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Addition Polymers From 1,4,5,8-tetrahydro-1,4;5,8-diepoxyanthracene and Bis-dienes II: Evidence for Thermal Dehydration Occurring in the Cure Process

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(NASA-TM-101385) ADDITION POLYMERS FROM 1,4,5,8-TETRAHYDRO-1,4;5,8-DIEPOXYANTHRACENE AND BIS-DIENES. 2: EVIDENCE FOR THERMAL DEHYDRATION OCCURRING IN THE CURE PROCESS (NASA) 8 p CSCL 11C G3/27

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SUMMARY

Diels-Alder cycloaddition copolymers from 1,4,5,8-tetrahydro-1,4;5,8-diepoxyanthracene and anthracene end-capped polyimide oligomers appear, by TGA, to undergo dehydration at elevated temperatures. This would produce thermally stable pentiptycene units along the polymer backbone, and render the polymers incapable of unzipping through a retro-Diels-Alder pathway. High resolution solid ^{13}C NMR of one formulation of the polymer system before and after heating at elevated temperatures, shows this to indeed be the case. NMR spectra of solid samples of the polymer before and after heating correlated well with those of the parent pentiptycene model compound before and after acid-catalyzed dehydration. Isothermal gravimetric analyses and viscosities of the polymer before and after heat treatment support dehydration as a mechanism for the cure reaction.

INTRODUCTION

We recently reported that 1,4,5,8-tetrahydro-1,4;5,8-diepoxyanthracene, 1, forms high molecular weight Diels-Alder addition copolymers with anthracene end-capped polyimide oligomers, for example, oligomer 2 (ref. 1). The polymers are soluble in common organic solvents, like N,N-dimethylformamide and N-methylpyrrolidinone, but on heating at elevated temperature, become insoluble and very thermally stable. The unique thermal behavior of this system makes it a good candidate as a matrix resin for high temperature composites.

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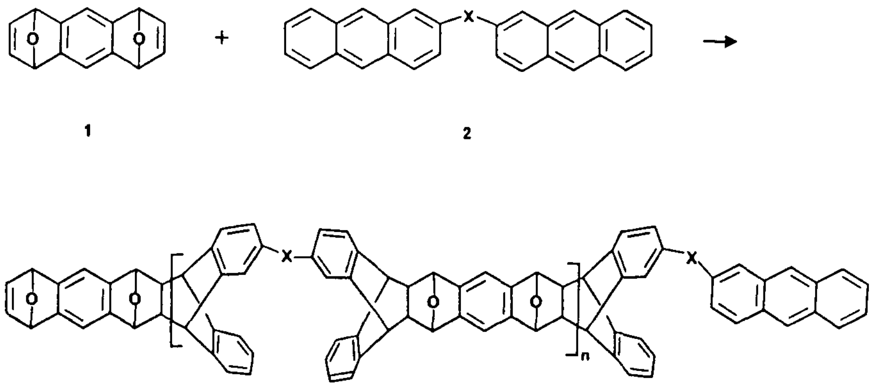

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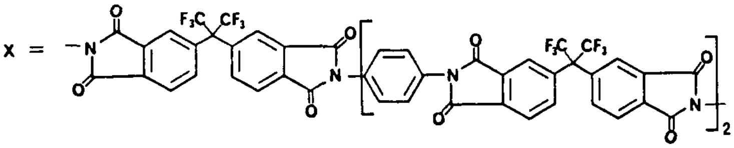
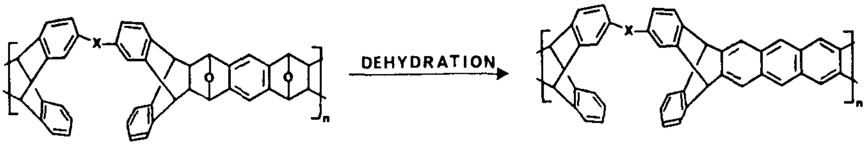


It was suggested (ref. 1) that the polymers, on heat treatment, undergo dehydration. This reaction would produce highly stable pentiptycene units along the polymer backbone, and make it impossible for the polymer to unzip by a retro-Diels-Alder mechanism. Dehydration was consistent with the degree of weight loss recorded with thermogravimetric analysis (TGA) of the untreated polymers. However, previously, we were unable to obtain direct spectral evidence that such a process was occurring.



