P. M. *Polym. Prepr.* **1992**, *33* (1), 910−911.

(8) Hergenrother, P. M.; Bryant, R. G.; Jensen, B. J.; Smith Jr. J. G.; Wilkinson, S. P. *Soc. Adv. Mater. Proc. Eng.* **1994**, *39* (1), 961−968.

(9) Bryant, R. G.; Jensen, B. J.; Hergenrother, P. M. *J. Appl. Polym. Sci.* **1996**, *59*, 1249−1254.

(10) Hergenrother, P. M.; Bryant, R. G.; Jensen, B. J.; Havens, S. J. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*, 3061−3067.

(11) Fang, X.; Rogers, D. F.; Scola, D. A.; Stevens, M. P. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 461−470.

(12) Baugher, A. H.; Espe, M. P.; Goetz, J. M.; Schaefer, J.; Pater, R. H. *Macromolecules* **1997**, *30*, 6295−6301.

(13) Meador, M. A. B.; Johnston, J. C.; Cavano, P. J. *Macromolecules* **1997**, *30*, 515−519.

(14) Takekoshi, T.; Terry, J. M. *Polymer* **1994**, *35*, 4874−4880.

(15) Hergenrother, P. M.; Smith Jr. J. G. *Polymer* **1994**, *35,* 4857−4864.

(16) Cano, R. J.; Jensen, B. J. *J. Adhes.* **1997**, *60*, 113−123.

(17) Hinkley, J. A. *J. Adv. Mater.* **1996,** *27,* 55−59.

(18) Harrington, K. A.; Orwoll, R. A.; Jensen, B. J.; Young, P. R, *Int. SAMPE Symp. Exhib.* **1996,** *41*, 135−148.

(19) Wood, K. H.; Orwoll, R. A.; Young, P. R.; Jensen, B. J.; Mcnair, H. M. *Int. SAMPE Symp. Exhib.* **1997,** *42,* 1271−1282.

MA991197M