

Novel phenylethynyl-terminated polyimide with excellent processability and high thermal stability

Abstract: Highly soluble and processability phenylethynyl-terminated polyimide oligomers with different molecular weight (degree of polymerization: $n=1\sim 9$) were successfully prepared from 2,3,3',4'-biphenyltetracarboxylic dianhydride (α -BPDA) and ether ketone diamine, 4,4'-Bis(3-aminophenoxy)benzophenone (BABP), and utilizing 4-phenylethynylphthalic anhydride (4-PEPA) as end-capped reagent. The uncured imide oligomers showed good solubility in aprotic solvents such as 1-methyl-2-pyrrolidinone (NMP), dimethylacetamide (DMAc) and so on. The oligoimide resins exhibited minimum melt viscosities of less than 10 Pa.s at around 300 °C to 330 °C, indicating wide melting processing windows for these prepared polyimide resins. Imide oligomers were cross-linked at an elevated temperature of 370 °C for one hour, and the cured polyimides exhibited excellent thermal stability both under N_2 and air atmosphere. The 5% weight loss in N_2 and air atmosphere were above 454 °C and 440 °C respectively.

Keywords: polyimide, imide oligomer, processability, solubility, thermal properties.

1. INTRODUCTION

Aromatic polyimides are well known with outstanding mechanical properties and high temperature stabilities. They can be utilized for a wide variety of applications such as in the electronic, automotive, and environmental protection^[1-3]. Over past 30 years, aromatic polyimides have been developed for advanced composites in aerospace. In aerospace industry, thermosetting polyimides have been used as matrix resins in carbon fiber reinforced composites as replacements for metallic components, due to their high strength-to-weight ratio and outstanding thermal stabilities. However, these materials usually have some defects, such as poor solubility in the vast majority of organic solvents as well as high melt viscosity, which limited their widespread application^[4]. Therefore, seeking for strategies to improve the processability of aromatic polyimides and maintaining their outstanding properties is a hot issue of research^[5]. In the past few years, phenylethynyl-terminated oligoimides (PEPA-oligoimides) have gained tremendous attention,

especially for the relationship between their chemical structures and melt viscosities and thermal properties. Many researchers, especially in NASN Langley Research Center, have studied various kinds of phenylethynyl terminated imide oligomers. For instance, PETI-5 prepared from 3,3',4,4'-biphenyltetracarboxylic dianhydride (*s*-BPDA), 3,4'-oxydianiline (3,4'-ODA) and 1,3-Bis(3-aminophenoxy)benzene (1,3,3-APB) has good processability. However, high melt viscosity of PETI-5 oligomer has limited its application^[6].

In order to search for balance between melt-processable aromatic polyimides with excellent processability and high thermal properties, there has been a lot of reports focusing on decreasing the melt viscosities and improving T_g of cured resin by reducing the degree of polymerization of the oligoimide^[7-8]. It was found that the low melt viscosity could be achieved by reducing the M_n of resin, meanwhile, the toughness of the material also could be reduced. An effective approach to solve this problem is the incorporation of bulky pendent groups^[9-10], noncoplanar or twisted monomers^[11-12] and flexible links^[12,13].

