Acetylene-Terminated Polyimide Cure Studies Using ^{13}C Magic-Angle Spinning NMR on Isotopically Labeled Samples

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ABSTRACT: The solid-state cure mechanisms of an acetylene-terminated polyisoimide have been studied using solid-state ^{13}C cross-polarization magic-angle spinning (CPMAS) nuclear magnetic resonance (NMR) spectroscopy on samples which had been selectively labeled using ^{13}C labeled precursors. The polymer backbone was labeled at sites which were expected to be involved in the cure chemistry: the benzophenone carbonyl carbon, the isoimide/imide carboxyl carbon, the C-1 (quaternary acetylene) ethynyl carbon, or the C-2 (terminal acetylene) ethynyl carbon. After preparing and subsequently curing the selectively labeled and unlabeled (control) resins identically, difference spectroscopy techniques were used to subtract the resonances due to the natural abundance ^{13}C nuclei, thereby resulting in spectra which were due to the selective label alone. Combining this technique with delayed decoupling experiments in which one allows the ^{13}C nuclei that are coupled to protons (^1H) to relax, those resonances which are protonated and nonprotonated were identified. The results were correlated with model and related compounds. The carbonyl function remained unchanged in the cured product. The isoimide/imide carboxyl carbons underwent an isomerization reaction to produce the expected imide structure. The solid-state ethynyl cure products were found to contain aromatic structures, condensed polycyclic aromatic structures, backbone addition and bridge structures. Steric factors and population densities of reactive sites in the polymer could influence the ratio of these products.

Introduction

The acetylene group has been used as a cure site for many different polymer classes including polyimides,[1] poly(aryl ether sulfones),[2] polyphenylenes,[3] polyesters,[4] poly(phenyl-*as*-triazines),[5] poly(perfluoroalkylene ether benzoxazoles),[6] and poly(phenylquinoxalines).[7] One of the advantages of this cure site is that no volatile byproducts are evolved during its cure. This can result in void-free polymer structures. An understanding of the solid-state reaction mechanisms which could determine cross-link density, mechanical properties, and thermal stability of the final material would be desirable. Unfortunately, the cured polymers are cross-linked and insoluble, making solution spectroscopic analysis difficult. The actual cure chemistry has therefore been subject to conjecture and uncertainty.

It has been speculated that the probable cure reaction is cyclotrimerization[1] to an aromatic ring structure which would result in a thermally stable cure site. However, model compound studies have been carried out which have led to the proposal of biradical[8-11] mechanisms forming linear or cyclic conjugated linkages. Other proposed mechanisms[7] include Glaser coupling to diyne structures, Straus coupling to form ene–yne structures which further rearrange to cyclic structures, Diels–Alder reactions with the polymer backbone to form condensed polycyclic aromatic structures, and Friedel–Crafts alkenylation of the polymer backbone.[12] The products of these mechanisms could further react to form phenylnaphthalene,[13] polyene,[14] polystyrene,[15] and azulene–naphthalene rearrangement products,[16] and poly(phenylphenanthrene),[17] and aromatic products.

Recently, the cure states of acetylene-terminated polymers have been studied using some solid-state techniques including FTIR, NMR, and ESR.[18,19] There have also been several reports[12,19,20] of work in which acetylene polymer chemistry was investigated using solid-state ^{13}C cross-polarization magic-angle spinning (CPMAS) NMR on samples in natural abundance. The NMR results suggest that the products formed are either aromatic, linear polyene chains or alkene addition products, but the interpretation of the data is subject to the limitations inherent in studying the subtle spectroscopic changes which occur on curing amorphous polymers. Thus, although previous experiments using natural abundance ^{13}C NMR have provided insight, the results are not conclusive in identifying actual cure products.

This paper reports the results of a study of the solid-state chemical reactions in a ^{13}C-labeled polyimide which had been prepared using starting materials labeled at sites that are thought to be involved in the cure reactions. The resulting polymers and unlabeled controls were subsequently studied using solid-state ^{13}C NMR. There are several advantages to this approach. First, by performing spectral subtraction on labeled and unlabeled samples that had been made and cured identically, the difference spectra will be that of only the labeled resonances since all other carbons in the samples should be in identical chemical environments and thus have the same chemical shifts and intensities. Also by selectively labeling and observing only one labeled site, one can look at the evolution of only one resonance at a time. Finally, by selectively labeling far above the natural abundance of the ^{13}C nuclei (1.1%), one can reduce the errors due to instrumental artifacts since the relative amount of background signal is reduced. Consequently, one can selectively look at specific resonances in the solid state, observe their evolution, and obtain information which is not attainable with use of optical, X-ray, and other types of spectroscopy.

