Investigation of the Structure of Acetylene-Terminated Polyimide Resins Using Magic-Angle Carbon-13 Nuclear Magnetic Resonance

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ABSTRACT: Magic-angle cross-polarization ^{13}C-NMR spectra have been obtained of the prepolymeric, cured, and postcured versions of an acetylene-terminated polyimide resin. Analysis of the differences between the spectra establishes that all acetylenic functionality is lost by prolonged curing and that not more than 30% of the acetylenic end groups undergo cyclotrimerization in the cross-linking process.

Polyimide polymers have been developed over the last decade for applications as coatings, adhesives, and thermosetting laminates where stability at temperatures up to 400 °C is required.[1] Although polyimides can be prepared by condensation polymerization of polyamic acids, such reactions liberate volatile byproducts such as water during the cure and consequently produce void-filled fabricated structures. The problem of void formation during cure and subsequent postcure has been solved mainly with the use of acetylene-terminated polyimide resins in which homopolymerization at elevated temperatures and pressures occurs without the formation of volatile byproducts.[2] Polyimide polymers formed in this fashion are void free and exhibit excellent thermal and physical properties. The mechanism of cure is believed to be aromatization of the acetylenic end groups but this has been impossible to verify due to the intractability of the cross-linked resin. We have examined these materials with carbon-13 NMR using cross-polarization techniques and magic-angle spinning[3] in order to determine the cross-linked structure of cured polyimide polymers prepared from acetylene-terminated oligomers.

The resin and cured polymers were obtained from Gulf Oil Co. and consisted of Thermid 600 polyimide resin, cured Thermid, and postcured Thermid. The prepolymer may be prepared by the copolymerization of benzophenonetetracarboxylic dianhydride and 1,3-di(3-aminophenoxy)benzene in a 2:1 ratio.[2] This intermediate is end capped with acetylene groups by reaction with (3-aminophenyl)acetylene, which is followed by imidization of the polyamic acid. The theoretical structure of the prepolymer is shown below (I), but the resin may also contain oligomers with varying ratios of these components. The cured sample was prepared by heating the resin at 180 °C for 10 min, followed by molding at 2500 psi and heating at 250 °C for 20 min. Postcuring treatment consisted of additional heating at 340 °C for 4 h and then 4 h at 370 °C.

Although the uncured resin is soluble, it is useful for purposes of comparison to examine this material in the solid state. The carbon-13 NMR spectrum of the resin (Figure 1, bottom) has sufficient resolution to identify peaks arising from the acetylenic carbons (84 ppm), various aromatic carbons (125–140 ppm), the amide carbonyl and aryl carbons with oxygen substituents (160 ppm), and the benzophenone carbonyls (193 ppm). The resonance at 176 ppm cannot be accounted for in the theoretical structure of the prepolymer (I), but its chemical shift and chemical history suggest its assignment to a carboxylic acid resulting from incomplete imidization of the prepolymer. Spectra of the insoluble cured and postcured polyimides are shown in Figure 1.[4] Significant line broadening is evident as might be expected for the overlapping, unresolved lines of a cross-linked material which has become structurally more diverse. Changes in the line shape of the aromatic-carbon region and the diminution of intensity in the acetylenic-carbon region are clear.

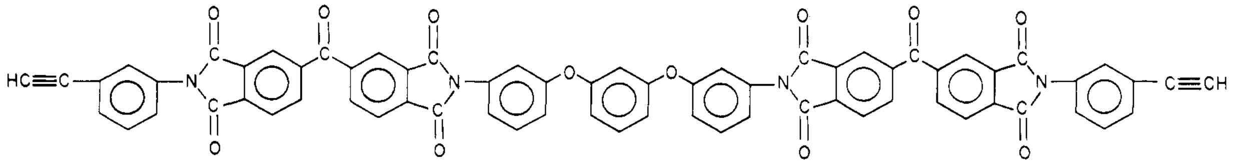
Table I

chemical shift, ppm from Me_4Si	percent change[a] gain	loss
84		−6.5
127–131	+6	
139		−0.5
144	+1	
151		−0.5
157–160	+1	

[a] Areas are expressed as a percent of the total NMR intensity of the carbons observed. The total change does not equal zero due to rounding errors.

The 15.1-MHz ^{13}C-NMR spectra shown in Figure 1 were each obtained from the time average of approximately 50 000 transients collected overnight, with magic-angle spinning of the powdered solids at 2.2 kHz in a 700-μL Beams-Andrew[5] Kel-F hollow rotor, using matched spin-lock cross-polarization techniques[6] with 1-ms single contacts and 38 kHz H_1's. The spectra were unchanged by the use of 2-ms long cross-polarization contacts indicating that 1-ms transfers were sufficient to produce full intensity for all types of carbons. No significant depolar broadening survived the 38-kHz decoupling field.