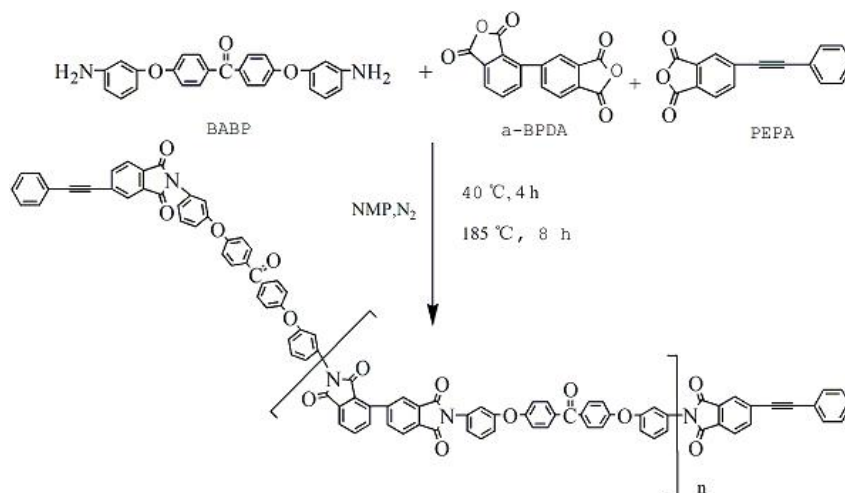
Based on the above considerations, in this study, a series of novel phenylethynyl-encapped oligoimides (PEPA-oligoimides) with different molecular weight (degree of polymerization: $n=1\sim 9$) were successfully prepared from 4,4'-Bis(3-aminophenoxy)benzophenone (BABP) and 2,3,3',4'-biphenyltetracarboxylic dianhydride (α -BPDA) by utilizing 4-phenylethynylphthalic anhydride as end-capped reagent at high temperatures. For the purpose of obtaining resin matrix with excellent processability through the combination of flexible ether ketone chain segment with diamine and asymmetric structure of aromatic dianhydride. Oligomers were prepared to study the relationship between their molecular weight and properties.

2 EXPERIMENTAL

2.1 Materials

2,3,3',4'-biphenyltetracarboxylic dianhydride(α -BPDA, 99%), 4,4'-bis(3-aminophenoxy)benzophenone (BABP, 98%), and 4-phenylethynylphthalic anhydride (PEPA, 99%) were purchased from Changzhou Sunlight Fine Chemicals Co. Ltd (China). N-methyl-2-pyrrolidone (NMP) were purchased from LingFeng Chemicals Co., Ltd. (Shanghai China). Other solvents were all used as received from their respective vendors and without further purification.

2.2 Preparation of the PEPA-imide oligomer with designed polymerization degree.



Scheme 1. Preparation of PI oligomers

The PEPA terminated oligomers based on BABP, α -BPDA, and PEPA with designed degree of polymerization of 1~9 were synthesized according to a typical method as shown in Scheme 1. The synthesis of polyimide oligomers PI-4, which has the polymerization degree of 4 ($n=4$), is used as an example to illustrate the detailed synthetic procedures. BABP (20.9035 g, 0.05 mol) and NMP (110 ml) were added in a dried 250 ml three-necked round-bottom flask, which was equipped with nitrogen inlet and magnetic stirrer, thermometer, dean stark trap and condenser. After the diamine was dissolved completely, α -BPDA (12.4109 g, 0.04 mol) was added and the reaction mixture was stirred for 4 h at 40 °C. Then, PEPA (5.2355 g, 0.02 mol) was added with extra NMP (40 ml) to adjust the solid content to 20 wt%, the mixture was stirred at 60 °C for another 24 hours to obtain the viscous poly(amic acid) resin solution. Next day, the solution was heated and refluxed at 185 °C for 8 h. After cooling down, the resin solution was poured into an excess of anhydrous ethanol and dried in vacuum oven at 150 °C for 4 h to afford oligomer powders with yield of 95%. Similarly, PEPA terminated oligomers PI-1, PI-2, PI-6, and PI-9 (the PI-number 1,2,6,9 represent the degree of polymerization) were also synthesized with an analogous procedure as described.

2.3 preparation of the Thermal-cured Polyimide Neat Resins.

The PEPA-oligoimide powders were dissolved in NMP with 10 wt% of solid content, and stirred for overnight at room temperature. The homogeneous oligoimide solution was poured

into a clean and dry plate-glass and dried in vacuum oven at 60 °C for 12 hours, 120 °C, 150 °C, 180 °C, 250 °C, 280 °C, and 350 °C for 1 h, respectively, and finally at 370 °C for another 1 hours. When the temperature drops to room temperature, the thin films were removed from the glass by immersion in hot water and then cut into required sized for the subsequent thermal and mechanical tests.

