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Addition Polymers From 1,4,5,8-Tetrahydro-1,4;5,8-diepoxyanthracene and Bis-dienes: Processable Resins for High Temperature Applications

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ADDITION POLYMERS FROM 1,4,5,8-TETRAHYDRO-1,4;5,8-DIEPOXYANTHRACENE

AND BIS-DIENES: PROCESSABLE RESINS FOR HIGH TEMPERATURE

APPLICATIONS

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SUMMARY

1,4,5,8-Tetrahydro-1,4;5,8-diepoxyanthracene reacts with various anthracene end-capped polyimide oligomers to form Diels-Alder cycloaddition copolymers. The polymers are soluble in common organic solvents, and have molecular weights of approximately 21,000 to 32,000. Interestingly, these resins appear to be more stable in air than in nitrogen. This is shown to be due to a unique dehydration (loss of water ranges from 2 to 5 percent) at temperatures of 390 to 400 °C to give thermo-oxidatively stable pentiptycene units along the polymer backbone. Because of their high softening points and good thermo-oxidative stability, the polymers have potential as processable, matrix resins for high temperature composite applications.

INTRODUCTION

It has been established that 1,4,5,8-tetrahydro-1,4;5,8-diepoxyanthracene, 1, is an effective bis-dienophile for the rapid construction of fused-ring systems (refs. 1 and 2). For example, the dihydrated pentiptycene, 2, can be prepared in one step from anthracene and 1. Extension of this chemistry
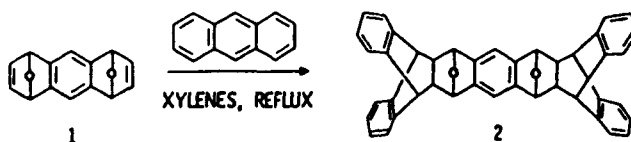
to the synthesis of ladder or partial ladder polymers can be accomplished by reacting bis-dienophile 1 with a bis-diene (ref. 3).

Compounds such as 2 have extremely high melting points and decomposition temperatures (ref. 4). Thus, polymers made from 1 and thermally stable bis-dienes have potential for high temperature applications.

Although many Diels-Alder polymers have been investigated in the past, only three studies have employed anthracenes as the reactive diene (refs. 5 to 7). These have lead only to low molecular weight polymers. This has been attributed to several different factors, including steric congestion at the site of cycloaddition, competing vinyl polymerization, stoichiometric imbalance and ease of reversibility of the Diels-Alder reaction (ref. 3).

In this paper, the synthesis of thermally stable copolymers from the reaction of anthracene end-capped polyimide oligomers acting as bis-dienes and bis-dienophile 1 will be discussed. The anthracenes are linked through the two-position, remote from the site of cycloaddition, and the bis-epoxide 1 does not undergo vinyl polymerization at the same temperature that cycloaddition takes place.

RESULTS AND DISCUSSION

Anthracene end-capped oligomers, 6 to 8, were prepared from 2-aminoanthracene, 3, 4,4'-(hexafluoroisopropylidene)bis(phthalic anhydride), 4, and p-phenylenediamine, 5. All of the oligomers were synthesized using the

6 m = 0
7 m = 1
8 m = 2
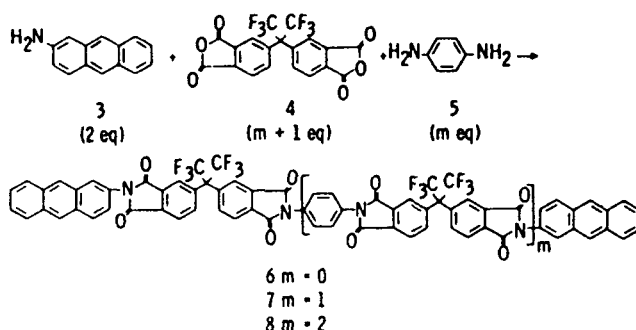
same procedure with different monomer stoichiometries. The number of moles of monomeric reactants in each case was governed by the ratio m:(m+1):2, where m, (m+1), and 2 are the number of moles of dianhydride, diamine, and 2-aminoanthracene, 3, respectively.

Addition polymerization was carried out as shown below. A one-to-one mixture of bis-epoxide 1 and the bis-diene were dissolved in a minimum amount of solvent, and heated to 155 °C under 300 to 400 psi nitrogen for 72 hr. The

