

Synthesis and characterization of phenylethynyl-terminated polyimideoligomers with a good processability derived from pyromellitic dianhydride and 4,4'-bis(3-aminophenoxy)diphenyl sulfone

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ABSTRACT Novel addition-type polyimide oligomer (degree of polymerization: $n = 4, 6, 9$) derived from pyromellitic dianhydride (PMDA), 4,4'-bis(3-aminophenoxy)diphenyl sulfone (m-BAPS), and 4-phenylethynylphthalic anhydride (PEPA) was synthesized for the matrix resin of high heat resistant composites. The melt viscosity, solubility of the oligomers and the thermal, mechanical properties of cured resins were studied in this paper. The results show that the processability of uncured imide oligomers is good. They showed very low viscosity and good solubility in aprotic solvents. The polyimide oligomers were successfully converted to cross-linked structures after curing at 370 °C. The cured resins exhibit excellent thermal stability and mechanical properties.

Keywords: Polyimide oligomers, phenylacetylene endcapped, low melt viscosity, flexible structure

1. Introduction

Over past 30 years many addition-type polyimides have been developed for advanced composites in aerospace applications^[1]. In recent years, PEPA have been receiving more attention as a novel end cap for the synthesis of addition-type polyimide due to offering a larger processing window and better thermo-oxidative stability compared with traditional reactive end caps^[2]. However, most of PI have high melting, softening temperatures and bad solubility in organic solvents. These properties make them difficult to process, thus limiting their application. PETI-5 and Tria-PI have excellent thermal properties, but they are not suitable for low melt viscosity processing areas because of high melt viscosities^[3]. PETI-298, PETI-330 and other small molecules oligomers, have low melt viscosities and wide processing windows. But the poor thermal stability and mechanical performances of PETI-298 and PETI-330 make it difficult to apply in highly heat-resistant composites^[4].

It is important for us to develop a novel polyimide. On the one hand, it is expected to obtain the PI oligomers with lower melt viscosity and better solubility. On the other hand, cured resin should have excellent thermal stability and mechanical properties. In this paper, we describe molecular design. PMDA was adopted as diacids because its symmetric and planar structures can bring thermal stability^[5]. We introduce m-BAPS as bisamine to make sure that large amounts of bent, distorted structures^[6] and flexible ether^[7], sulfuryl^[8] units are contained in our PI. For investigating the structure-property relations, the melt viscosity, solubility of the oligomers and the thermal, mechanical properties of cured resins were studied in this paper. The uncured PI oligomers showed low viscosity and good solubility. The cured resins exhibit excellent thermal stability and mechanical properties.

2. Experimentation

2.1. Materials

m-BAPS was purchased from Changzhou Sunlight Fine Chemical Co. Ltd. It was dried in vacuum at 80 °C for 10 h. PMDA and PEPA were purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. N,N-dimethylacetamide (DMAc) were purified by distillation under reduced pressure over

CaH₂ and stored over 4 Å molecular sieves. Xylene and ethanol were supplied by Beijing Chemical Works. These solvents were used without further purification.

2.2. Measurements

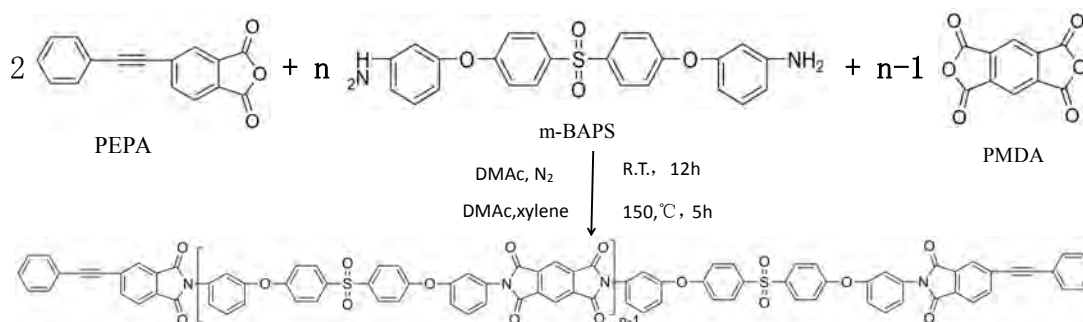
Differential scanning calorimetric (DSC) analysis was carried out on a TA instrument DSC Q100 with the sample sealed in an aluminum pan. Glass transition temperatures (T_gs) were determined with DSC at a scanning rate of 10 °C / min under nitrogen with 50 mL/min gas flow. Melt viscosity measurements were performed on a TA Instruments Co. AR-2000 dynamic rheometer at heating rate of 5 °C/min. Thermo gravimetric analysis (TGA) was performed with a heating rate of 10 °C/min under nitrogen or air atmosphere by the TA 2050. Dynamic mechanical analysis (DMA) was performed on thin film specimens on a TA instrument DMA Q800 at a heating rate of 5 °C/min with a load frequency of 1 Hz in nitrogen. Mechanical properties were measured on a Shimadzu AG-I universal testing apparatus with crosshead speed of 8 mm/min, tensile modulus, tensile strength and elongation at break were calculated as the average of five film strips^[9].