Changes in the NMR spectra due to the curing process are more easily seen in Figure 2 which shows the difference spectrum obtained by subtraction of the spectrum of the uncured resin from that of the cured resin. The line widths of the uncured resin spectrum have been artifically broadened to approximate the line widths in the highly



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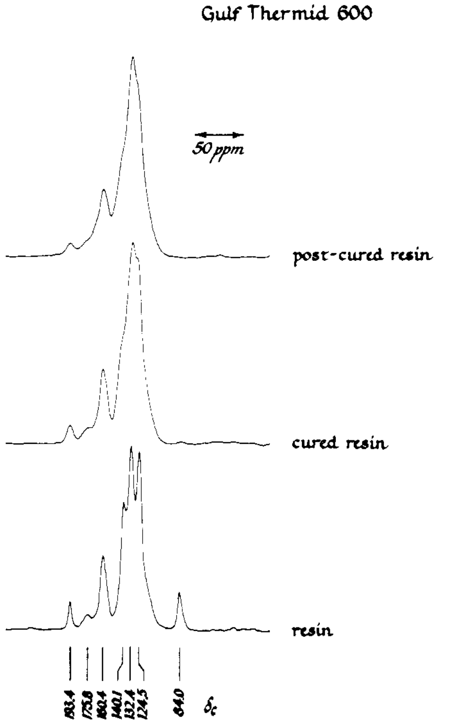


Figure 1. Magic-angle cross-polarization ^{13}C-NMR spectra of Thermid 600 acetylene-terminated polyimide resin (bottom); cured polyimide polymer (middle); and postcured polyimide polymer (top).

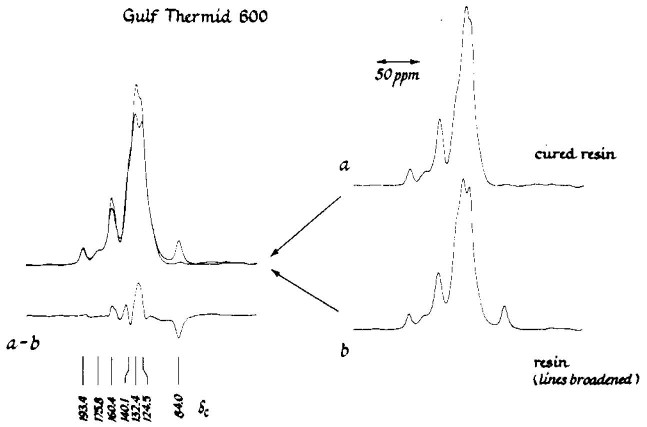


Figure 2. Difference spectrum (a–b) obtained by subtraction of the polyimide resin spectrum (with lines artifically broadened, b) from that of the cured polyimide polymer (a). Small deviations in the difference spectrum should be ignored since line broadening across the cured polymer spectrum may not be uniform.

cross-linked material. The difference spectrum (labeled a–b in Figure 2), whose net integrated area is approximately zero, clearly shows regions of intensity loss as peaks extending below the base line, while regions which gain in integrated intensity in the curing process appear as positive peaks. These results are summarized in Table I which lists the approximate chemical shift and change in relative area as a percent of the total carbon signal.

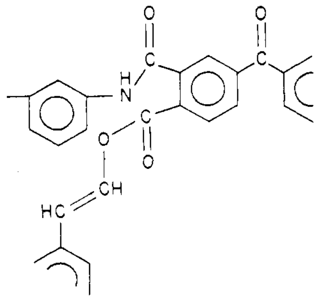
The results shown in the difference spectrum and Table I establish that the major mechanism for cross-linking involves loss (i.e., reaction) of the acetylenic end-capping groups. Examination of Figure 1 shows that over 90% of the acetylenes are consumed in the curing process. No acetylenic functions remain after postcuring.

Thermal condensations of acetylene and its derivatives generally occur above 400 °C yielding a wide variety of products including vinylacetylene, divinylacetylene, benzene, and cyclooctatetraene.[7] Similar condensations can be made to occur at much lower temperatures with the aid of catalysts ranging from Ziegler and Friedel-Crafts to metal salts and mineral acids.[7] The observation[2] that curing of the Thermid 600 resin can be achieved at temperatures as low as 200 °C suggests that catalytic as well as thermal reactions of the terminal acetylenes can occur.