6 m = 0
7 m = 1
8 m = 2

9 m = 0
10 m = 1
11 m = 2

2
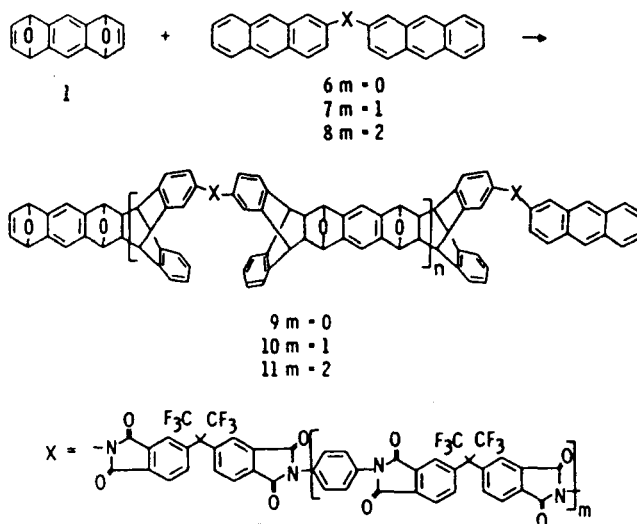
polymers were obtained as light tan powders in quantitative yields. Thermo-mechanical analysis (TMA) gave softening points of 349.5, 347.4, and 349.4 °C for 9, 10, and 11, respectively.

The molecular weight of the polymers can be controlled by varying the reaction times. An indication of molecular weights was obtained by integration of the NMR spectra. In each spectrum, there was a very small peak at 5.60 ppm belonging to bridgehead proton from the unreacted epoxide endgroup. In the repeat units, this bridgehead proton occured at 4.83 ppm. Assuming the polymer is capped by an epoxide on one side and an anthracene on the other side, then there should be two endgroup bridgehead protons, He, for every 4n+1 repeat unit protons, Hr, (where n is the number of repeat units) per polymer chain. Hence, integration of these two peaks should give an estimate of number average molecular weight.

For polymer 9, integration of the ^{1}H NMR indicated a molecular weight of approximately 21,000, based on 20 to 21 repeat units. Polymer 10 gave about a 32,000 molecular weight, also for 20 to 21 repeat units. For polymer 11, the peak at 5.60 was too small to integrate with any degree of accuracy.

The polymers were soluble in common organic solvents, such as chloroform, methylene chloride, and N,N-dimethylformamide. Brittle, amber-colored films of 9 and 10 could be cast from these solvents. Polymer 11 was much less soluble. Films of 11 could be formed from N,N-dimethylformamide only with careful control of evaporation rate.

The thermogravimetric analysis (TGA) of the polymers is shown in figures 1(a) to (c). Interestingly, the polymers appear to be more stable in air than nitrogen. In air, each polymer exhibited an initial weight loss of a few percent at approximately 390 °C, the curve leveled off, and the final onset of decomposition occurred at 560 to 570 °C. In contrast, decomposition of the polymers in nitrogen occurred rapidly starting around 390 to 400 °C.

Apparently, there are two different degradation pathways operating in the 390 to 400 °C range. One is a chain scission process, probably retro-Diels-Alder reaction, and the other leads to a more stable structure. The stabilizing reaction is dehydration of the epoxide moieties, leaving anthracene-containing pentiptycene units along the polymer backbone.
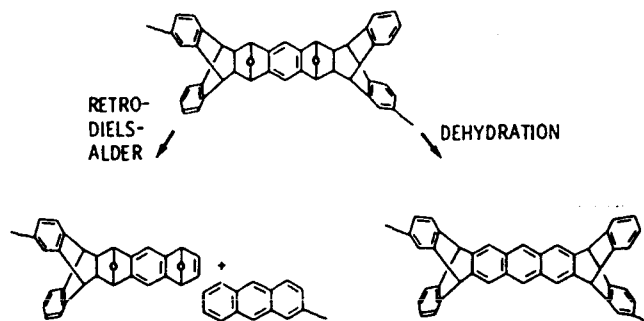
In nitrogen, judging from the rapid weight loss at 390 to 400 °C shown by the TGA, both dehydration and retro-Diels-Alder reaction are occurring. In

3

air, the retro-Diels-Alder reaction appears to be either stopped, or at least slowed down considerably, making dehydration the dominant process. This strongly suggests that the retro-Diels-Alder reaction, in this case, is not concerted, but rather goes through a biradical intermediate. In air, this biradical can be quenched by oxygen.

Actual weight loss in air at approximately 450 °C, the point that the TGA leveled off, were as follows: the m=0 polymer, 9, lost close to 5 percent, initially; the m=1 polymer, 10, lost 3.5 percent; m=2 polymer, 11, lost 2 percent. The calculated weight loss which can be accounted for by dehydration of polymers 9, 10, and 11, respectively, is 3.6, 2.4, and 1.8 percent. The approximately 1 percent difference between actual and calculated values can be accounted for by residual solvent or moisture absorption in the samples.

Since dehydration occurred faster than chain scission reaction in air at 390 to 400 °C, the resulting polymer was more stable. After dehydration, the aromatic structure formed cannot undergo retro-Diels-Alder reaction.

As further verification that dehydration occurred and was responsible for the initial weight loss in air, polymer 10 was treated with concentrated hydrochloric acid in acetic anhydride. This is the same method as that used by Hart and coworkers to dehydrate adduct 3 (ref. 2). TGA in both air and nitrogen of the dehydrated polymer is shown in figure 2. Here, the onset of decomposition is aproximately 570 °C in air, and 580 °C in nitrogen. There is no initial weight loss at 390 to 400 °C, as seen in the TGA of undehydrated polymer 10.

