

## **2,3,2',3'-biphenyltetracarboxylic dianhydride-based phenylethynyl-terminated imide oligomers with excellent processability and thermal stability**

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**Abstract:** A series of imide oligomers were synthesized by two-step polymerization method using 2,3,2',3'-biphenyltetracarboxylic dianhydride and (3, 3'-BPDA) and aromatic diamines as the monomers, 4-phenylethynyl phthalic anhydride (4-PEPA) as the end-capping reagent. These imide oligomers were characterized by means of gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), rheological measurements, and solubility tests. Compared with their analogues based on 4,4'-BPDA, 3, 3'-BPDA-based imide oligomers showed much better solubility in low boiling point solvents (THF and dioxane), and lower melt viscosity, which can be attributed to their unique bent architecture. High performance thermosetting polyimides were produced from these oligomers via the thermal crosslinking reaction of phenylethynyl group. The properties of the thermosets were studied using mechanical property measurements, dynamic mechanical thermal analysis (DMTA), and thermogravimetric analysis (TGA). The cured polyimides exhibited very high glass transition temperatures of up to 443 °C, and 5% weight loss temperatures of up to 569 °C in air.

**Keywords:** Phenylethynyl endcapped imide oligomers, solubility, melt viscosity, high-temperature polymers, 2, 3, 2', 3'-biphenyltetracarboxylic dianhydride

### **1. Introduction**

Aromatic polyimides are considered to be a class of high-performance polymers featured with high glass transition temperatures, high thermal stability, excellent mechanical and electrical properties, and good chemical resistance.<sup>1,2</sup> The excellent overall properties of polyimides are regarded as a consequence of their chain rigidity and strong inter- and intra-molecular interactions. However, these interactions in polyimides also give rise to high melt viscosity and limited solubility in organic solvents, which augments the difficulties in the fabrication of composites and articles. To improve processability, PMR-type (Polymerization of Monomer Reactants in-situ) polyimide resins were developed by Serafini et al, using a methanol solution of monomers and end-capping reagent. Mostly notably, PMR-15 (based on 3, 3', 4, 4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4, 4'-diaminodiphenylmethane) and PMR-II-50 (based on 4, 4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and *p*-phenylenediamine) have been widely utilized as thermosetting resins for carbon fiber reinforced composites.<sup>3,4</sup> These composites showed a long-term use temperature of 316 °C (PMR-15-based) and 343 °C (PMR-II-50-based), respectively. However, there are some obstacles existing in PMR-type resins and composites, including the brittleness of cured resins and the release of

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volatiles during processing. Under NASA's High Speed Civil Transport (HSCT) program, 4-phenylethynylphthalic anhydride (PEPA)-terminated imide oligomers, such as PETI-5 (based on 3, 3', 4, 4'-biphenyltetracarboxylic dianhydride (4, 4'-BPDA), 1, 3-bis(3-aminophenoxy)benzene (1, 3, 3-APB), 3, 4'-oxyaniline (3, 4'-ODA), had been extensively investigated as adhesives and composite matrix resins for airframe applications since it afforded polyimides with an excellent combination of thermal stability, adhesion, and toughness. However, these polyimides exhibited only a moderate glass transition temperature of 270 °C.<sup>5</sup>

Imide oligomers are usually synthesized as amide acid solution in aprotic solvents due to their limited solubility in fully imidized form. In this route, water was released as the by-product of imidization in fabricating process. The evaporation of water and other volatiles after applying consolidation pressure can cause voids or pin holes in the finished composites. To achieve void-free laminates, many research efforts have been aimed at developing imide oligomers with high solubility in organic solvents in their fully imidized form. Approaches to improving the solubility of polyimides included the incorporation of flexible links (-O-, -S-, -CO-, -SO<sub>2</sub>-, -CH<sub>2</sub>-, etc.), and the attachment of bulky pendent groups. However, the thermal and mechanical properties of modified polyimides were usually compromised for better oligomer solubility in organic solvents.