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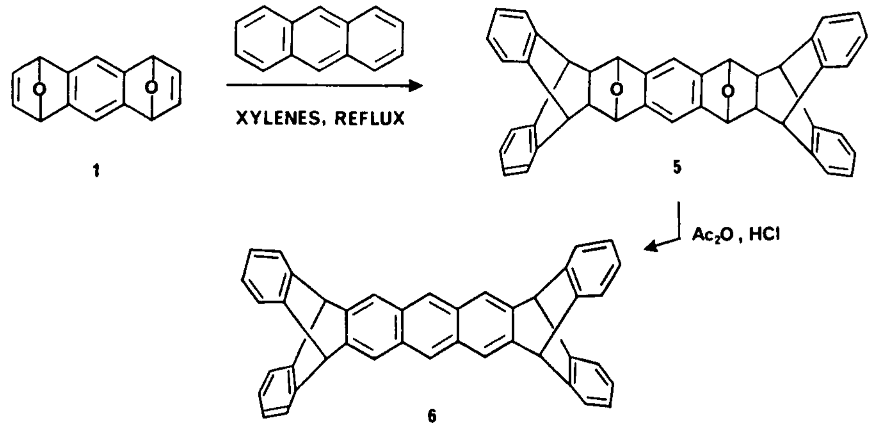
In this paper, such direct evidence will be presented. A comparison between the magic angle spinning (MAS) ^{13}C NMR of solid polymer samples before and after heat treatment with those of suitable model compounds will be shown.

RESULTS AND DISCUSSION

Polymer 3 was synthesized as previously reported (ref. 1) with some minor modifications. A one-to-one mixture of anthracene end-capped oligomer 2 and endoxide 1 in N,N-dimethylformamide (DMF) were heated at 155 °C under 400 psi nitrogen for 36 hr. The polymer was obtained in quantitative yield as a dark brown solid after removal of solvent.

MAS ^{13}C NMR of polymer 3 (fig. 1(a)) gave nine peaks: (a) a broad line at 48.32 ppm, (b) a broad multiplet at 65.50 ppm corresponding to the carbon bearing two $-CF_3$ groups (long-range coupled to the fluorines), (c) a peak at 80.52 ppm, (d) five aromatic peaks at 110.31, 123.84, 131.68, 138.44, and 143.90 ppm, and (e) a broad carbonyl line at 164.95 ppm. Most of the aromatic peaks (d), the carbonyl peak (e), and peak (c) can be assigned to the imide oligomer chains. The other peak assignments can be made based on comparison with the solution ^{13}C NMR of bis-adduct 5 reported by Hart and coworkers (ref. 2). In addition to aromatic peaks, the spectrum of 5 contains three aliphatic peaks at 47.47, 49.07, and 81.09 ppm belonging to the three aliphatic bridgeheads. Hence, peaks (a) and (c) can be assigned to the bridgeheads in the polymer. (The two peaks at 47.47 and 49.07 ppm which are resolved in the solution NMR of 5 show up as one broad peak at 48.32 ppm in the polymer.)