The polymer chosen for this study was prepared by the condensation of benzophenonetetracarboxylic acid dianhydride (BTDA) and 1,3-bis(3-aminophenoxy)benzene (APB) in a 2:1 molar ratio with subsequent addition of 3-(aminophenyl)acetylene (APA) to produce the acetylene-terminated amic acid oligomer that is known by the trade name Thermid.[21] Subsequently, this oligomer was chemically dehydrated from the amic acid to an isoimide/imide mixture which was isolated for the cure studies using procedures detailed in the literature.[22] The reaction scheme is shown in Figure 1.

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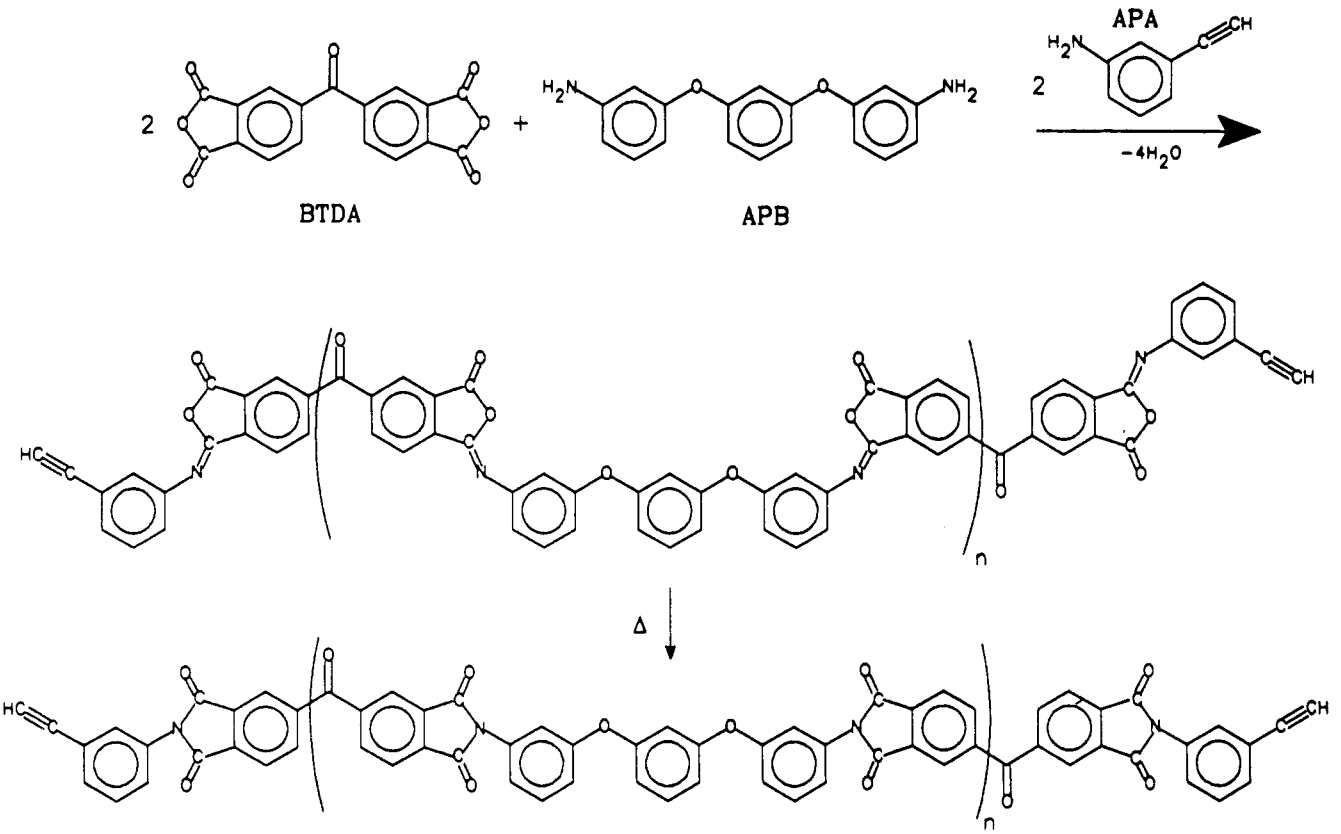


Figure 1. Synthesis of acetylene-terminated isoimide oligomer and cure to imide oligomer.

