

Synthesis, Crosslink and Properties of Novel Phenylethynyl-Terminated PAEK Oligomer

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INTRODUCTION:

High temperature, solvent resistant materials which also display good mechanical properties are desired for use as aerospace structural adhesives and polymer matrix/carbon fiber composites. However, the high performance/high temperature polymers typically exhibit high melt viscosities and insoluble in common organic solvent, as a consequence, processability by compression and injection moulding for use as composite matrices and adhesives is often difficult or unachievable.

In recent years, in an effort to address the problem of high melt viscosities, development of low molecular weight oligomers with phenylethynyl terminated group as cross-linking precursor for the preparation of high performance thermosets has attracted considerable attention¹⁻⁵. Since the oligomeric glass transition temperature value or melt temperature can be designed to be below 200 °C (or T_g be below 250 °C) there is a desirable large melt processing window for these materials between $T_g(T_m)$ and T_{cure} . Moreover, the melt viscosity of general oligomeric poly(arylene ether)s is very low, between 250 °C and 350 °C, suggesting applicability to processing techniques such as resin infusion (RIM) and/or resin transfer molding (RTM) which are attractive methodologies for the economical manufacture of polymer matrix/carbon fiber composites.

Herein a new star-branched, phenylethynyl-terminated aryl ether oligomer which possesses lower melt viscosities and/or high solubility and lower melt temperature before cure was prepared. While its cured polymer exhibits high T_g , thermo-oxidatively stable, solvent-resistant networks. DSC data clearly showed that the uncured oligomer has a low melt temperature and displayed a wide process window. While a low melt viscosity at 280 °C and a discrete data was obtained by dynamic rheometer due to its good fluidness. IR spectra was used to follow the cure of the oligomer and showed the time-dependent and temperature-dependent disappearance of the phenylethynyl groups. This oligomer with low molecular weight underwent thermally curing to yield a network at 370 °C for 1h, as a result obtaining the polymer which has excellent composite properties. The TGA and DMA spectra suggest that the cured polymer possesses excellent thermooxidative stability and a good retention of storage modulus

above the glass transition temperature(to 400°C).

EXPERIMENTAL:

Starting materials

commercially obtained 4-bromobenzoyl chloride (mp 36~39°C) was purified by recrystallization in ketone as a solvent and dried at 23°C in vacuo before use. Bis(triphenylphosphine) palladium(II) chloride ($\text{PdCl}_2(\text{PPh}_3)_2$) and phenylethynyl were obtained from Fluka Co. and used as received. Triethylamine(b.p. 88.9°C) and phenylethynyl(b.p. 140~143°C) were freshly distilled before use. Anhydrous potassium carbonate(K_2CO_3) was dried at 100°C and stored in a desiccator. Other solvents, reagents and catalysts were used as received.

Monomer synthesis

Synthesis of 4-fluoro-4'-phenylethynylbenzophenone(FPEB)

The FPEB was synthesized via the palladium-catalyzed coupling reaction of 4-bromo-4'-fluorobenzophenone and phenylethynyl using the known procedure⁶ as shown in Scheme 1.

Oligomer synthesis

A 250ml three-neck round bottom flask equipped with a mechanical stirrer, a nitrogen inlet-outlet, a Dean-Stark trap and a reflux condenser was added 7.2g(0.024mol) of FPEB, 2.5g(0.018mol, 50mol% excess) of anhydrous potassium carbonate(K_2CO_3), 150ml of DMAc and 40ml of toluene. The solution was heated to reflux and the toluene/water mixture was removed by azeotropic distillation. A solution of 1.008g(0.008mol) of 1,3,5-trihydroxybenzene(THB) in 30ml of DMAc was added dropwise over 10h. After the addition, the reaction was further conducted at reflux temperature for 6h. Then, the mixture was cooled to 23°C and poured into 1000ml of acidic(HCl) water. The precipitate was collected by filtration and washed with distilled water three times and washed with ethanol once. The crude product was recrystallized from DMAc to provide objective oligomer.