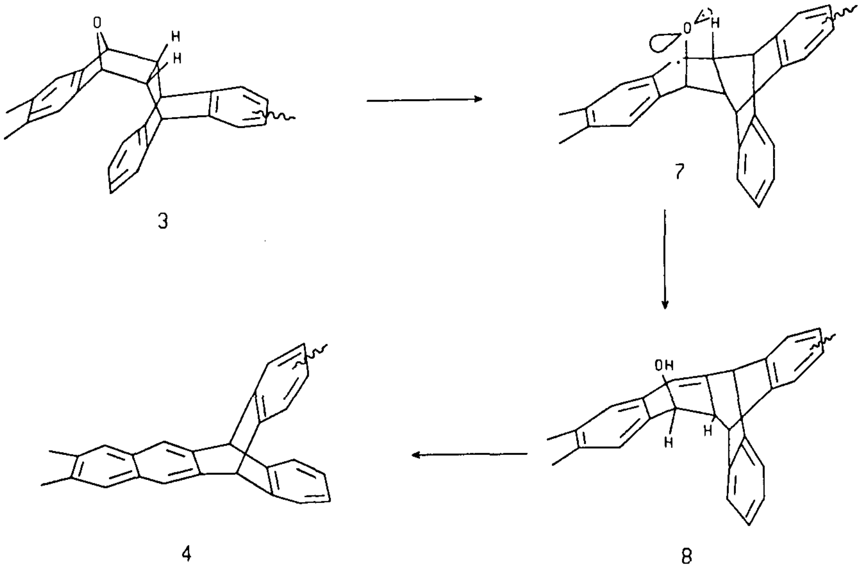
When polymer 3 is heated at 315 °C for 5 hr, changes occur in the solid ^{13}C NMR spectrum (fig. 1(b)). The peaks at 48.32, 80.52, and 110.31 ppm begin to disappear, and a new peak (f) at 53.42 ppm develops. For longer heating times or at higher temperatures, the (a) and (c) peaks disappear completely (fig. 1(c)), leaving, in the aliphatic region, only the new peak (f) at 53.42 ppm.

Two possible explanations could account for the disappearance of the two bridgeheads: (1) depolymerization (retro-Diels-Alder reaction), or (2) dehydration. In order to differentiate between the two processes, the inherent viscosities of the polymer before and after heat treatment were monitored. If depolymerization is the primary process, the viscosity should dramatically decrease. In contrast, dehydration should result in virtually no change in the viscosity. Before heat treatment, polymer 3 had an inherent viscosity of 0.15; after heating for 5 hr at 315 °C, the viscosity of the resin increased to 0.18.

The appearance of the new peak at 53.42 ppm confirms that dehydration is occurring. This peak corresponds to the chemical shift of the aliphatic bridgehead carbon (53.81 ppm) in parent pentiptycene 6, the product of acid catalyzed dehydration of adduct 5.

The driving force for thermally activated dehydration would be aromatization to form a more stable structure. Formation of an aromatic system by dehydration of an endoxide ring has been proposed previously as a cure mechanism for other such polymers (ref. 3). However, no evidence that this was occurring was shown. Other Diels-Alder addition copolymers have been shown to aromatize through loss of carbon monoxide (ref. 4), carbon dioxide (ref. 5), and hydrogen (ref. 6).

A proposed mechanism for dehydration is shown below. Initial cleavage of one of the epoxide oxygen-carbon bonds in 3 affords the corresponding biradical 7. The driving force for this cleavage would be the reduction of considerable steric interactions between the benzene rings in 3. In the second step, 1,4-hydrogen transfer from the c-bridgehead carbon to the oxygen radical center proceeds via formation of a highly favored five-center transition state to provide intermediate 8. Dehydration of this intermediate would then proceed via either a concerted or two-step process.



Thermogravimetric analysis (TGA) of the completely dehydrated polymer 3 was run in air and nitrogen (fig. 2). The cured neat resin shows no initial weight loss at lower temperatures, and has an onset of decomposition in excess of 600 °C in both air and nitrogen.

CONCLUSIONS

Clearly, dehydration is the dominant cure process in this polymer system. This leads to a polymer which is incapable of unzipping by a retro-Diels-Alder mechanism, since the reaction produces aromatic pentiptycene units along the chain. We have proposed a mechanism for dehydration, and have shown direct spectral evidence that this is occurring. MAS ^{13}C NMR of solid samples is a very powerful technique in probing the reactions occurring at elevated temperatures in otherwise intractable polymer systems. We hope to use this as a tool to bring new insight into the cure chemistry of other such systems.