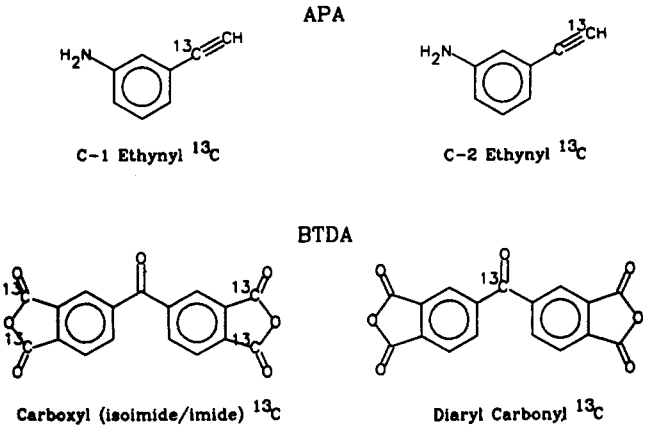


Figure 2. ^{13}C-labeled monomers.

Experimental Section

The unlabeled BTDA was obtained from Aldrich and was sublimed at 200 °C under reduced pressure. The APA and APB were obtained from National Starch and Chemical Corp. The APB was purified by elution down a silica gel column with ethyl acetate/hexanes (1:1). The APA was distilled in a Kugelrohr apparatus under reduced pressure. The selectively labeled compounds, 3-(aminophenyl)acetylene-*1*-^{13}C (99 atom % ^{13}C), 3-(aminophenyl)acetylene-2-^{13}C (99 atom % ^{13}C), benzophenone-$^{13}C_1$-tetracarboxylic acid dianhydride (ketone, 99 atom % ^{13}C), and benzophenone-3,3′,4,4′-tetracarboxylic-$^{13}C_2$ acid dianhydride (99 atom %), are shown in Figure 2 and were obtained from Merck & Co. Each labeled monomer was purified as above.

A typical polymerization is as follows: BTDA (1.46 mmol) and 4.72 mL of dry tetrahydrofuran (THF) were placed in a three-necked 15-mL round-bottomed flask equipped with a thermowell, septum, reflux condensor, nitrogen inlet, and magnetic stirrer, and the flask was heated to reflux with an oil bath. APB (0.749 mmol) was dissolved in 1.73 mL of dry THF and was added slowly through the septum over a period of 1 h. After the addition was complete, the reaction was refluxed for an additional 30 min. The APA (1.46 mmol) in 0.5 mL of dry THF was then added, and the reaction was allowed to reflux for an additional 30 min. The solution was cooled in an ice bath and was diluted with 4.72 mL of dry THF. Trifluoroacetic acid anhydride (8.21 mmol) was added slowly, and the solution was allowed to warm to room temperature overnight. The oligomer was then precipitated in 60 mL of hexanes. The powder was isolated by filtration, washed with additional hexanes, and dried under reduced pressure at 85 °C for 4 h and at room temperature overnight. This yielded approximately 0.76 g of oligomer. The oligomer structure was verified by infrared spectroscopy. Assuming that the polymerization has gone to 100% conversion, the number average degree of polymerization, $\bar{X}_n = (1+r)/(1-r)$, for this oligomer is expected to be 3 on the basis of the stoichiometric imbalance ($r = 0.5$) in the condensation reaction.

Curing of the oligomers was carried out by placing vials of oligomer samples in an 85 °C oven under UHP (99.999%) nitrogen atmosphere. The ramp rate of the oven was controlled at 5 °C per minute. The oven was held at the following temperatures and time intervals during the cure: 85 °C/10 min, 170 °C/30 min, 200 °C/30 min, 300 °C/30 min, and 400 °C/4 h. All samples were prepared identically.

Nuclear magnetic resonance was performed using an IBM Instruments WP-200SY spectrometer equipped with an accessory for high power decoupling and a Doty Scientific magic-angle spinning probe. Chemical shifts for solid-state spectra were referenced with use of adamantane and hexamethylbenzene as external references. The carbon and proton frequencies were 50.328 and 200.13 MHz, respectively. Solution spectra of the uncured oligomers were acquired using 16 384 data points. Solid-state spectra were recorded using 2048 data points and zero-filled to 8192 data points before Fourier transformation. The spectral width was typically 12 500 Hz. The proton 90° pulse width was 5 μs. The spin lock and decoupling fields were 57 kHz, and the speed of the MAS spinner was 3.8 kHz.

