Evidence for Thermal Dehydration Occurring in Diels–Alder Addition Polymers

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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** (Scheme I).[3] 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.

It was suggested[3] 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 (Scheme II). 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. In this paper, such 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 are shown. Kinetics of the reaction at elevated temperatures were examined in order to establish cure conditions for the resin system.

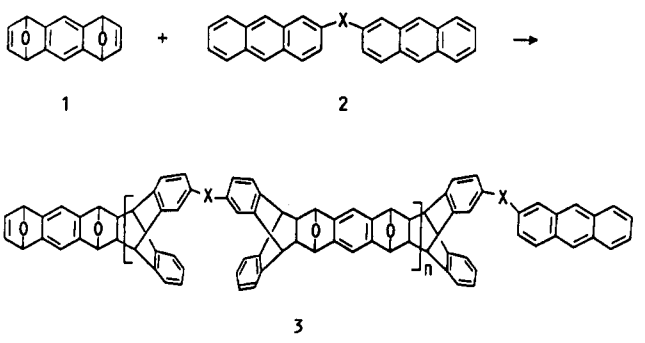
Experimental Section

All NMR spectra were recorded with a Bruker AM-300 spectrometer. The solid NMR spectra were run with a high power solid attachment with a probe equipped with a dual air bearing capable of magic angle spinning (MAS) at rates up to 5 kHz and tunable over the frequency range from ^{14}N to ^{63}Cu. Solution samples were prepared with $CDCl_3$ as solvent and tetramethylsilane as internal standard. Infrared spectra were done as solid KBr pellets using a Perkin-Elmer 1750 Fourier transform spectrometer. All thermal analysis were recorded on an Omnitherm data station. Thermogravimetric analyses were performed with a Perkin-Elmer TGS-2 at a scan rate of 10 °C/min. Isothermal gravimetric analyses were done with the same instrument by ramping to temperature at 5 °C/min and holding for up to 15 h. Thermomechanical analyses were carried out with a Du Pont Instruments 943 TMA using a scan rate of 20 °C/min. Inherent viscosity was run by using an Ubbelohde viscometer in a constant temperature bath at 25 °C with *N,N*-dimethylacetamide as solvent (concentration of 0.5 g of polymer/100 mL of solvent).

The anthracene end-capped oligomer **2** was synthesized as previously described.[3] Bis(epoxide) **1** was purchased from Daychem Laboratories, Dayton, OH, as a mixture of syn and anti isomers and was used without further purification.

Preparation of Polymer 3. A solution of 1,4,5,8-tetrahydro-1,4;5,8-diepoxyanthracene (1) (2.10 g, 10 mmol) and oligomer (**2**) (18.27 g, 10 mmol) in 100 mL of *N,N*-dimethylformamide was placed in a 300-mL Parr stirred-pressure reactor. The reactor was pressurized to 300 psi with nitrogen. The reaction mixture was heated to 155 °C, at which point the pressure was 400 psi, and was held for 36 h. After this time, the reaction was cooled and the solvent was removed. The brown solid remaining was dried at 200 °C for 4 h and 288 °C for 1 h to give 20.35 g (quantitative yield) of polymer, softening temperature (from TMA) 359 °C (lit.[3] 350 °C). ^1H NMR (ppm): 2.18 (br s, 4 H), 4.43 (br s, 4 H), 4.85 (br s, 4 H), 6.93–7.39 (m, 10 H), 7.63 (s, 8 H), 7.83–8.08 (m, 24 H). IR: 1363, 1728, 1786 cm^{-1}.

Scheme I



Scheme II

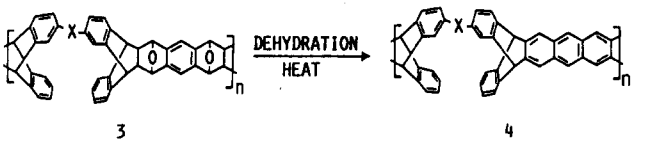


Table I

T, K	$1/T$, $\times 10^{-3}$ K	ln k
583	1.72	−10.37
588	1.70	−10.10
603	1.66	−9.65
613	1.67	−9.47
623	1.61	−9.31
628	1.59	−9.06

Heat Treatment of Polymer 3. Bulk samples of polymer **3** were ground to a fine powder and placed in a beaker. The samples were then heat treated in a Blue M oven equipped with flowing air and preheated to temperature. After regrinding, the samples were used for MAS ^{13}C NMR.

Kinetics Experiments. Samples of polymer **3** (approximately 10 mg each) were run isothermally in air at 310, 315, 330, 340, 350, and 355 °C (three samples at each temperature) for 15 h. The approximate rate was estimated from the slope of the weight loss curve using the method of initial rates. At temperatures below 310 °C, the slope was too small to measure with any accuracy. Above 355 °C, reaction occurred too rapidly, and it appeared that degradation was beginning to compete with dehydration. Hence, no part of the weight loss curve was linear. At 310 °C, the slope was linear for 13 h, but at 355 °C, the reaction was essentially complete after 2–3 h.