2.4 Characterization and Measurements

The chemical structure and crosslink characterization of The PEPA-oligoimide powders were measured using Fourier transform infrared (FTIR) spectra with presses KBr pellets and the cured thin films were measured using FT-IR with an ATR accessory (FTIR; Nicolet 8700). X-ray diffraction (XRD) patterns were collected in a Rigaku Dmax-2550 diffractometer with Cu K α radiation. Rheological behavior measurements were performed on a HAAKE MARS III Rotational Rheometer, with a fixed strain of 5% and a fixed angular frequency of 10 rad/s. Sample specimen discs of 2.0 cm diameter and 2 mm thickness were prepared by press molding (5 MPa) the oligomer powders at room temperature. Complex viscosity (g^*) was measured from 100 to 400 °C at a heating rate of 4 °C/min under a continuous nitrogen flow. Differential scanning calorimetry (DSC) was performed on a TA DSC Q20 at a scan rate of 20 °C/min in flowing nitrogen. The T_g of cured films was measured with DMA Q800. The rectangular-shaped specimens with the dimensions of 15 \times 5 \times 0.3 mm were held by vertical clamps subjected to tensile modes. Measurements were conducted over a range of 50 to 350 °C at heating rate of 5°C/min and a loading frequency of 1 Hz. Thermogravimetric analysis (TGA) test was carried out on Netzsch TG 209 F1 Iris carrying out on approximately 5~10 mg samples at a heating rate of 10 °C/min under nitrogen or air atmosphere. Tensile tests of the cured films were performed on Instron 5567 tensile testing machine. Five specimens were tested for each sample at room temperature with a constant cross-head speed of 5 mm/min.

RESULTS AND DISSCUSSION

Synthesis and Characherization of PEPA-oligoimides

FT-IR. In Fig. 1(a), The asymmetric and symmetric stretching absorption bands around 1778 and 1722 cm^{-1} , as well as the bending vibration absorption band around 725 cm^{-1} were attributed to

the imide groups (C=O) in the oligoimide backbone. Meanwhile, the absorption at 1380 cm^{-1} assigned to the vibration of the C-N in the imide five-membered ring was also detected, characteristic peak of ketone carbonyl can be observed at 1650 cm^{-1} due to 4,4'-Bis(3-aminophenoxy) benzophenone moiety as diamine content. Additionally, the absorption at 2210 cm^{-1} was attributed to the stretching vibrations of phenylethynyl groups ($-\text{C}\equiv\text{C}-$) in the oligomer, and the absorption at 2210 cm^{-1} became weakened in intensity as the degree of polymerization increased, implying the content of PEPA gradually diminished. Evidently, the