The CPMAS NMR experiment is carried out by transferring polarization from the proton spin population to the rare spins (^{13}C) via Hartmann-Hahn matching[23,24] and acquiring the spectrum using dipolar decoupling[25] to eliminate dipolar broadening of the carbon resonances while spinning the sample at the so-called magic angle at a speed fast enough to average out the

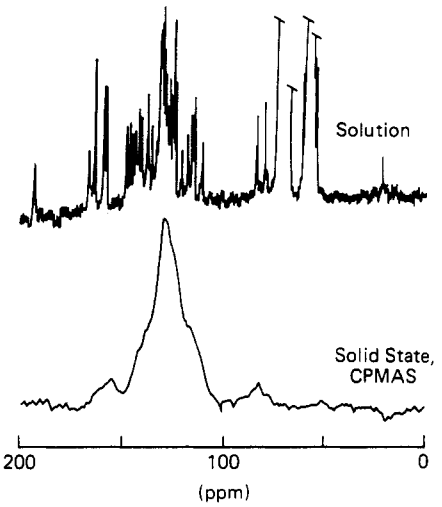


Figure 3. Solution and solid-state CPMAS ^{13}C NMR of uncured unlabeled acetylene-terminated isoimide oligomer (resonances due to the diglyme-d_{14} solvent are marked \).

chemical shift anisotropies to their isotropic values.[26,27]

The spectra were recorded using a 2-ms Hartmann–Hahn contact time and the total suppression of spinning sidebands (TOSS) sequence[28-30] which refocuses the intensity of the spinning sidebands into the respective center frequencies since difference spectroscopy is not reliable with spinning sidebands present. All solid-state spectra were similarly obtained.

Results

A high-resolution solution ^{13}C NMR spectrum of the uncured isoimide oligomer in diglyme-d_{14} along with the 15-MHz solid-state CPMAS spectrum of the same material is shown in Figure 3. The resonances at 70.7, 70.0, and 57.7 ppm in the solution spectrum are from the deuterated solvent, diglyme-d_{14}. The solution spectral shifts are very similar to those reported for the amic acid version of this oligomer[31] with the expected exceptions of the isoimide carbons. Comparing the solution and the solid-state spectra one can see that although there is sufficient resolution in the CPMAS spectrum to distinguish regions of the spectrum, one cannot differentiate most individual resonances as is possible for the solution spectrum. These broad resonances are due primarily to the chemical shift distributions of the polymer in the amorphous solid state. Unfortunately, even though the uncured oligomer is soluble, the cured material is not, so that we are forced to use solid-state techniques rather than the highly resolved solution techniques.

The solid-state 15-MHz CPMAS ^{13}C NMR spectra of the cured and uncured unlabeled oligomer are shown in Figure 4. The disadvantages of the unlabeled solid-state techniques are illustrated here. One can see that several resonances change upon curing but no information is gained about which uncured reactant resonances produce the cured product resonances. The changes upon curing are relatively small compared to the total ^{13}C resonances and are easily confused with the background noise. It is also expected that the mobility of the cured oligomer is reduced in the solid state, which can affect the overall spectrum, and makes interpretations of changes even more suspect. Thus we are forced to selectively label the oligomer in order to obtain meaningful information about the cure sites and products.

In order to be sure we are observing the products from the selectively labeled site, we utilize a "difference" technique which subtracts out the resonances of the naturally abundant ^{13}C resonances. The ability to observe

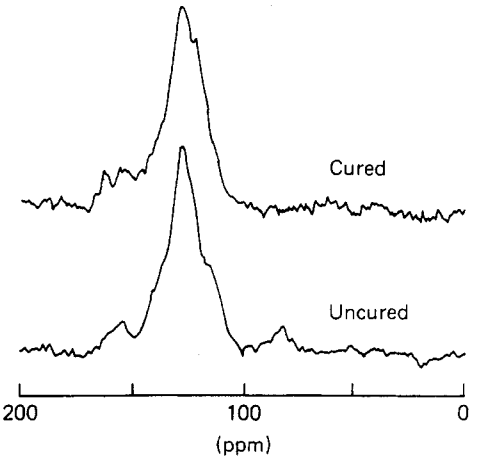


Figure 4. Cured and uncured solid-state CPMAS ^{13}C NMR of unlabeled acetylene-terminated oligomer.

