Isomeric Dianhydrides(i-BPDA and s-BPDA) Based Modified Phenylethynyl-terminated Imide Oligomers

Xiang Wang (王响), Chunhai Chen (陈春海), Guodong Dang (党国栋), Xiaogang Zhao (赵晓刚)
Alan G. MacDiarmid Institute, Jilin University, Changchun 130012 , P. R. China
(吉林大学麦克德尔米德实验室 130012)

Abstract

In recent years, TriA-PI, a new phenylethynyl terminated addition-type a-BPDA/4, 4'-ODA with PEPA imide oligomer, has been exploited as a high-performance materials with higher Tg, good mechanical properties and lower melt viscosity. But a-BPDA is very expensive, limiting their application. In this paper, new kinds of all-aromatic phenylethynyl-terminated imide oligomers were prepared by the reaction of 3,3′,4,4′- biphenylenetetracarboxylic dianhydride(s-BPDA) and isomeric 2,2′,3,3′-biphenylenetetracarboxylic dianhydride (i-BPDA) with 4,4'-ODA and PEPA. The molar ration of i-BPDA and s-BPDA was 50/50 and designed the molecular weights of imide oligomers were about 1000, 2000, 3000, 5000g/mol (n=1, 3, 5, 9). The Olig-5(n=5) showed good tensile properties with strength at break of 112MPa, modulus of 2.2GPa and 17.0% elongation. It also had excellent thermal stability, the temperature of 5% weight loss was 558℃ in N_2, the Tg of the cured polymer was 339℃, and the oligomer possessed low melt viscosity above 300℃. Most of properties i.e. the mechanical properties, the thermal stability properties and the melt viscosity, were almost comparable with TriA-PI having molecular weight of 2500g/mol. The thermal curing process of the oligomers was also investigated by differential scanning calorimetry(DSC) by monitoring the change of Tg and the exothermic peak. Melt viscosity, thermal and tensile properties of oligomers with different molecular weight were also investigated.

Key Words: Oligomer, isomeric biphenylenetetracarboxylic dianhydride, melt viscosity, 4-phenylethynylphthalic anhydride, thermoset polyimide

1. Introduction

Aromatic polyimides are well known as polymers with outstanding mechanical properties and high temperature capabilities. They can be utilized for a wide range of applications: such as matrices for high-performance advanced composite materials, high temperature insulators for aircraft wire coatings, and membranes for gas separation. However, most of them are difficult to process, because of their insolubility in organic solvents as well as high glass transition and melt temperature. Therefore, considerable efforts have been devoted to the synthesis of tractable polyimides that maintain excellent combinations of properties [1-5].

In recent years, more and more attention has been focused on the study of imide oligomers with phenylethynyl terminated groups, because they demonstrated many advantages in both favorable processability and good material properties, and could provide high-performance composites with broad potential applications. [6-9]. For example, PETI-5 prepared from 3, 3′, 4, 4′- biphenylenetetracarboxylic dianhydride(s-BPDA) and two diamines have been evaluated as adhesive and composite matrix resin.

The cured resin has excellent mechanical properties , good processability and thermo-oxidative stability, but it has relatively lower Tg of sample at 270℃ [10-11].

Recently, TriA-PI, a new phenylethynyl terminated addition-type a a-BPDA/4,4'-ODA with PEPA imide oligomer, has been exploited as a high-performance materials with higher Tg, good mechanical properties and lower melt viscosity. But a-BPDA is very expensive, limiting their application [12-13].

In this paper, two dianhydrides(i-BPDA and s-BPDA)and 4,4′-ODA with PEPA imide oligomers were synthesized. And the series of imide oligomer had higher Tg, good mechanical properties, and low melt viscosity. The properties of the cured oligomers were compared with TriA-PI having the molecular weight of 2500g/mol. Oligomers with different molecular weight were prepared to study the relationship between their structure and property.