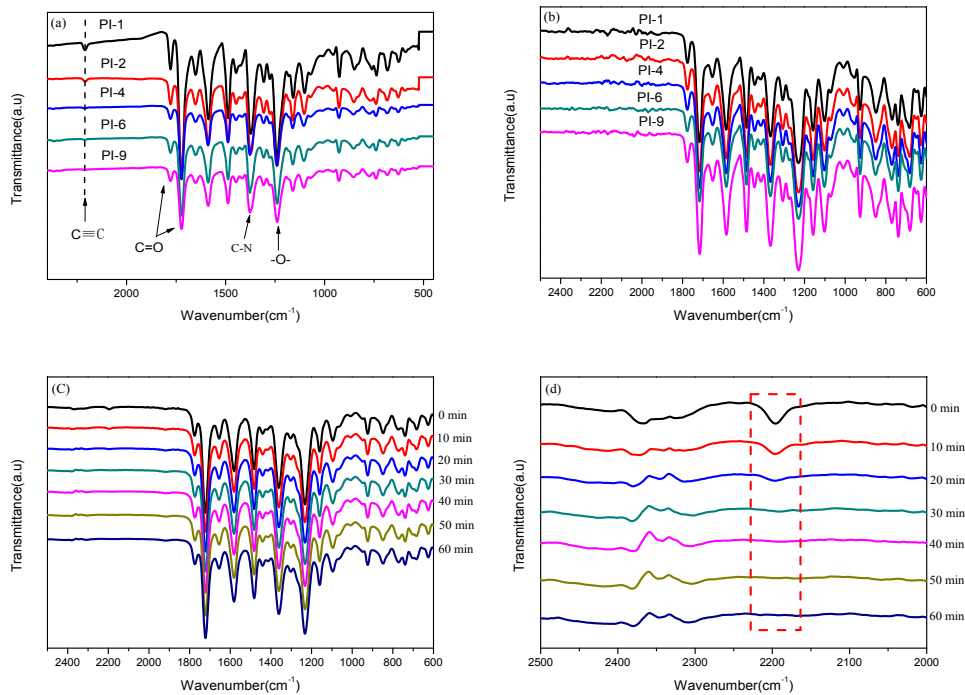


Fig.1 FT-IR spectra of (a) uncured PEPA-oligoimide powders, (b) cured thin films (ATR), (c) PI-2 oligomer at $370\text{ }^{\circ}\text{C}$ for 1 h with ranges from 2500 cm^{-1} to 600 cm^{-1} , (d) PI-2 oligomer at $370\text{ }^{\circ}\text{C}$ for 1 h with ranges from 2500 cm^{-1} to 2000 cm^{-1} .

oligoimides with phenylethynyl end-capping groups have been definitely acquired. In Fig.1 (c) and (d), the crosslink reaction of phenylethynyl group $\text{C}\equiv\text{C}$ was monitored by FT-IR as illustrated by PI-2. From the Fig.1 (c), the skeleton structure of the oligoimides has not changed at $370\text{ }^{\circ}\text{C}$ for 1 h, indicating that PEPA-oligoimide has excellent thermal stability. It can be seen from Fig.1 (d) that the absorption peak around 2213 cm^{-1} decreased gradually and almost vanished after 30 min when cured at $370\text{ }^{\circ}\text{C}$, which demonstrated the sample heated at $370\text{ }^{\circ}\text{C}$ for 1 hour can be completely cured. Therefore, cured polyimide films in Fig.1 (b) were lack of the characteristic peak of phenylethynyl group $\text{C}\equiv\text{C}$ at around 2210 cm^{-1} , meaning that the films has been cured

completely.

XRD. Fig.2 shows the XRD curves of the oligoimide powders, and all the curves show wide peaks and no sharp crystal peaks. These results indicated that low crystallizability of all of these oligoimides^[13], which may be owed to the introduction of flexible ethers and ketone carbonyl structure of diamines (BABP) as well as asymmetric structural dianhydride (α -BPDA) in the main chains.

Thermal properties of the oligoimides and cured polyimides. The glass transition temperature (T_g) of uncured oligoimides were determined by DSC at a heating rate of 20 K/min under N_2 atmosphere. Each oligoimide was dried under vacuum oven at 60 °C for 6 hours before testing. As can be seen from DSC curves of Fig.3, all the PI oligomers exhibited similar thermal behavior. Obviously, each oligomer has only one T_g within the temperature range of 150-210 °C, and a remarkably exothermic peak in the range of 405-425 °C. No sharp melting exothermic peak on