Another method was the incorporation of asymmetric or bent monomers, such as isomeric dianhydrides which had been proven to be an effective approach to attaining processable polyimides without sacrificing other excellent properties. Since 2000, a series of imide oligomers based on 3, 4'-linked dianhydrides were developed. These oligomers showed improved solubility, lower viscosity, and higher glass transition temperature after curing in comparison with those based on 4, 4'-linked dianhydrides due to the decrease of intermolecular interaction stemmed from its asymmetric architecture, as well as the restricted rotation around the single bond adjacent to phthalimide. Rozhanskii *et al* reported a series of polyimides derived from 3, 3'-BPDA and aromatic diamines. These polymers showed high glass transition temperatures, good solubility in organic solvents, and low dielectric constants.<sup>6</sup> However, to the best of our knowledge, no reports dealing with PEPA-terminated imide oligomers based on 3, 3'-BPDA can be found in the literature.

In this study, we report the synthesis and characterization of phenylethynyl-terminated imide oligomers derived from 3, 3'-BPDA. These oligomers showed much better processability (solubility and melt flowability) than those based on 4, 4'-BPDA, which is highly desired for the fabrication of void-free composites. The imide oligomers were then cured at elevated temperature, and the thermal and mechanical properties of cured polymers were also investigated. The structure-property relationship for this series of thermosetting polymers was elucidated.

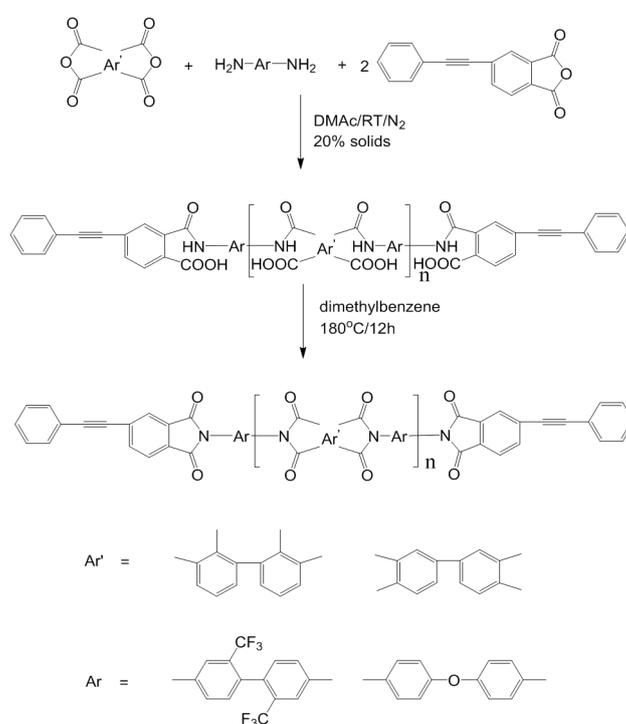
## 2. Results and discussion

### 2.1 Oligomer synthesis

As depicted in Scheme 1, two series of phenylethynyl-encapped imide oligomers were prepared via a two-step procedure, using 3, 3'-BPDA and aromatic diamines (4, 4'-ODA, TFMB) as the monomers. Stoichiometric amounts of anhydride and amine groups were used in all cases. Amic acids were firstly formed by reacting anhydrides with amines in DMAc, and then thermally converted into imide oligomers. The oligomers were named by the chemical nature and degree of polymerization, e.g. PI-ODA-1 is 4, 4'-ODA-based imide oligomer derived from 3, 3'-BPDA with a degree of polymerization of 1, and PI-TFMB-2 is the TFMB-based imide oligomer derived from 4, 4'-BPDA with a polymerization degree of 2

FTIR spectra of PI-ODA-2, PI-TFMB-2 are shown in Figure 1. The bands around 1780 and 1720  $\text{cm}^{-1}$  were assigned to the characteristic absorptions of asymmetric and symmetric stretching  $\text{C}=\text{O}$ , respectively. The peak around 1375  $\text{cm}^{-1}$  was assigned to the characteristic absorptions of  $\text{C}-\text{N}$  bond in imide group, which demonstrated the successful synthesis of imide oligomers. The characteristic peaks at 2212  $\text{cm}^{-1}$  was attributed to the stretching vibration of  $\text{C}\equiv\text{C}$  group, which confirmed the existence of end group.