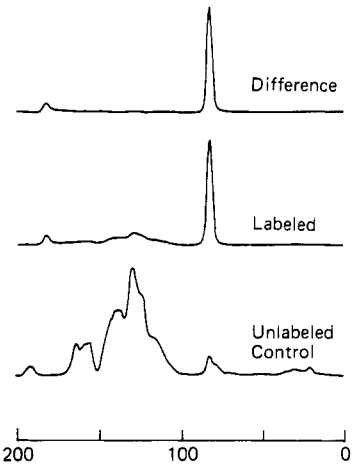


Figure 5. ^{13}C NMR difference spectroscopy: spectrum of the uncured, unlabeled acetylene-terminated oligomer (bottom), spectrum of oligomer labeled at the C-1 ethynyl position (middle), and difference spectrum (top).

only the ^{13}C labeled sites in the labeled samples is illustrated in Figure 5 which shows the spectrum of the uncured, unlabeled control sample, the spectrum of the uncured sample labeled at the C-1 position of the ethynyl groups, and the normalized difference spectrum. (These were all run at 50 MHz with use of a more stable sample probe which gives a better signal-to-noise ratio, thus the improvement in the spectra compared to Figures 3 and 4.) One can observe that all resonances due to natural abundance nuclei are eliminated in the difference spectrum leaving only the isotopically labeled resonance at 84.1 ppm and its spinning sideband.

Another technique used in this set of experiments is delayed decoupling. This is illustrated in Figure 6, a set of spectra of the uncured oligomer labeled at both the diaryl carbonyl (ketone) carbon and at the C-2 ethynyl position. In the delayed decoupling experiment, proton decoupling is turned off for a time between the cross polarization and aquisition steps. This permits carbons with nearby protons to relax rapidly via carbon–proton dipolar coupling. The remaining signal that is acquired is due to carbons with weak proton dipolar coupling. The resulting spectrum is thus due to nonprotonated carbons if the decoupling delay time is chosen correctly, typically 40 μs. Thus, the unprotonated carbonyl carbon resonance at 193 ppm remains unchanged at all delayed decoupling times while the protonated ethynyl carbon at 81 ppm vanishes at a decoupling delay of 40 μs.

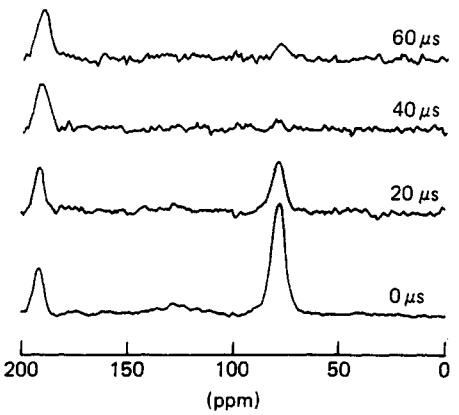


Figure 6. Delayed decoupling experiments of acetylene-terminated oligomer labeled at the diaryl carbonyl and C-2 ethynyl positions.

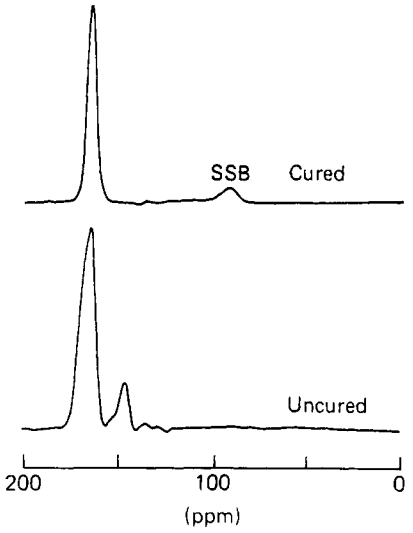


Figure 7. ^{13}C NMR difference spectra of acetylene-terminated oligomer labeled at the carboxyl (isoimide/imide) positions.

The chemical evolution of the isoimide/imide carboxyl carbons can be seen in Figure 7 which shows difference spectra for the oligomer which is ^{13}C labeled at that site. By using *N*-phenylphthalisoimide and *N*-phenylphthalimide as model compounds, the isoimide carbonyl, the C=N isoimide, and the imide carbonyl carbons should have resonances at 166, 145, and 169 ppm, respectively.[32] The difference spectrum confirms that the uncured resin has two peaks at 148.0 and 166.7 ppm for the two different carboxyl carbons in the isoimide ring. The larger resonance at 166.7 is actually due to the overlay of some preimidized carboxyl resonance with the isoimide carbonyl. The partial imidization of the oligomer during chemical dehydration can also be confirmed by the appearance of characteristic imide bands in the IR spectrum of the oligomer. The smaller peak at 148.0 is due to the C=N isoimide carbon. The cured resin has only a single resonance at 166.7 ppm. No additional peaks are observed in the cured sample and resolution enhancement shows that the peak is in fact a single peak rather than two or more closely spaced resonances. Thus, in the process of curing the sample the isoimide/imide carbons produces a single species. This is consistent with the thermal isomerization of the isoimide to the imide.[31,32] The absence of other resonances in the cured sample suggests that acetylene addition reactions at residual amide groups[12] is not a significant mechanism for this oligomer. Since we did not observe resonances for amide groups in the uncured oligomer, this is not surprising.