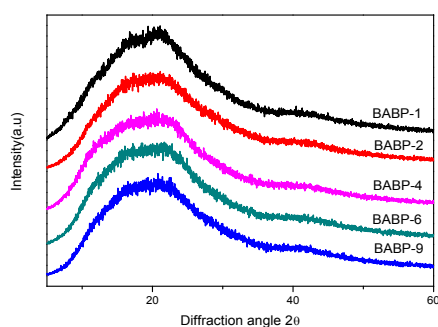


Fig.2 XRD patterns of phenylethynyl terminated oligomers

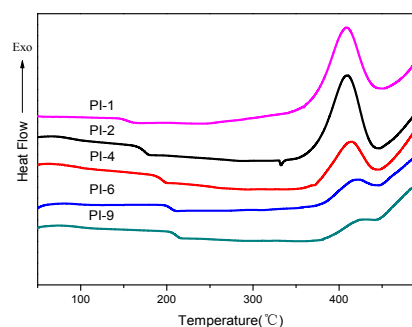


Fig.3 DSC curves of PEPA-oligomer

the DSC curves, and this phenomenon was consistent with the XRD results. The increase of the T_g can be observed from 154 °C to 210 °C due to the degree of polymerization increased. On the contrary, the T_g of the cured imide oligomers determined by DMA at the heating rate of 5 K/min and a loading frequency of 1 Hz (Table 1) were reduced with the degree of polymerization increased, owing to the T_g of cured resin is not only affected by the molecular weight but also related to the crosslink density. Generally, crosslink density increases as the degree of

Table 1. Thermal properties of oligoimides

Samples	Uncured powders				Cured Tg_2 (°C)	ΔTg (°C)
	DSC (first scan)					
	Tg_1 (°C)	Ti (°C)	Tp (°C)	ΔH (J/g)		
PI-1	154.16	372.65	407.87	171.9	313.19	159.03
PI-2	172.98	374.07	409.03	143.1	291.46	118.48
PI-4	193.22	377.59	413.24	58.76	289.12	95.9
PI-6	203.95	388.18	416.38	20.81	276.11	72.16
PI-9	210.38	401.39	422.15	2.71	265.12	54.74

Tg_1 : glass transition temperature of oligomers determined by DSC at the heating rate of 20 K/min under N_2 atmosphere Ti : onset crosslink temperature of the oligomers. Tp : the temperature of exothermic peak on DSC curves. Tg_2 : glass transition temperature of cured films determined by DMA at the heating rate of 5 K/min and a loading frequency of 1 Hz. $\Delta Tg = Tg_2 - Tg_1$.

varied from 54 to 159 °C with the degree of polymerization and the content of phenylethynyl groups. In addition, the exothermic peak were attribute to the complex reaction of the phenylethynyl groups in the chain of oligoimides, and the value of Ti and Tp moved to higher temperatures as the degree of polymerization increased due to segment motion and chain extending were restricted. Similarly, ΔH number was gradually reduced from PI-1 to PI-9.

Processability of the imide oligomers. The solubilities of the oligoimides with different degree of polymerization were listed in Table 2. The solubilities of the oligomers in different solvents was determined by dissolving 10 mg of oligomers powders in 1ml of solvent. The solution stability of oligomers in NMP and DMAc was also tested at 50 wt% of solid content. The results indicated that all the imide oligomers exhibited excellent solubility not only in polar aprotic solvents like N,N-dimethylacetamide, N,N-dimethylformamide, and NMP, but also in less polar solvents such as dimethylsulfoxide (DMSO) and tetrahydrofuran (THF). Meanwhile, the solubilities of all the imide oligomers were over 50%, which were mianlyattributed to incorporation of aromatic ether ketone structure and asymmetric structure into the main chain backbone. As we all know, the precursor of the composite is the prepreg, which is the intermediate material of the composites, and were usually made by immersing reinforcing fibers in the the resin matrixs . The preparation of thermosetting resin matrix prepregs are mainly based on two methods, namely solution impregnation method and melting method. Solution impregnation method is dissolved the

Table 2. Processability of the oligoimides.