Molded specimens

The obtained aryl ether oligomer was molded by using $6 \times 6 \times 0.05 \text{ cm}^3$ polyimide film frame on a $20 \times 20 \text{ cm}^2$ stainless steel plate with UPILEX-S separator films under 1.4MPa by heating initially to above T_m for 10min and subsequently to 370°C for 1h. The dark red film-like specimens of $6 \times 6 \times 0.05 \text{ cm}^3$ thick were obtained.

Characterization

Differential scanning calorimetry(DSC) was performed on a Mettler Toledo DSC821^e thermal analyzer with the sample sealed in an aluminum pan. The T_g of polymer was determined with DSC at a heating rate of 20°C/min in a nitrogen atmosphere. The infrared spectra of melted oligomer as deposited onto silicon wafers

and KBr powder-pressed pellets were recorded on a BRUKER VECTOR22 spectrometer. Dynamic thermogravimetric analyses(TG) were determined on films using a PERKIN-ELMER TGA7 series in the range 30~900°C at a heating rate of 10 °C/min in an air atmosphere. Dynamic mechanical analyzer(DMA) was performed on thin film specimens(23.7mm long, 5mm wide, and 0.05mm thick) on Rheometric Solids Analyzer RSA II instrument at a heating rate of 5°C/min and load frequency of 1Hz in an air atmosphere.

RESULTS AND DISCUSSION:

Aryl ether oligomer synthesis

FPEB was chosen as an endcapping agent because it has been reported to be very reactive in aromatic nucleophilic displacement reactions⁶. The fluorine atom is activated for displacement by the electron-withdrawing carbonyl group in the para-position. The phenylethynyl-terminated, branched aryl ether oligomer has been synthesized at 160°C, via a nucleophilic route by using FPEB and THB as the branching unit, and shown as scheme 2. In order to get a high yield of final product, 30ml of the DMAc solution of the THB was added into the reaction system with a dropwise addition over 10h, and get a temporal high reaction concentration of FPEB for the dropped THB. The structure of aryl ether oligomer can not be confirmed by NMR because of its difficult solubility in CDCl₃ and DMSO-d₆. However, its theory molecular weight is accordance with the result of MS, as shown in Figure 1. Similarly, the element analysis for aryl ether oligomer has also proved the results.

Uncured aryl ether oligomer thermal behavior

To study the crosslinking of the oligomer and the thermal behavior of the cured material, DSC analysis was performed. As shown in Figure 2, the oligomer displayed a sharp melting endothermic peak at 252°C and an exothermic peak onset near 330°C peaking at 403°C as the first scan. The exothermic peak has been associated to cross-linking reaction⁷. It is advantageous to processibility such as resin infusion or resin transfer molding because the aryl ether oligomer exhibits a lower melting point compared with PEEK(m.p.334°C), and its high temperature cure exotherm also demonstrates the wide curing window from meltability to crosslinking. After annealing, DSC curve did not showed a distinct transition when the sample was rerun. However, disappearance of melting endothermic peak and curing exothermic peak indicated those phenylethynyl functional groups have been cured completely in the first heating run. Unexpectedly, no further glass transition of the cured polymer was observed when the second scan.

On the other hand, the aryl ether oligomer displays a low melt viscosity at 280°C because of its highly crystal. Its melt viscosity at 280°C was below 0.1Poise and a

discrete data was obtained by dynamic rheometer due to its good fluidness.

Cross-linking behavior of phenylethynyl-terminated aryl ether oligomer

The crosslink reaction of phenylethynyl end group was demonstrated by IR spectroscopy by following the disappearance of the phenylethynyl absorption band at 2210 cm^{-1} . The molecular modeling results earlier mentioned, which revealed the ethynyl bonds to be most probable sites for radical attack suggested monitoring the time-dependent variations in the intensity of the $\text{C}\equiv\text{C}$ stretching vibration peak at around 2210 cm^{-1} as a good measure of the progress of the curing reaction. As shown in Figure 3, the IR spectra displayed that the absorption band of the phenylethynyl triple bond for uncured portions of the oligomer decrease gradually with cure time and consumed totally within 1h at a constant temperature (370°C). The time-dependant disappearance of the ethynyl indicated that the $\text{C}\equiv\text{C}$ bond in endcapper group have been completely cured at 370°C for 1 h.