2.3 Preparation of uncured PI oligomers

PEPA terminated imide oligomers derived from PMDA and m-BAPS were synthesized according to a previous literature^[1]. The degree of the polymer can be controlled by adjusting the mol ratio of monomers attend the polycondensation. The synthesis of polyimide oligomers (n=4) is used as an example to illustrate the detailed synthetic procedures (as shown in Scheme 1). m-BAPS (8.6498 g, 0.04 mol) and DMAc (50 ml) were added in a dried 250 ml three necked round-bottom flask which was equipped with nitrogen inlet and magnetic stirrer. After the diamine was dissolved completely, PMDA (3.2718 g, 0.03 mol) was added and the reaction mixture was stirred for almost 6 h at room temperature. After then PEPA (2.4312 g, 0.02 mol) was added with extra DMAc (12 ml) to adjust the concentration of total solids to 20% wt. The solution was stirred for another 6 h at room temperature to obtain the PEPA end-capped amide acid oligomer. And then, Xylene (25 percent of the total volum) was added into the solution. After the attachment of a water segregator and a reflux condenser to the flask, the amide acid oligomers in DMAc solutions were imidized at 150 °C in oil bath for 5 h. After cooling the flask to room temperature, the obtained solution was completely clear without precipitations. The solutions were poured into ethanol (300 ml) to reprecipitate the imidized oligomer. The precipitates were filtrated, washed with ethanol three or four times and dried in vacuum oven at 160 °C for 10 h.

2.4 Preparation of cured PI film

The obtained imide oligomers were molded by using a 6 cm × 6 cm × 0.05 mm polyimide film frame on a 20 cm × 20 cm stainless steel plate with UPILEX-S separator films under 1.4 MPa by heating initially to 260 °C for 30 min and subsequently to 370 °C for 1 h. The brown-colored film-like specimens of 6 cm × 6 cm × 0.05 mm were obtained.



Scheme 1. preparation of PI oligomer

3.Results and discussion

A serie of novel addition-type imide oligomer derived from PMDA, m-BAPS and PEPA was designed to synthesize. Our PI oligomers were synthesized using two-step methods, which were carried out via polyamic acid (PAA) intermediate. Inherent viscosities (η_{inh}) of PAA were measured with an Ubbelohde viscometer at 25°C in DMAc at a concentration of 0.5 g/dL. The result were $\eta_{inh}(n=4) < \eta_{inh}(n=6) < \eta_{inh}(n=9)$, which suggests that different molecular weights of polyimide oligomers were successfully obtained.

Fig. 1 demonstrates IR spectra for the uncured imide oligomers. All the PIs exhibited characteristic imide group absorptions around 1780 cm^{-1} (asymmetrical C=O stretching), 1721 cm^{-1} (symmetrical C=O stretching), 1394 cm^{-1} (C-N stretching). In addition, an absorption of PI oligomers curves around 2210 cm^{-1} (C≡C) suggests that phenylethyne-terminated PI oligomers were prepared successfully. The PI oligomers were converted to cross-linked structures after curing at 370 °C. The absorption of cured PI films curves around 2210 cm^{-1} (C≡C) disappeared, which indicated the PI oligomers had been fully cross-linked.