2. Experimental

2.1. Materials

2,2′,3,3′-biphenylenetetracarboxylic dianhydride (i-BPDA) was synthesized according to the literature, m.p.272℃. 3,3′,4,4′- biphenylenetetracarboxylic dianhydride (s-BPDA) from Chriskev Company Inc, m.p.305-308℃; 4-phenylethynylphthalicanhydride (PEPA) from MANAC Corp.,Japan, m.p.152℃; N,N-Dimethylacetamide(DMAc) was distilled under reduced pressure before use.

2.2. Measurements

Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC Q100 thermal analyzer at a heating rate of 20 ℃/min under a nitrogen atmosphere, Each oligomer was scanned twice; Dynamic mechanical analysis (DMA) was performed on a TA instrument DMA Q800 at a heating rate of 5℃/min and at a load frequency of 1 Hz in an nitrogen atmosphere; Thermogravimetric analysis (TGA) was performed using TA Instruments Pyris Diamond TG/DTA thermogravimetric analyzer at a heating rate of 5 ℃/min in a nitrogen and air atmosphere; Melt viscosity measurements were performed on a Physica MCR300 dynamic rheometer at a ramp rate of 4℃/min in a nitrogen flow; Tensile properties such as the tensile modulus, tensile strength and elongation of the films at break were measured as the average using specimens on a Shimadzu AE-1 tensile apparatus, Sample average size: 3.00mm×40.00mm×0.04mm, strain rate: 8mm/min.

2.3. Polyimide synthesis

2.3.1. The synthesis of PEPA end-capped oligomers

Scheme 1 represents the experimental procedure used to prepare the oligomers and their cured polymers, The molar ration of i-BPDA and s-BPDA is 50/50 and designed the molecular weights of imide oligomers were about 1000, 2000, 3000, 5000g/mol(n=1,3,5,9). For convenience, in this paper, all the samples are denominated in shortened forms. For example, "Olig-1" means the sample with an oligomer degree of 1.

The amide acid oligomer was prepared by the slow addition of a calculated stoichiometric offset of i-BPDA scurried with an electron stirred mixture of the 4,4′-ODA and DMAc at room temperature for 4 h. Then slowly introduce s-BPDA ($n_{s\text{-}BPDA}=n_{i\text{-}BPDA}$), stirred for an additional 4 h. After then PEPA was added, the reaction solution was stirred for 3 h and remained 30% (m/v) concentration [14].

The solution of amide acid oligomer in DMAc was cast on a glass plate, and dried in an air oven at 80℃ and 150℃ for 1 h each, and then the material was imidized at 200℃ for 1h and 250℃ for 1h in a vacuum oven, and finally ground to obtain yellow imide oligomer powder.