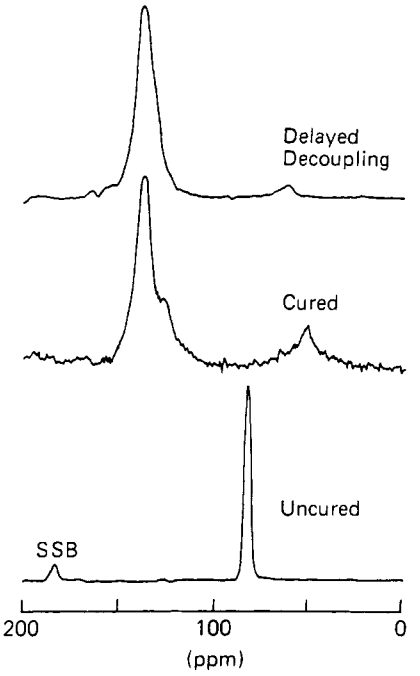


Figure 8. ^{13}C NMR difference spectra of acetylene-terminated oligomer labeled at the C-1 ethynyl position.

The difference spectra for the cured and uncured samples which had been selectively ^{13}C labeled at the C-1 ethynyl carbon are shown in Figure 8. The uncured resin has a well-defined single resonance at 84.1 ppm due to the isotopic label. The corresponding spectrum for the cured sample exhibits a large resonance at 139.5 ppm and a smaller resonance at 129.6 ppm in the aromatic region. In addition, a fairly broad resonance is found in the aliphatic region centered at about 52 ppm. The delayed decoupling spectrum reveals that the carbon at 139.5 ppm is nonprotonated while the carbons at 129.6 and 52 ppm are protonated. A small peak at 63 ppm which was hidden under the broad protonated carbon resonance at 52 ppm is revealed in the delayed decoupling experiment. This carbon is also nonprotonated. These aliphatic peaks are not artifacts or spinning sidebands in that the peaks are invariant to spinning speed, transmitter pulse offset, or other instrumental parameters. Although the peaks are broad and it cannot be determined from the present data if each peak is due to several different but similar products, it appears that at least four classes of products are formed during the thermal cure and that two of these products have become protonated.

Figure 9 presents the difference spectra for the cured and uncured samples which had been selectively ^{13}C labeled at the C-2 (protonated terminal) ethynyl carbon. The well-defined single resonance at 80.8 ppm is due to the isotopic label of the uncured material. The cured C-2 sample produces a distinct peak at 128.7 ppm, a broad resonance between 58 and 70 ppm, and a shoulder on the downfield peak at about 138 ppm. Delayed decoupling spectroscopy discloses that the shoulder is a nonprotonated resonance at 138.0 ppm while the resonance at 128.7 is from protonated carbons. The delayed decoupling spectrum has been normalized and the small shoulder in the cured spectrum has been brought to full peak height. Therefore, the baseline of the delayed decoupling spectrum has become very irratic and makes interpretation difficult. However, if the broad resonance between 58 and 70 ppm were nonprotonated, the resulting resonance in the delayed decoupling spectrum would be expected to be at least $^1/_4$ of the full peak height and above the observed baseline

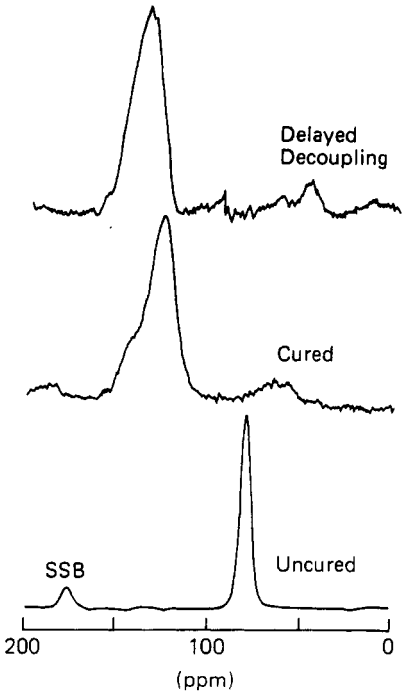


Figure 9. ^{13}C NMR difference spectra of acetylene-terminated oligomer labeled at the C-2 ethynyl position.