To develop this resin system into a useful high temperature material, optimum cure conditions must be developed, and flow properties of the polymer must be maximized by formulation studies, without detrimentally affecting the thermal stability. This is the subject of a current study.

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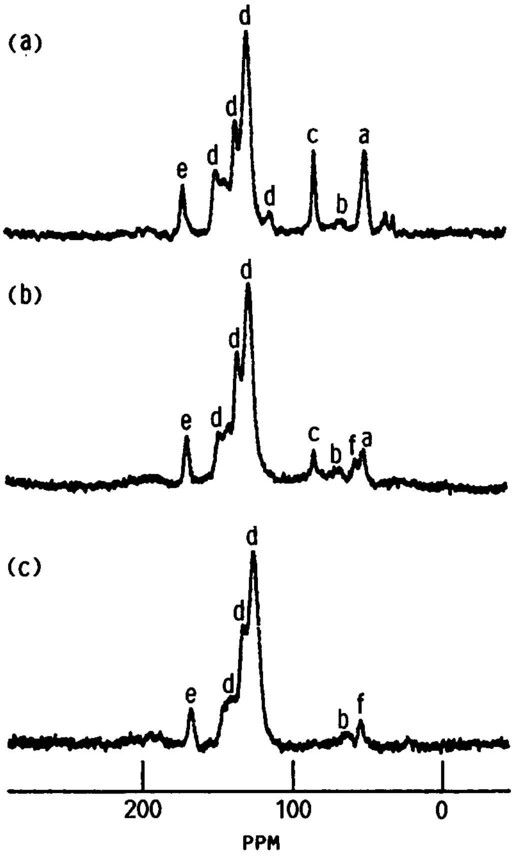

FIGURE 1. - MAS ^{13}C NMR OF POLYMER 3. (a) BEFORE HEATING, (b) AFTER HEATING FOR 5 HR AT 315 °C, (c) AFTER HEATING FOR 2 HR AT 350 °C.

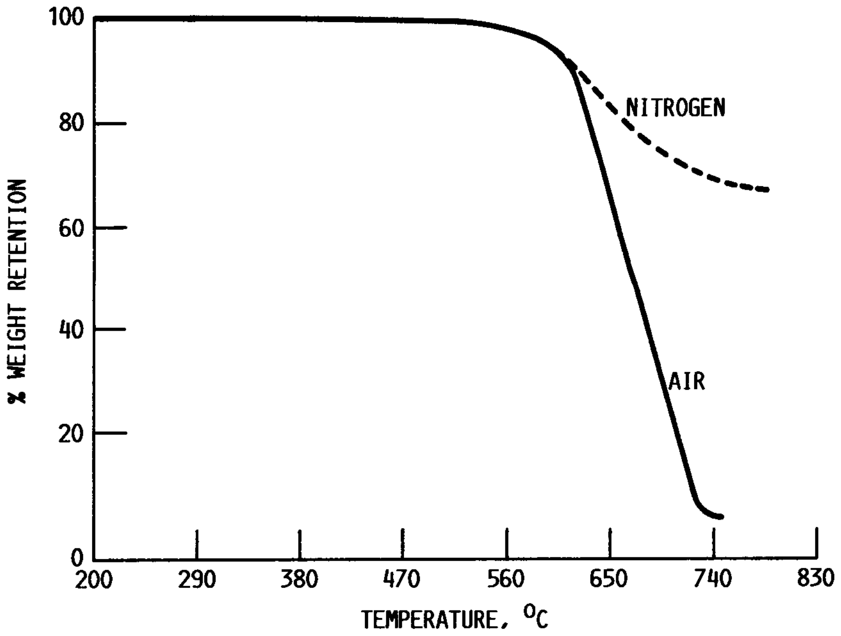

FIGURE 2. - TGA OF POLYMER 3 IN AIR AND NITROGEN SHOWS ONSET OF DECOMPOSITION TO BE IN EXCESS OF 600 °C.

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16. Abstract

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