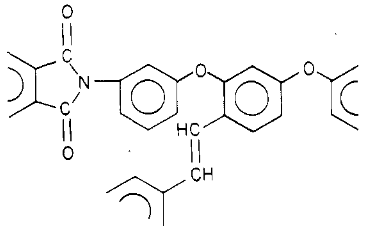
Several possible condensation reactions which would result in cross-linking of the polyimide resin will now be considered in view of the expected changes in the NMR spectrum. Terminal acetylenes can be dimerized to vinylacetylenes or further reacted to divinylacetylenes under acid conditions of the Straus coupling reaction.[8] However, the absence of an acetylenic resonance in the postcured polymer indicates that such products could only exist as intermediates which would be unstable to prolonged curing. Terminal acetylenes may undergo cyclization to substituted benzenes, cyclooctatetraenes, or higher annulenes; this has, in fact, been suggested as the mode of cross-linking in these polyimide polymers.[9] Cyclotrimerization of the acetylenic groups would lead to the formation of trisubstituted benzenes which may be either 1,2,4 or 1,3,5 isomers or some mixture of these. Using triphenylbenzene as a model[10] for this type of polymerization, we can estimate that the newly formed aryl carbons would exhibit chemical shifts of about 125–129 ppm for the unsubstituted carbons and 140–144 ppm for the substituted carbons. Consequently, cyclotrimerization during curing should result in an increase in intensity of the carbon resonances in the regions of 125–129 and 140–144 ppm and a loss of intensity in the 84-ppm region, in ratios of 1:1:2, respectively. (As a second-order effect we expect the aryl-carbon resonance, arising from the carbon attached to the acetylene group in the prepolymer, to shift to lower field upon cyclization, changing from 123 toward about 135 ppm.)

Based on this analysis, cyclotrimerization could account for the complete 1% increase at 144 ppm as well as a 1% gain in the 127–131-ppm region and a 2% loss (or 30% of the total 6.5% loss) in the acetylenic region. Thus we can conclude that no more than 30% of the acetylene end groups trimerize to benzene during cross-linking. (Cyclooctatetraene formation is expected to contribute to regions of the NMR spectrum which are shifted 3–5 ppm downfield from those for cyclotrimerization. We see no evidence for the formation of cyclooctatetraene in the spectra of Figure 1.)

After accounting for the effects of cyclotrimerization during the curing process, the major change remaining in the difference spectrum is the conversion of the acetylenic carbons (84 ppm) to vinyl carbons (125–130 ppm). There are at least three types of addition reactions which could account for this result and which seem feasible under the conditions of curing. The first is addition to a carboxylic acid functional group.[11] Although not present in the theoretical structure of the polyimide resin, the NMR spectrum of the resin (Figure 1, bottom) shows a resonance at 176 ppm which we assigned to a carboxylic acid residue from incomplete imidization. (In fact, these are expected to occur in pairs with amides, as will be mentioned below.) Addition of acetylene to carboxylic acids leads to the formation of alkenyl esters (II). A second addition reaction is a Friedel-Crafts type aromatic alkenylation[12] of the acidic aryl carbons in the central arylene ethers (III),

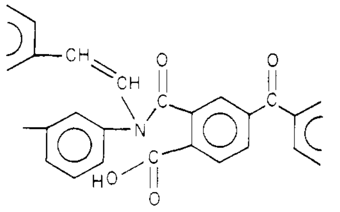


II

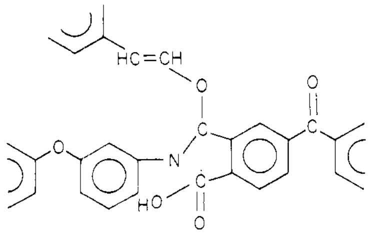


III

which can be promoted by the ortho- and para-directing effects of the ether oxygens. And finally, addition might also occur at an amide which, by inference, should be associated with the observed carboxylic acid. Addition could occur at either the amide nitrogen[13] or at the oxygen[14] of its tautomer forming the *N*-alkenyl amide (IVa)



IVa



IVb

or the alkenyl imidate (IVb). Thermal rearrangement and cyclization of the addition prducts II–IV are possible during curing and subsequent postcuring treatment.

At elevated temperatures and pressures a wide variety of catalysts are known to promote the addition of acetylenes to carboxylic acids.[11] The alkenyl esterification should have a significant effect on the carboxylic carbon resonance. Using acetic acid and vinyl acetate as models,[15] the resonance for the carboxylic carbon shifts upfield by about 11 ppm upon esterification and suggests a similar shift could be expected as a second-order effect in the cured polyimide. In fact, no change was noted in the carboxylic acid region of the NMR spectra, and hence we do not believe esterification plays a significant role in cross-linking the polyimide resin.

The other addition reaction products (III, IVa, and IVb) will all result in increased NMR intensity over the range of 120–140 ppm at the expense of the acetylenic-carbon region. The NMR data of Figure 1 support the formation of vinyl carbons during curing of the polyimide resin, thereby providing a reasonable accounting for the disappearance of the remainder of the acetylenic groups. With the present results, and in the absence of detailed chemical shift data from model compounds, we are unable to draw any quantitative conclusions regarding the extent to which any one of these reaction products may be involved in the cross-linking of the polyimide polymer.

The results presented here have shown conclusively that reactions involving the terminal acetylenic groups of Thermid 600 polyimide resin are involved in the homopolymerization and that all acetylenic character is lost in the postcuring process. Not more than 30% of the acetylenes undergo cyclotrimerization or other condensation reactions, while the remainder appear to be consumed by addition reactions. We have eliminated esterification as a cross-linking mechanism and have presented several other specific addition reaction products which are consistent with the chemistry of acetylenes and the NMR results. The relative degrees to which the various other addition products are involved in cross-linking remains uncertain.

References and Notes

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