Molecular weights of imide oligomers were determined by GPC, the results of which are summarized in Table 1. The molecular weights of the oligomers were controlled by stoichiometrically adjusting the ratios of dianhydride, diamine, and end-capping reagent. In general, the measured number average molecular weights ( $M_n$ ) agreed with the calculated ones, indicating that oligomers with targeted molecular weights were achieved. The PI'-ODA-2 and PI'-TFMB-2 could't be measured due to their limited solubility in *N,N*-dimethylformamide (DMF).



Scheme 1 synthesis of imide oligomers

Table 1. Molecular weights and thermal properties of imide oligomers

Oligomer	$M_n$ (g/mol)		PDI (measured) <sup>a</sup>	$T_g$ ( $^{\circ}\text{C}$ ) <sup>b</sup>
	Calculated	Measured <sup>a</sup>		
PI-ODA-1	1119	2900	1.11	166
PI-ODA-2	1578	3600	1.22	185
PI-ODA-3	2036	4400	1.34	201

PI'-ODA-2	1578	—	—	279
PI-TFMB-1	1359	2600	1.53	185
PI-TFMB-2	1938	3900	1.67	210
PI-TFMB-3	2516	4600	1.80	223
PI'-TFMB-2	1938	—	—	245

<sup>a</sup> determined from GPC. <sup>b</sup> determined from DSC at a heating rate of 10 °C min<sup>-1</sup>

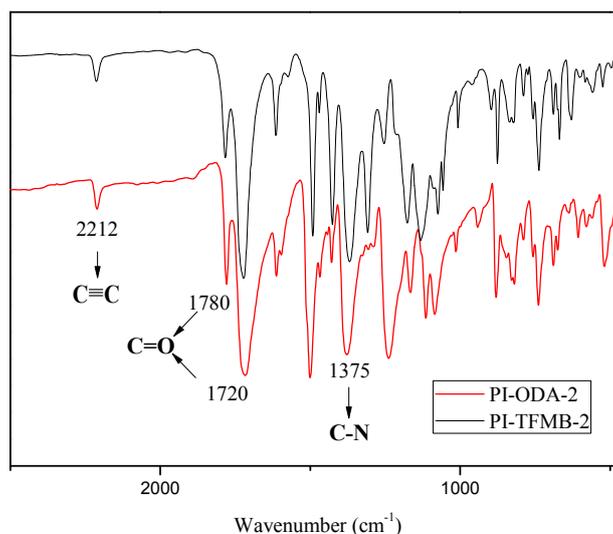


Figure 1. FTIR spectra of imide oligomers

## 2.2 Properties of imide oligomers

### 2.2.1 Thermal properties of the imide oligomers

The glass transition temperatures ( $T_g$ ) of 3, 3'-BPDA-based imide oligomers determined by DSC were in the range of 166-223 °C. The molecular weights and the structures of imide oligomers had a great impact on the thermal properties of the oligomers. For a given diamine, the  $T_g$  values increased with the molecular weights as expected. Meanwhile, the  $T_g$  values of 3, 3'-BPDA-based imide oligomers were lower than the counterparts derived from 4, 4'-BPDA, which can be attributed to the decrease of intermolecular interaction stemmed from its non-coplanar architecture.

### 2.2.2 Solubility of imide oligomers

Most of imide oligomers were prepared in amic acid or PMR form due to their limited solubility in fully imidized form. Water or methanol was released as the by-product of imidization at elevated temperature. Furthermore, the imidization temperature usually overlaps with crosslinking temperature of end groups, which makes the depletion of volatiles impossible before the application of pressure. Therefore, fully imidized oligomers with good solubility are highly desired for the fabrication of void-free composites. As shown in Table 2, 4, 4'-ODA-based imide oligomers were soluble in NMP and DMAc at room temperature, while TFMB-based ones were soluble in NMP, DMAc, THF, dioxane and butanone at room temperature. These oligomers showed much better solubility than the analogues based on 4, 4'-BPDA. The enhanced solubility for imide oligomers derived from 3, 3'-BPDA can be

explained in terms of their bent architectures, which hinder the chain packing and therefore reduce the formation of charge transfer complex. Among all the imide oligomers, TFMB-based ones exhibited the highest solubility due to the low polarity of fluorine and the twisted biphenyl segments.