The amount of water produced, $[H_2O]_t$, is related to the weight loss according to the expression, $[H_2O]_t \propto (w_0 - w_t)$, where w_0 is the initial weight of the sample and w_t is the weight at a given time t. For the kinetic data analysis we have used the weight loss ratio

$$(w_t - w_\infty)/(w_0 - w_\infty) = \{[H_2O]_\infty - [H_2O]_t\}/[H_2O]_\infty = k\Delta t$$

where w_∞ and $[H_2O]_\infty$ denote the long time limiting values. The results of the preliminary analysis of the weight loss data assuming the first order initial rate process is given in Table I. An Arrhenius plot of ln k versus $1/T$ is given in Figure 3. Standard deviation calculated for ln k (population = $n - 1$) was 0.089.

Results and Discussion

Polymer **3** was synthesized as previously reported[3] with some minor modifications. A one-to-one mixture of anthracene endcapped oligomer **2** and endoxide **1** in *N,N*-

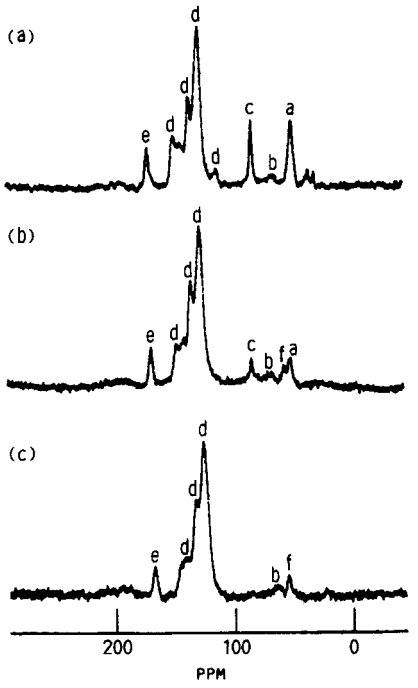
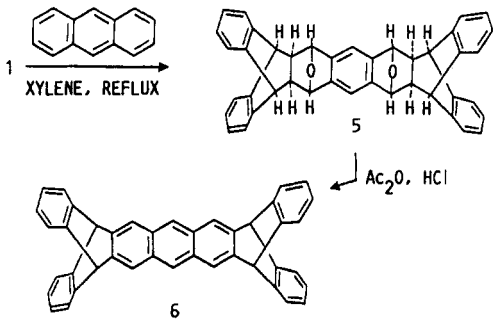


Figure 1. MAS ^{13}C NMR of polymer **3**: (a) before heating, (b) after heating for 5 hours at 315 °C, and (c) after heating for 2 h at 350 °C.

Scheme III



dimethylformamide (DMF) were heated at 155 °C under 400 psi of nitrogen for 36 h. The polymer was obtained in quantitative yield as a dark brown solid after removal of the solvent.

MAS solid ^{13}C NMR of polymer **3** (Figure 1a) 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 on comparison with the solution ^{13}C NMR of bis adduct **5** reported by Hart and co-workers (Scheme III).[4] In addition to aromatic peaks (ranging from 110.04 to 145.79 ppm), 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 that are resolved in the solution NMR of the model compound show up as one broad peak at 48.32 ppm in the polymer.)

When polymer **3** is heated at 315 °C for 5 h, changes occur in the solid ^{13}C NMR spectrum (Figure 1b). 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

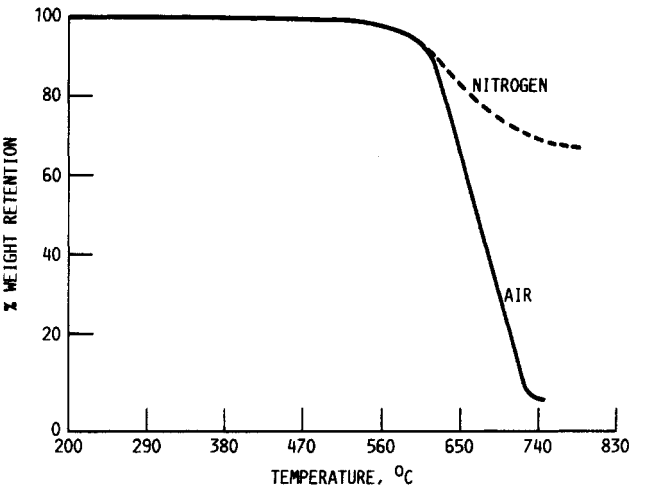


Figure 2. TGA of fully cured polymer **3** in air and nitrogen shows onset of decomposition to be in excess of 600 °C.

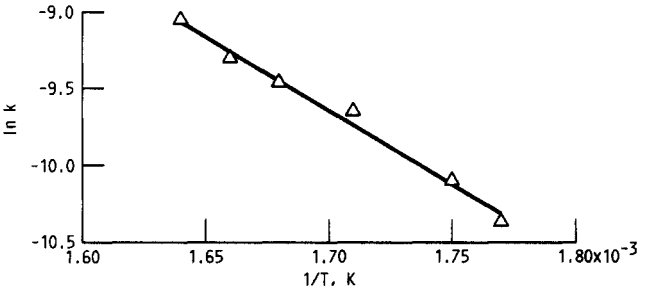


Figure 3. Arrhenius plot for dehydraton of polymer **3**.

heating times or at higher temperatures, peaks (a) and (c) disappear completely (Figure 1c), 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** has an inherent viscosity of 0.15; after heating for 5 h at 315 °C, the viscosity of the resin increased to 0.18.