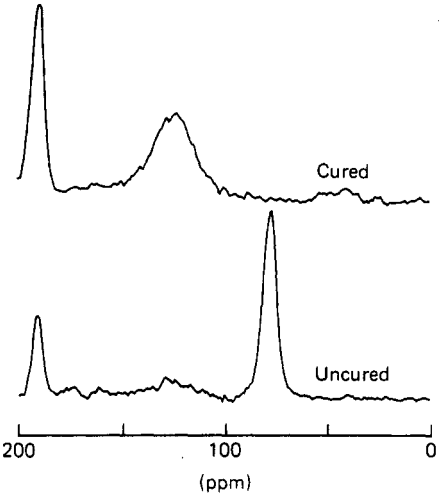


Figure 10. ^{13}C NMR spectra of acetylene-terminated oligomer labeled at both the diaryl carbonyl and C-2 ethynyl positions.

noise. Since this is not the case, this resonance is from a protonated carbon. Again, it appears that at least three classes of products are formed during the thermal cure and that one of these products is now nonprotonated.

The spectra for a polymer sample labeled at both the diaryl carbonyl carbons and at the protonated C-2 ethynyl carbons are in Figure 10. These are not difference spectra and the natural abundance ^{13}C spectra for the oligomer can be seen just above the baseline. The labeled C-2 ethynyl carbon is found at 80.8 ppm in the uncured resin and is the largest peak. However, in the cured resin, the resonance is distributed between the three or four product peaks described above and accounts for the broad peaks at 100–150 ppm and 40–60 ppm. The major peak in the cured resin is due to the carbonyl carbon at 193 ppm. There is no change in the peak position or intensity of the carbonyl resonance after cure. These spectra have been normalized for the highest peak and since the C-2 carbon is distributed between several products, the carbonyl is now larger in intensity. Thus, for fully cured material, the NMR shows that the carbonyl carbon is unchanged in the cure products.

Discussion

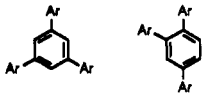
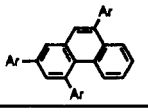
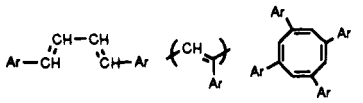
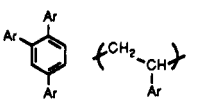
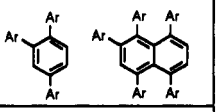
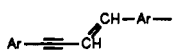
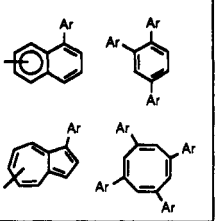
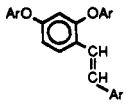
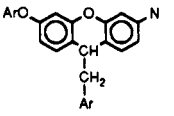
Table I lists some of the cure site structures formed by acetylene groups as proposed in the literature[1,8-12] as well as thermal degradation products of the proposed cure structures.[13-17] The lack of resonances in various parts of the NMR spectrum can eliminate some of these structures as final cure products. In the Glaser and Straus coupling reactions, the diyne and ene–yne structures are formed. Both have triple bond structures and can be modeled by 1,4-diphenylbutadiyne.[33] These resonances would be expected between 75 and 85 ppm and are not present in the fully cured material. The biradical, first-order termination products, conjugated double-bond structures shown in the table, can be modeled by acepleidylene[34] and the C-2 protonated carbon would be expected at about 135–137 ppm. The cured material does have a resonance at 138.0 ppm but it is nonprotonated. Therefore, this class of structure is also not evident in the final cured state. The polystyrene-like structures which are proposed as thermal degradation products of the conjugated double-bond structures would have resonances near 35 ppm based on the model compounds, 1,1,4,4-tetraphenylbutane[35] and [2.2]paracyclophane.[36] No resonances are apparent in this aliphatic region. The phenylazulene structure, suggested as a thermal degradation product of the ene–yne Straus product, should have a C-2 protonated resonance at 117.6 corresponding to the C-3 position in 1-phenylazulene.[37] Again, the absence resonance in this region eliminates this possible cure product.