Table 2. Solubility of the imide oligomers

Oligomer	NMP	DMAc	THF	Dioxane	Butanone
PI-ODA-1	+	+	+	+	—
PI-ODA-2	+	+	±	±	—
PI-ODA-3	+	+	±	—	—
PI'-ODA-2	±	±	—	—	—
PI-TFMB-1	+	+	+	+	+
PI-TFMB-2	+	+	+	+	+
PI-TFMB-3	+	+	+	+	+
PI'-TFMB-2	±	±	±	—	—

+: soluble at room temperature; ±: partially soluble on heating; —: insoluble.

### 2.2.3 Rheological properties of imide oligomers

The viscosity profiles of the imide oligomers were detailedly characterized by rheological measurements, the results of which are shown in Table 3 and Figure 2. For a given oligomer composition, the minimum melt viscosity values of imide oligomers increased with molecular weights. For a given diamine and molecular weight, oligomers from 3, 3'-BPDA showed much lower melt viscosity values than those from 4, 4'-BPDA, which can be rationalized in terms of the reduced chain linearity and inter-molecular interaction stemmed from the bent architecture of 3, 3'-BPDA residue.

Table 3. Complex viscosity data of imide oligomers

oligomer	Minimum melt viscosity (Pa.s/°C)
PI-ODA-1	2/277
PI-ODA-2	5/330
PI-ODA-3	19/350
PI'-ODA-2	18000/334
PI-TFMB-1	5/295
PI-TFMB-2	11/337
PI-TFMB-3	20/353
PI'-TFMB-2	4700/348

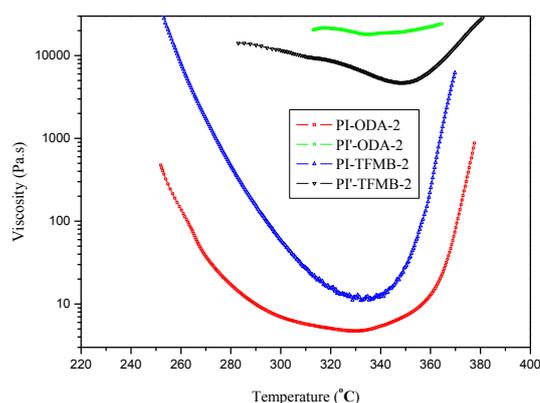


Figure 2 Complex viscosity curves of imide oligomers derived from 3, 3'-BPDA and 4, 4'-BPDA

## 2.3 Properties of cured polyimides

### 2.3.1 Thermal properties of cured resins

The thermal properties of cured polyimide thermosets were characterized by thermogravimetric analysis (TGA), the results of which are listed in Table 4 and Figure 3. The  $T_{5\%}$  values of the thermosets in air and nitrogen spanned a range of 550-569 °C and 540-572 °C, respectively. As shown in Figure 3, no obvious weight loss of cured resins was detected until the temperature was ramped to 500 °C. These results demonstrated that all thermosets possessed excellent thermo-oxidative and thermal stability.

The glass transition temperatures ( $T_g$ ) of cured resins were characterized via DMTA, the results of which are summarized in Table 4 and Figure 4. For a given degree of polymerization, The  $T_g$  values followed the trend of PI-TFMB>PI-ODA, ranging from 364 to 443 °C. Thermosets based on 4, 4'-ODA showed lower  $T_g$  values due to their flexible ether linkage. For a given oligomer architecture,  $T_g$  values increased with the decrease of oligomer molecular weights. Lower oligomer molecular weights lead to higher crosslink densities and therefore higher glass transition temperatures of cured resins.