The unique thermal behavior of this system makes it a good candidate as a matrix resin for high temperature composites. Since the polymers are soluble in common solvents before dehydration occurs, they can be used to coat fibers, dried, and easily handled as prepreg materials. After heating past the softening and dehydration temperatures, a resin is formed which is very thermally stable. This is presently under investigation.

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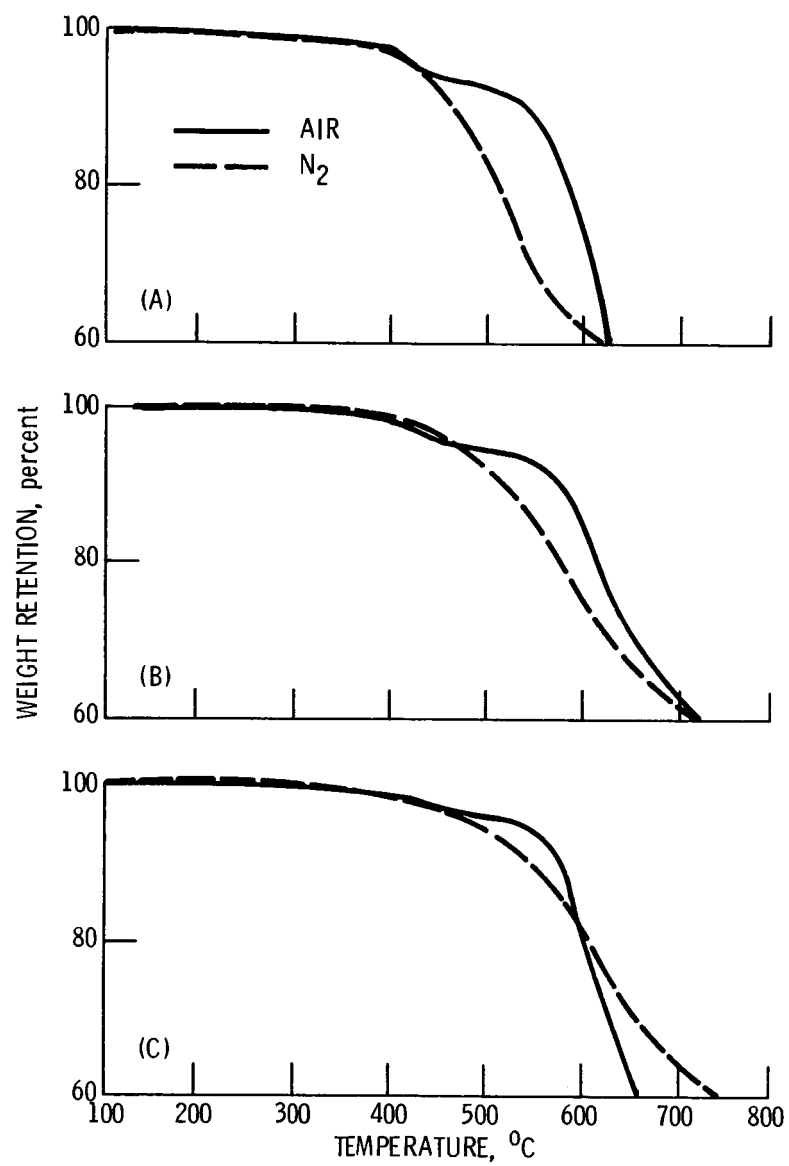7. Stevens, M.P. J. Polym. Sci. Polym. Lett. Ed., 1984, 22, 467.

FIGURE 1.

FIGURE 2.
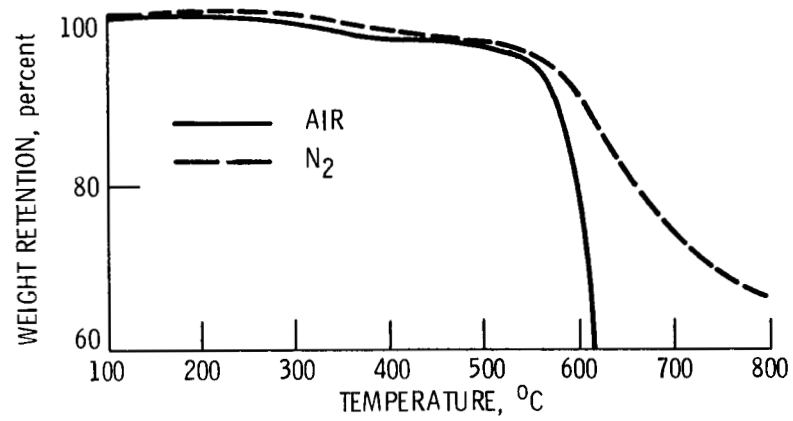
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