Samples	NMP ^a	DMAc	DMF	CHCl ₃	DMSO	THF	Acetone	Min. Melt viscosity (Pa.s)
PI-1	>50%	>50%	++	++	+	+	-	0.29 at 311 oC
PI-2	>50%	>50%	++	++	+	+-	-	0.68 at 307 oC
PI-4	>50%	>50%	++	++	+	+-	-	7.21 at 316 oC
PI-6	>50%	>50%	++	++	+	+-	-	10.53 at 315 oC
PI-9	>50%	>50%	++	++	+	+-	-	7.84 at 332 oC

++: completely dissolved at room temperature;

+ : completely dissolved on heating;

+ -: partially dissolved on heating;

- : insoluble even on heating.

components of the resin matrix in solvent in a prescribed ratio to prepare a solution. The high content of prepregs is beneficial for reducing the formation of porosity in the composites, therefore, the higher solubilities of imide oligomers more than 50% are suitable for solution impregnation method to prepare composites. In addition, the minimum melt viscosities of the oligomers were carried out, and the data were listed in the Table 2. All the PEPA-oligoimides showed minimum viscosity 0.29-11 Pa.s at 307-332 °C, resulting in aromatic ether ketone structure in the BABP and asymmetric structure in the α -BPDA have improved polyimide conformational freedom and help to reduce viscosity, which were suitable for Resin Transfer Model (RTM).

Thermal Stability and Mechanical Properties of cured films.

The thermal stabilities of the cured polyimides prepared from oligomers cured at 370 °C for 1 h was evaluated by TGA under N₂ and air atmosphere at a heating rate of 10 °C min⁻¹. The main data were summarized in Table 3. All cured oligomer films the temperature of 5% weight loss were around 450 °C whether in nitrogen or in the air exhibiting excellent thermal stabilities, and the char yields were all above 60%. Table 3. also summarized the room temperature tensile properties of the thermal cured films. The films with small degree of polymerization were too brittle to obtain the mechanical properties due to a relatively higher crosslinking density. All the thermoset PI films cured at 370 °C for 1 h exhibited good mechanical properties with tensile strengths at the range of 80-115 MPa, tensile modulus of 3.0-1.8 GPa and elongation at breakage of 3.3%-9.9%. Compared with other oligoimides, PI-4 showed the highest

Table 3. Thermal stability and mechanical properties of cured films.

Samples	Cured thin films										
	TGA(N ₂)					TGA(air)			Tensile properties		
	<i>T_i</i> (°C)	<i>T_{d5}</i> (°C)	<i>T_{d10}</i> (°C)	<i>T_{max}</i> (°C)	<i>R_w</i> (%)	<i>T_{d5}</i> (°C)	<i>T_{d10}</i> (°C)	<i>T_{max}</i> (°C)	Tensile Strength (MPa)	Modulus (GPa)	Elongation at break (%)
PI-1	443	464	491	492	63.9	472	498	583	80.2	3.00	3.3
PI-2	451	464	487	497	66.1	464	488	570	84.6	1.87	7.4
PI-4	441	454	478	484	62.4	449	474	549	115.0	2.22	9.9
PI-6	440	469	497	479	71.4	440	469	553	95.1	2.41	7.7
PI-9	435	463	492	478	68.8	459	483	541	94.1	2.10	7.5

T_i: initial decomposition temperature; *T_{d5}* temperature at 5 wt% loss; *T_{d10}* temperature at 10 wt% loss; *T_{max}* temperature of maximum rate of decomposition; *R_w*: char yield at 800°C.

tensile strengths. The thin films prepared by PI-1 and PI-2 with 1 and 2 degree of polymerization exhibit higher crosslink densities than PI-4. In general, cured films prepared by PI-4 possessed best tensile properties.

Conclusions

In this work, a series of novel phenylethynyl-endcapped oligoimides (PEPA-oligoimides) with different molecular weight (degree of polymerization: n=1~9) were successfully prepared from thermal imidization of BABP、 α -BPDA and PEPA was found to have high solubility (50%) and low melt viscosity, which can adapt to various of composite molding methods, such as lution impregnation method and RTM. At the same time, all the cured PIs exhibit good thermal stability, mechanical properties indicated the sample of PI-4 possessed best tensile properties.

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