In addition, in order to determine the best temperature of the crosslinking reaction, IR spectroscopy was used to monitor the curing reaction at two different temperatures, 300 and 370°C . As shown in Figure 4, the absorption band of the phenylethynyl triple bond was still observed after cured at 300°C for 1 h while the absorption band of the triple bond have disappeared after cured at 370°C for 1 h, suggesting that phenylethynyl could be cured completely at 370°C within a constant reactive time(1h).

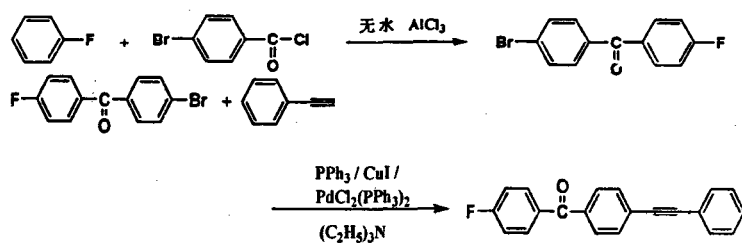
Cured polymer

The cured aryl ether polymer film was obtained from compressive molding at 370°C for 1h. A typical DMA curve of the cured polymer was shown in Figure 5. Regarding the peak temperature in the E'' curve as the glass transition temperature, the polymer exhibits a higher T_g at 350°C . Unexpectedly, the cured sample displayed a high storage modulus and have a good retention even above the T_g (about 400°C). The high modulus may be due to high crosslinking density resulting from the low molecular weight of the oligomer before cure and presence of the polar carbonyl group and rigid structures in the oligomer backbone.

TGA curves of the cured film were measured at a heating rate of $10^\circ\text{C}/\text{min}$ in an air atmosphere. As shown in Figure 6, the cured polymer did not begin to lose weight until 500°C , even in air, and the 5% weight loss values occurred at 528°C . The TGA data indicated that the cured polymer film had excellent thermal stability. The tensile properties of the material can not be detected because of the lower fracture toughness of the film. The low fracture toughness result from the lower molecular weight and hyper branched oligomer that led to the higher crosslink density.

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Scheme 1: Synthesis of the endcapper FPEB

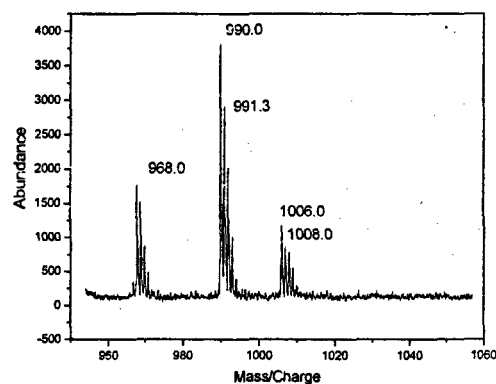
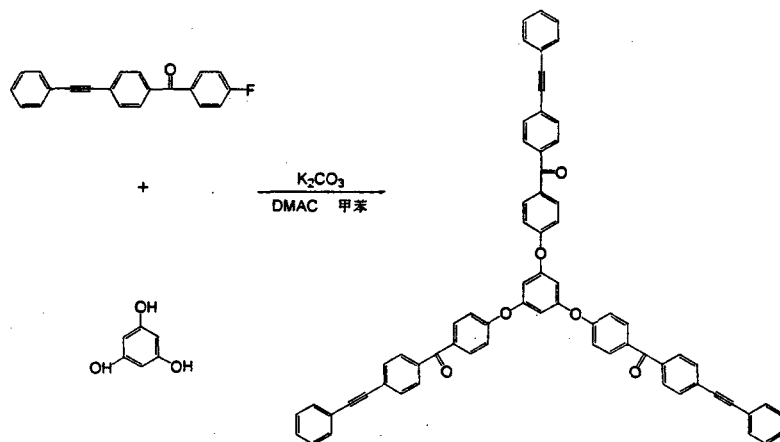