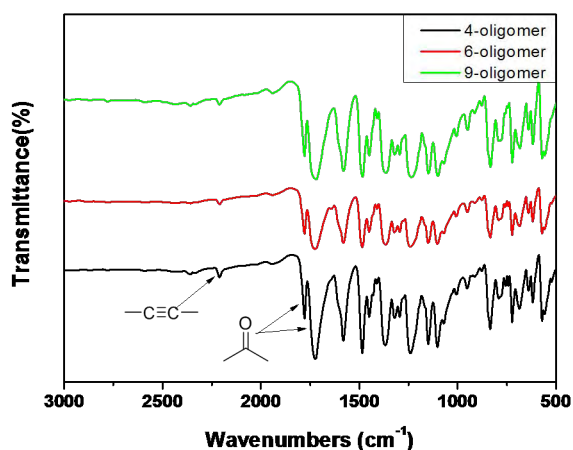


Fig.1 IR spectrum of uncured PI oligomers

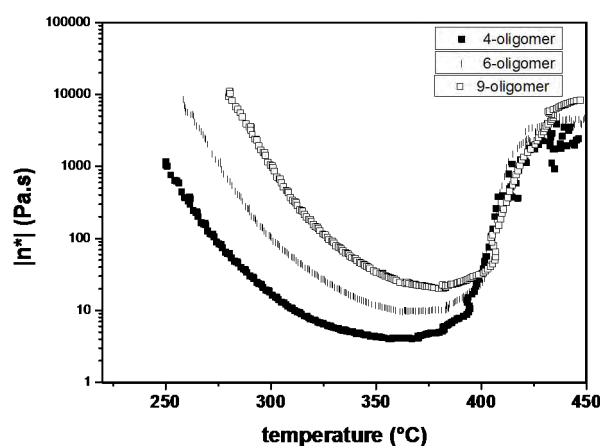


Fig.2 The rheological behaviors of uncured PI oligomers

3.2. Solubility, processability and thermal properties of the uncured PI oligomers

Table 1. Solubility, Tg and minimum melt viscosity of uncured imide oligomers

simple	Solubility in DMAc	Tg(°C) .	Min. melt viscosity (Pa·s)
n=4	>20%w.t.	212	4.08
n=6	>20%w.t.	226	9.77
n=9	>20%w.t.	236	23.74

Table 1. Shows Thermal, solubility properties and processability of the uncured PI oligomers. Oligomers showed good solubility in aprotic solvents. On the other hand, they were completely soluble in DMAc solution with high concentration even at room temperature (>20%wt.). Fig. 2 shows the dynamic rheological properties of the PI oligomers. The minimum melt viscosity of the imide oligomers also increased with increase of the degree of polymerization. These data shows that polyimide oligomer has a significantly better processability in compared with conventional PMDA-based polyimides. Especially, the oligomer (n=4) can be used to prepare the high performance resin-based composite materials via Resin Transfer Molding (RTM) due to their low melt viscosities (about 5 Pa·s). These excellent low melt viscosities is thought to be accomplished by their meta-phenyl and ether structures: bent and distorted polymer chain decrease the intermolecular interactions. In

addition, flexible sulfonyl units of m-BAPS component imparted PI better rheological properties. On the other hand, with higher heating temperature, the melt viscosity of the imide oligomers reduced initially then increased ($T > 370^\circ\text{C}$) due to crosslinking phenomenon.

Fig. 3 shows the DSC curves of PI oligomers, whose T_g at the range from 212 to 236°C . The increase behavior of T_g was observed because of an increase of the degree of polymerization. A large exothermic peak around 410°C was found due to cross-link phenomenon.

3.3. Thermal and mechanical properties of cured PI films

Thermal and mechanical properties of the cured rein (PMDA/m-BAPS/PEPA) are summarized in Table 2. All data were obtained from cured homogeneous brown-colored films.

The thermal properties of the cured PI films were evaluated by DSC, DMA, TGA. The results are summarized in Table 2. T_g of the polyimides were in the range of $268\sim 275^\circ\text{C}$ and $265\sim 270^\circ\text{C}$, as attributed to the different responses of the samples to the two characterization methods. Generally, T_g values of cured polymers are determined by chain rigidity of the polymer backbones and crosslinking density. As a result, it is observed that the T_g values of the cured PI films increased with decrease of the degree of polymerization in Table 2. This might be attributed to inhibition of free rotation of the polymer segments due to the existence of crosslinking sites [11].