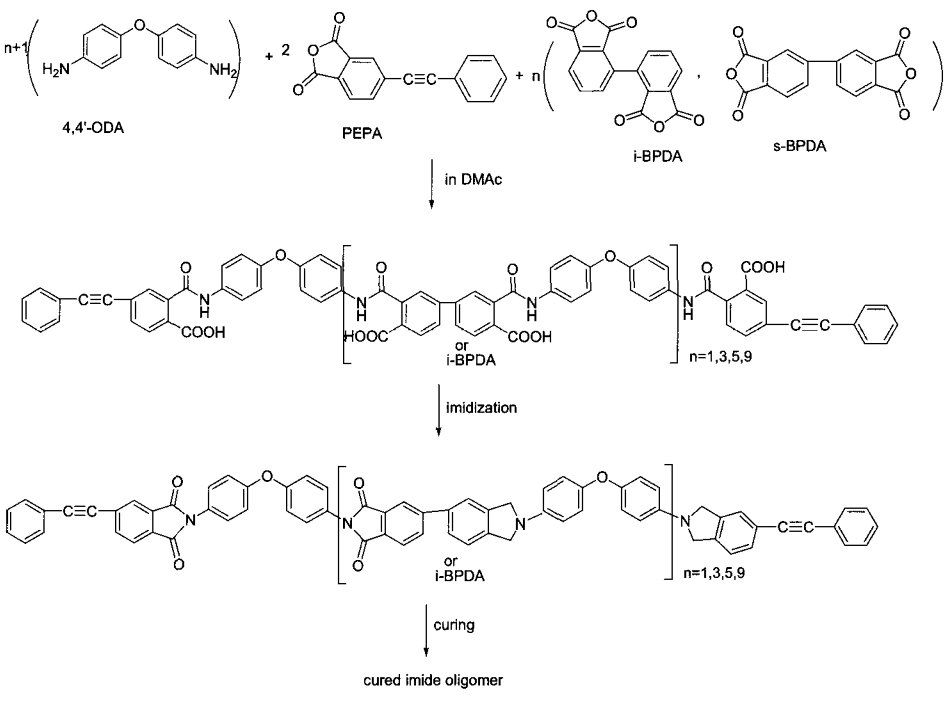
2.3.2. Films

The imide oligomers obtained were molded by using 6 cmx6 cmx0.05 cm polyimide film frame on a 20 cmx20 cm stainless steel plate with UPILEX-S separator films under 1.5 MPa by heating initially to Tg+60℃ for 20 min and subsequently to 370℃ for 1h. The dark red film-like specimens of 6 cmx6 cm x0.05 cm thick were obtained.

3. Results and discussion

3.1. Synthesis oligomer and cured oligomer

The imide oligomers with different molecular weight were prepared as shown in scheme 1. The amide acid oligomers were made by reaction of calculated stoichiometeric ratios of s-BPDA; i-BPDA and 4,4′-ODA with PEPA in DMAc and subsequently cyclodehydrated by thermal imidization at 250℃ to obtain a series of phenylethynyl -terminated imide oligomers.



Scheme 1. Synthesis of oligomers derived from i-BPDA and s-BPDA

The cured imide oligomers were obtained by compressive molding at 370℃ for 1h. The thermal curing process of the oligomers was also investigated by DSC by monitoring the change of Tg and exothermic peak. As shown in figure 1, exothermic enthalpy (△H) decreased, and Tg increased with cure time. When the cure time is 40 min, exothermic enthalpy vanished.

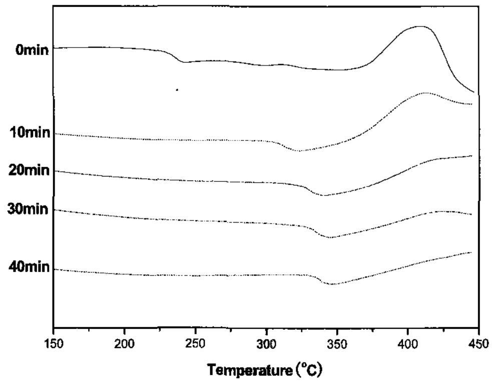


Figure 1. DSC of thermally treated olig-5 at 370℃ with different cure time

3.2. Properties of imide oligomers with different molecular weight

3.2.1. Thermal properties of imide oligomers

The thermal properties of uncured imide oligomers and their cured oligomer films with different molecular weight are shown in table 1.

Table 1. The thermal properties of uncured imide oligomers and their cured oligomer films with different molecular weight

Sample	Uncured imide oligomers						Cured Film Properties			
	DSC						Tg(℃)		$Td_{5\%}$(℃)	
	First run				Second	$\triangle$Tg (℃)	DSC	DMA	N_2	Air
	Tg^1 (℃)	T_{onset}(℃)	T_{exo} (℃)	$\triangle$H (J/g)	Tg^2 (℃)					
Olig-1	155	291	395	123	375	220	375	366	545	533
Olig-3	208	301	405	62	344	136	350	341	553	542
Olig-5	235	364	410	41	339	104	339	333	558	544
Olig-9	264	379	421	20	337	73	336	330	554	549

Tg^1 : glass transition temperature of the oligomers determined on powdered sample by DSC at a heating rate of 20℃/min in the first run; Tg^2: glass transition temperature determined on samples by DSC at a heating rate of 20℃/min in the second heating run; T_{onset}: onset crosslink temperature of the oligomers; T_{exo}: the temperature of exothermic peaks on DSC curves. $\triangle Tg = Tg^2 - Tg^1$

The Tg values of imide oligomers with different molecular weight were measured by DSC. Figure 2 shows the first heating run of DSC thermo-grams up to 450℃ for uncured imide oligomers. The initial Tg values increased with the increase of molecular weight, and the exothermic (T_{exo}) also shifted to higher temperature, but the enthalpy of the exothermic peak decreased gradually.