Figure 1: TOP MS of the oligomer



Scheme 2: Synthesis of the aryl ether oligomer

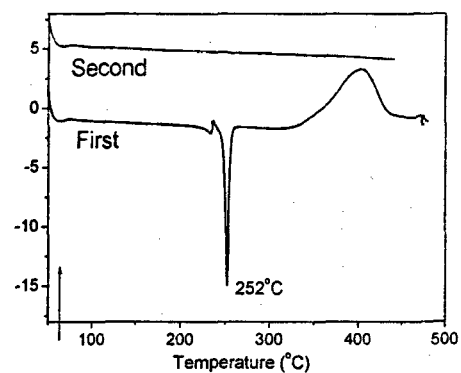


Figure 2: DSC curves of the oligomer

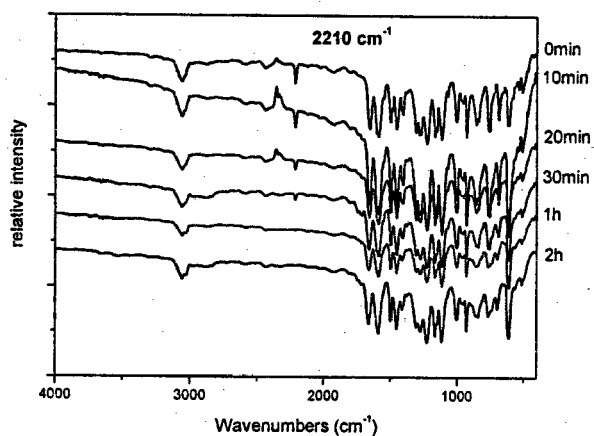


Figure 3: IR spectra of the oligomer for 370°C at different time

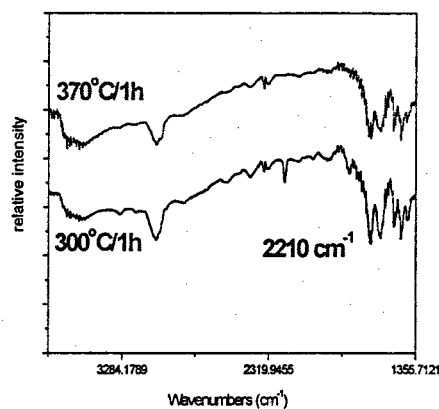


Figure 4: IR spectra of the oligomer at 300°C and 370°C for 1h

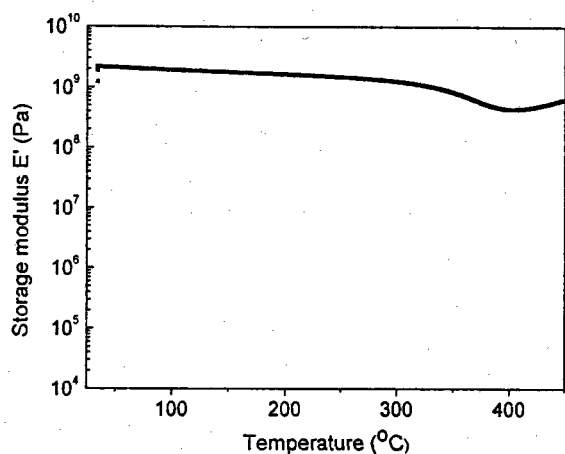


Figure 5: DMA curve of the cured polymer film

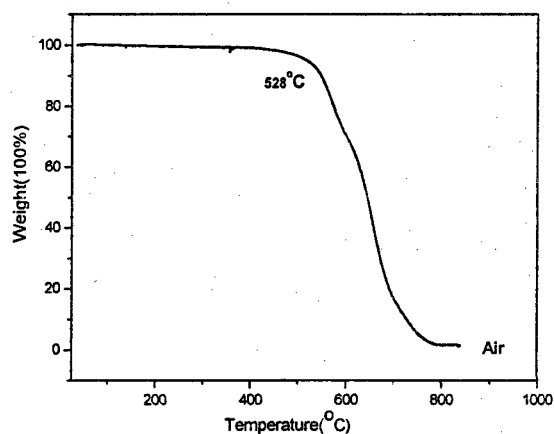


Figure 6: TGA curve of the cured polymer in an air atmosphere