Even if certain structures are absent after 400 °C cure, they could be present at lower temperatures and provide the pathways to other cure products. The Straus coupling product, the ene–yne structure, could thermally cyclize to the thermally stable phenylnaphthalene structure. In this pathway, one of the C-1 carbons becomes protonated and should have a resonance, based on the model compound, fluoranthene,[38] of 125–130 ppm accompanied by a C-2 protonated shift near 129 ppm. The second acetylene group involved in the coupling should have a nonprotonated C-1 shift at 135–140 ppm and a C-2 protonated shift at 121–126 ppm. The spectra for the acetylene-labeled materials suggest this as a possible cure product and pathway.

Trisubstituted benzenes are the proposed products of cyclotrimerization, of thermal cyclization of both coupling products, and of thermal degradation of the biradical products. By using 1,3,5-triphenylbenzene[39] as a model compound, the unprotonated chemical shifts for this aromatic product would appear at about 140–145 ppm for the C-1 carbon. The C-2 protonated carbon resonance would be expected at about 125–130 ppm. These resonances are present in the cured product spectra, so it appears that cyclotrimerization and the thermal cyclization of both coupling products, as well as of some biradical products, are all possible cure mechanisms to this aromatic product.

There is also evidence for the Diels–Alder addition to these aromatic structures forming condensed polycyclic aromatic systems with the C-2 resonance at 138.0 ppm. The model compound, pyrene,[40] would indicate a nonprotonated C-2 carbon product resonance in this viscinity for these condensed aromatic structures. An alternative mechanism for the formation of these systems is via the bimolecular aromatization of the diyne Glaser coupling products.[41]

Table I
Acetylene Cure Reaction Mechanisms and Associated Cure Site Products and Associated Reaction or Degradation Products

reaction mechanisms and products	further reaction or degradation products
cyclotrimerization 	Diels–Alder addition 
biradical mechanisms 	
Glaser coupling	
Straus coupling 	
Friedel–Crafts addition 	

A Friedel–Crafts type aromatic alkenylation of the oligomer backbone at the acidic aryl carbons in the central arylene ether structure has been suggested as a reaction product. As modeled by *trans*-stilbene,[42] in this type of structure both C-1 and C-2 carbons are protonated and have chemical shifts at ~127–131 ppm. Again, this structure is a potential cure product.

None of the cure products in Table I explain the resonances in the 50–70-ppm range. A possible interpretation is the further reaction of the Friedel–Crafts backbone addition product, the diaryl alkene, with the adjacent acidic aryl carbon[43] to form a bridged structure. By using 1,1,2,2-tetraphenylethane[42] as a model compound, the protonated C-2 carbon should appear at 55–60 ppm. The protonated C-1 carbon should appear slightly upfield at about 50–55 ppm. This structure would then account for the two largest peaks in the aliphatic region of the spectra.

Conclusions

The cure products of the acetylene-terminated polyisoimide, Thermid, have been studied with use of CP-MAS NMR techniques. By correlating the experimental data obtained with chemical shifts based on model compounds, one can deduce the probable cure products and eliminate others. The simple spectrum of the cured isoimide/imide carbonyl ^{13}C labeled oligomer suggests that these carbons are not involved in any reactions with the ethynyl carbons but undergo the expected isomerization to the imide structure. Similarly, the diaryl carbonyl is not involved in the cure chemistry.

The ethynyl carbons are the more interesting participants in the cure chemistry of this oligomer. The major products are aromatic groups as evidenced by the largest C-1 peak at 139.5 ppm and C-2 peak at 128.7 ppm. Another reaction product class is the condensed polycyclic aromatic structures (such as naphthalene or phenanthrene) as indicated by the deprotonation of the C-2 (138 ppm) and corresponding protonation of the C-1 (129.5 ppm) carbons in the spectra. Aromatic alkenylation of the backbone is also indicated by the protonated C-1 and C-2 peaks at ~129 ppm. The very small protonated C-1 resonance at 52 ppm and the corresponding C-2 resonance at 58 ppm could be attributed to the further reaction of a Friedel–Crafts backbone addition to form a bridge in the backbone. The results from the C-1 and C-2 labeled samples are mutually consistent. Relative intensities of peaks observed in the two samples match, and when one peak of one sample is protonated, a corresponding peak of the other sample is deprotonated.

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Registry No. (APB)(BTDA) (SRU) APA terminated isoimide, 137495-59-1; (APB)(BTDA) (SRU) APA terminated imide, 54061-60-8; (APB)(BTDA) (SRU) APA terminated amic acid, 67339-16-6.