Table 4. Thermal properties of cured polyimide thermosets

Oligomer	$T_g$ (°C)	N <sub>2</sub>	Air
		$T_{5\%}$ (°C)	$T_{5\%}$ (°C)
PI-ODA-1	406	540	550
PI-ODA-2	378	550	557
PI-ODA-3	364	545	551
PI-TFMB-1	443	567	562
PI-TFMB-2	409	571	566
PI-TFMB-3	384	572	569

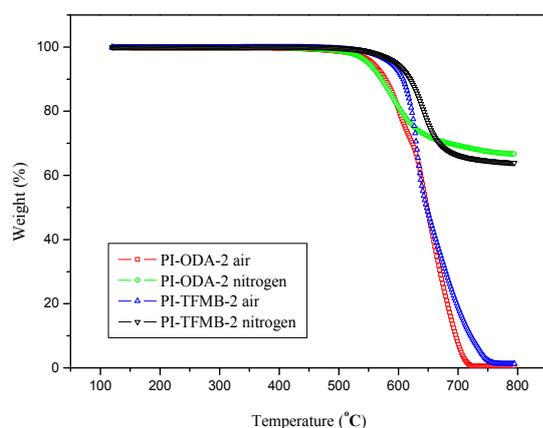


Fig 3 TGA traces of cured polyimides in air and N<sub>2</sub>

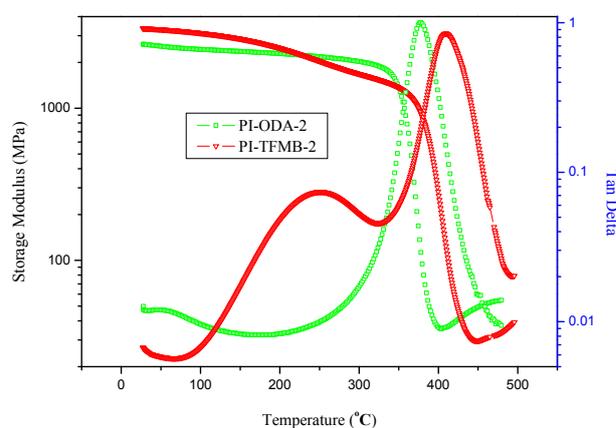


Fig 4 DMTA traces of cured polyimides

### 2.3.2 Mechanical properties of cured resins

Table 5 summarizes the mechanical properties of cured imide oligomers. After thermally curing at 371 °C for 2.5 hours, the tensile strength, modulus and elongation at breakage of polymers were 21-85 MPa, 1.4-3.6 GPa and 1.5-3.3%, respectively. The flexural strength and modulus of polymers were 60-131 MPa and 3.1-3.9 GPa, respectively. The tensile strength, flexural strength and elongation at break of thermosetting polyimides increased as the molecular weight of imide oligomers increased. Oligomers with higher molecular weights can produce thermosets with lower cross-linking densities, which led to higher toughness of the resulting thermosets.

Table 5. Mechanical properties of cured polyimide thermosets

oligomers	Tensile	Tensile	Elongation at breakage (%)	Flexural	Flexural
	strength	Modulus		Strength	Modulus
	(MPa)	(GPa)		(MPa)	(GPa)
PI-ODA-1	21	1.6	1.5	60	3.4
PI-ODA-2	42	1.4	3.3	65	3.1
PI-TFMB-1	24	1.6	1.8	70	3.2
PI-TFMB-2	85	3.6	2.9	131	3.9

### 3. Conclusion

In this work, a series of phenylethynyl-terminated imide oligomers were prepared using 3, 3'-BPDA and aromatic diamines (4, 4'-ODA and TFMB) as the monomers, and PEPA as the end-capping reagent. Due to their unique bent architecture, these imide oligomers showed much higher solubility in low boiling point solvents (THF and dioxane) and lower minimum viscosity compared with the corresponding imide oligomers derived from 4, 4'-BPDA. High solubility in low boiling point solvents and low melt viscosity are highly desired for high quality composites fabrication. After cured at 371 °C for 2.5 hours, 3, 3'-BPDA-based thermosetting polyimides displayed a glass transition temperature of 364-443 °C, and a 5% weight loss temperature of 550-569 °C in air atmosphere. Due to an excellent combination of improved processability and remarkable thermal properties of cured resins, these imide oligomers showed great potential in the applications of high temperature structural composites for aerospace industry.

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