Figure 3 shows the DSC curves of cured imide oligomers (the second scan), a higher Tg was observed in the second heating run as a result of phenylethynyl crosslinking in the course of the first heating run. And the Tg values decreased with the increase of molecular weight, because of lower crosslink density. For example, the cured Olig-1 has a Tg of 375℃, whereas the cured Olig-9 has a Tg of only 337℃.

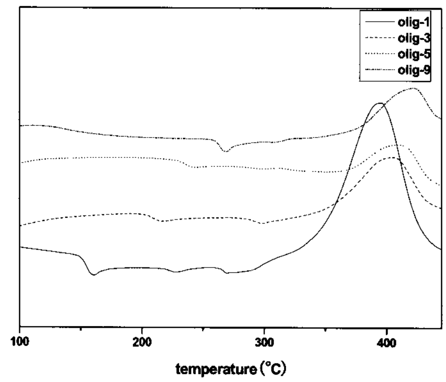


Figure 2. DSC curves of uncured imide oligomer

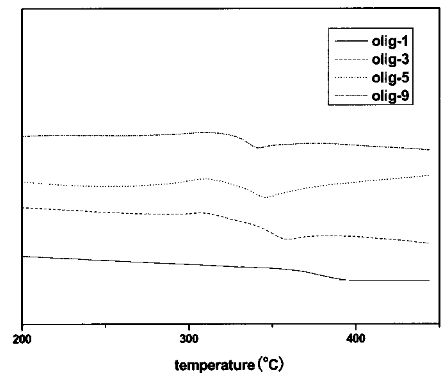


Figure 3. DSC curves of cured imide oligomer

The DMA curves of the oligomer films with different molecular weight were shown in Figure 4. The data is listed in Table 1 and consistent with the Tg values measured by DSC.

All of the cured oligomer films with different molecular weight showed excellent thermal stability. The temperatures of 5% weight loss, listed in table 1, are above 540℃ in N_2 and 530℃ in air.

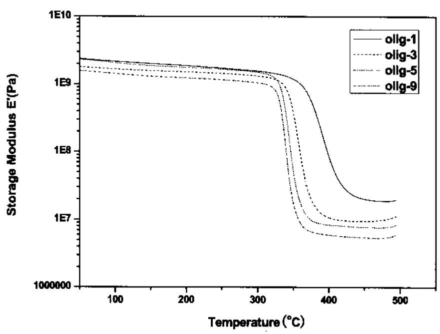


Figure 4. DMA curves of cured imide oligomer films

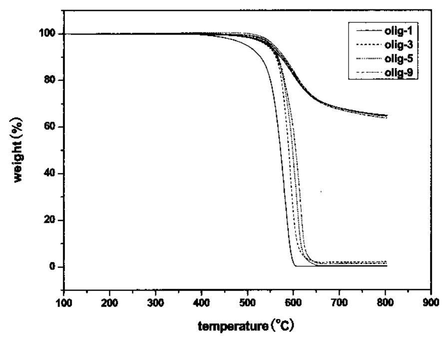


Figure 5. TGA curves of cured imide oligomer films in N_2 and air

3.2.2. Rheological behavior

The dynamic rheological properties of the imide oligomers are displayed in Figure 6. Olig-1, Olig-3, Olig-5, Olig-9 exhibited minimum melt viscosity as low as 0.44 Pa.s (334℃), 20 Pa.s (353℃), 108 Pa.s (364℃) and 1420 Pa.s (375℃), respectively. Obviously, decreasing the molecular weight of the oligomer led to a sharp decrease of the temperature at the minimum melt viscosity and a wider processing window. Compared with TriA-PI (1000 Pa. s (320℃)), the oligomers exhibited a lower dynamic melt viscosity above 300℃ and a broader rang of temperature.