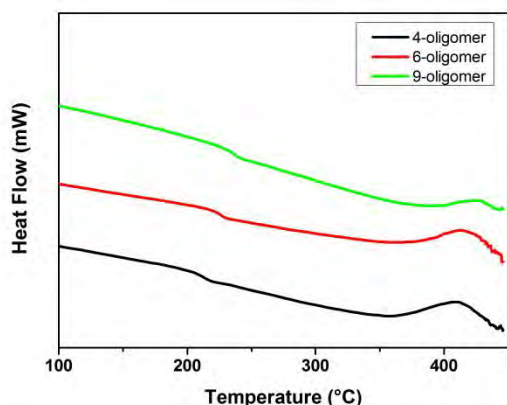


Fig.3 DSC curves of the uncured PI oligomers

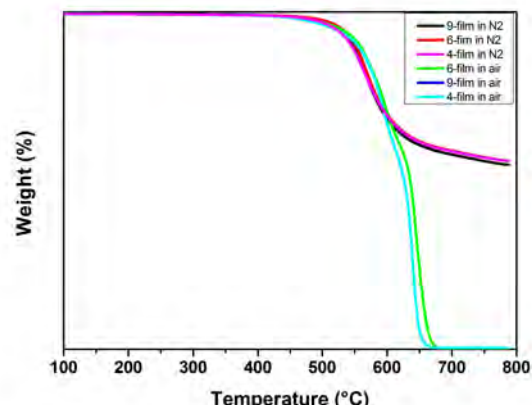


Fig.4 TGA curves of the cured films

Sample	Thermal and mechanical properties of						$R_{800^\circ\text{C}}$ (%)	Modulus (GPa)	Strength (MPa)	Elongation (%)
	T_g (°C)		$T_{5\%}$ (°C)		$T_{10\%}$ (°C)					
	DSC	DMA	Air	N ₂	Air	N ₂				
n=4	275	270	520	520	554	545	56	1.74	59.7	4.1
n=6	274	267	529	530	558	551	56	2.06	80.2	6.0
n=9	268	265	530	525	557	549	55	2.23	84.1	6.5

Fig. 4 show the TGA curves of the polyimide films. As can be seen from Fig.4, all the cured PI films showed fairly good thermal stability. They did not show obvious weight loss before 490°C , implying that no thermal decomposition occurred. 5% weight loss temperatures ($T_{5\%}$) were located over 520°C no matter in nitrogen or in air. This might be attributed to a large number of phenyl structures in polymer chain. The cured PI films were tested for mechanical properties at room temperature, as summarized in Table 2. The polyimide films had the tensile strength as high as 80 MPa, the tensile modulus in range of $1.74\sim 2.23$ GPa, and the elongation at break of 6%, indicating that the obtained cured PI films were tough and strong. These data might be supported by the high storage modulus of DMA curves. In comparison of the traditional cured PI, the PI derived from m-BAPS/PMDA/PEPA exhibited the higher elongation at break. It might be attributed to the bent and distorted structure and flexible units of polyimide backbone.

4. Conclusion

Novel phenylethynyl-terminated, addition-type imide oligomer containing ether and sulfonyl units were synthesized and characterized. The experimental results show that the introduction of flexible structure is an effective way to improve the solubility and processability. The uncured imide oligomers was found to have a good solubility and a good processability. Especially, the oligomer(n=4) can be used to prepare the high performance resin-based composite materials via RTM due to their low melt viscosities (about 5 Pa·s). These imide oligomers were successfully converted to cured resin which exhibit high Tg(Tg>260°C) and excellent mechanical properties.

In addition, through clarifying the relationship of degree and property, it is a great benefit to obtain the polyimide oligomers (degree of polymerization: n = 1, 2, 3) with lower melt viscosity and better solubility. We believe that these excellent properties of PMDA/m-BAPS-based addition-type polyimides suggest promising possibilities for application to highly heat-resistant composites prepared by polyimide wet prepreg and a RTM system.

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