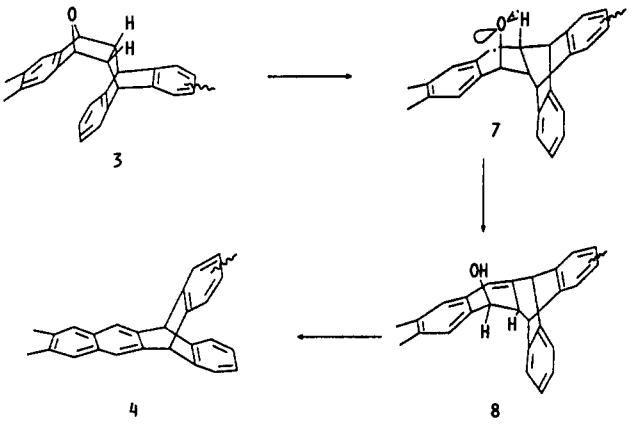
The appearance of the new peak at 53.42 ppm confirms that dehydration is occurring. This peak corresponds to the chemical shift of the aliphatic bridgehead carbon (53.81 ppm) in parent pentiptycene **6**, the product of acid-catalyzed dehydration of adduct **5** (Scheme III).[4]

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.[5] However, no evidence that this was occurring was shown. Other Diels–Alder addition copolymers have been shown to aromatize through loss of carbon monoxide,[6] carbon dioxide,[7] and hydrogen.[8]

Thermogravimetric analysis (TGA) of the completely dehydrated polymer **3** was run in air and nitrogen (Figure 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.

The rate of weight loss due to dehydration was monitored by isothermal gravimetric analysis from 310 to 355 °C. Initial slopes of these plots were linear with respect

Scheme IV



to time and eventually leveled off when dehydration was complete. Arrhenius treatment of this weight loss data provided a linear plot of ln k versus $1/T$ (Figure 3) with a slope of -9.54×10^3 and an intercept of 6.09. An activation energy (E_a) of 19.0 kcal mol^{-1} was calculated from the slope of this plot. At 310 °C, this corresponds to a $\Delta H^{\ddagger}$ of 17.8 kcal mol^{-1}, a $\Delta S^{\ddagger}$ of -47.7 cal mol^{-1} deg^{-1}, and a $\Delta G^{\ddagger}$ of 45.6 kcal mol^{-1}.

A plausible mechanism consistent with the weight loss curves observed for dehydration is presented in Scheme IV. 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 γ-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.

The rather large negative $\Delta S^{\ddagger}$ at 310 °C, calculated from the Arrhenius plot, reflects a highly ordered transition state for the rate-determining step in the dehydration mechanism. The only step in the proposed mechanism that contains such a transition state would be the second step involving 1,4-hydrogen transfer. The decay behavior of the weight loss curves after the initial portion may also suggest that the overall reaction rate, k, depends on the rate constants, k_1 and k_2, belonging to the first two steps in Scheme IV, respectively. The consecutive unimolecular reaction requires two exponential terms in the weight-loss curves. An attempt was made to numerically fit the experimental data assuming such a multistep mechanism. However, because of scatter in the experimental data (due to slight temperature overshoots or different amounts of adsorbed water in the samples), such a detailed fit was not possible. In any case, if $k_1 \ll k_2$ or if the intermediate **7** is at a steady-state concentration, a simple first-order decay would be expected.

It should be noted that this mechanism presupposes that the only cycloadducts formed during polymerization are those resulting from endo addition. Only in this orientation are the c-bridgehead hydrogen and the epoxide oxygen syn to each other, thus having the correct geometry in intermediate **7** for 1,4-hydrogen transfer. Model studies of the Diels–Alder cycloaddition of anthracene and bis(epoxide) **1** (shown in Scheme III) reveal that only one isomer of bis adduct **5** is formed from each of the isomers of **1**. Although the structures of these isomers have not been confirmed, it is likely they result from endo addition since this mode of attack is preferred for maximum orbital overlap in the transition state (Alder rule). In light of this, therefore, it is reasonable to assume that the same mode of attack is preferred in the polymer.

Conclusions

Clearly, dehydration is the dominant cure process in this polymer system. This leads to a polymer that is incapable of unzipping by a retro-Diels–Alder mechanism, since the reaction produces highly aromatic pentiptycene units along the chain. We have shown direct spectral evidence that this is occurring. MAS solid ^{13}C NMR 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.

We have proposed a mechanism that fits the kinetics experiments performed by using isothermal gravimetric analysis. These experiments have also lead to ways of curing this polymer into a highly thermally stable resin, suggesting the optimum cure temperature to be approximately 340–350 °C. To develop this resin system into a useful high-temperature material, flow properties at these temperatures must be optimized by formulation studies, without detrimentally affecting the thermal stability. This is the subject of a current study.

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References and Notes

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