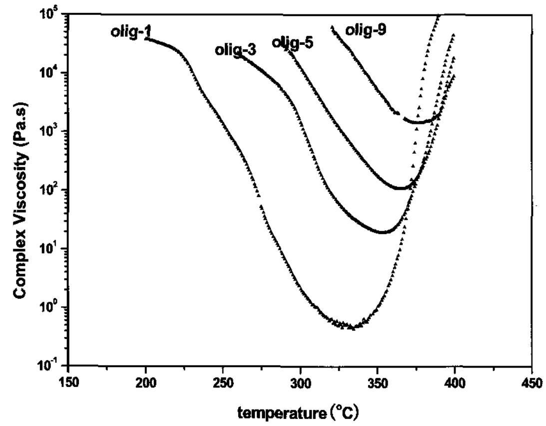


Figure 6. The dynamic rheological behaviors of uncured imide oligomers

3.2.3. Tensile properties

The room temperature tensile properties of cured oligomer films were presented in table 2. The cured imide oligomer films with lower molecular weight were easy to break due to higher crosslink density. In comparing their tensile properties, The Olig-5 showed the best tensile properties with strength at break of 112MPa, modulus of 2.2GPa and 17% elongation.

Table 2. The tensile properties of cured oligomer films with different molecular weight

Sample	Strength (MPa)	Modulus (GPa)	Elongation (%)
Olig-1	60	2.1	4
Olig-3	98	2.1	8
Olig-5	112	2.2	17
Olig-9	86	2.0	8

3.3. Comparison with TriA-PI

According to the literature [13, 15], the properties of TriA-PI are given in table 3.

In comparing the properties of cured oligomer films with different molecular weight, the Olig-5 having a calculated molecular weight of about 3000 g/mol approximately exhibited the best combination of properties as listed in table 3. Most of properties, i.e. the mechanical properties, the thermal stability properties and the melt viscosity, were almost comparable with TriA-PI with molecular weight of 2500g/mol.

Table 3. The properties of TriA-PI and Olig-5.

Sample	Mn(g/mol)	Tg(℃)	$Td_{5\%}$(℃)	Melt flow viscosity	Thesile properties		
			N_2	Minimum(Pa.S)	Strength (MPa)	Modulus (GPa)	Elongation (%)
TriA-PI	2500	343	556	1000 (320)	115	2.3	14
Olig-5	3000	339	558	108 (364℃)	112	2.2	17

4. Conclusions

A series of phenylethnyl-terminated imide oligomers consisting of s-BPDA ,i-BPDA and 4, 4′-ODA have been prepared by thermal imidization. The uncured oligomers with lower molecular weights exhibit lower initial Tg, yet lower minimum melt viscosities at low temperature, and their corresponding cured oligomers have higher Tg. All the oligomers can be compressed into films, and the films exhibit excellent thermal stability and good mechanical properties. The film of Olig-1 has higher Tg but poor tensile properties due to higher crosslink densities. Among them, Olig-5 offers the best combination of properties, and most of properties are almost comparable with TriA-PI.

REFERENCES

[1] Zhiming Qiu, Suobo Zhang. Polymer [J], 2005, 46: 1693-1700

[2] Chunhai Chen, Rikio Yokota, Masakatsu Kochi, Masakatsu Kochi, Kazuyuki Horie, Paul Hergenrother. High Performance Polymers [J], 2005, 17: 317-333

[3] P. M. Hergenrother, K. A. Watson, J. G. Smith Jr, J. W. Connella, R. Yokota. Polymer [J], 2002, 43: 5077-5093

[4] Ding Mengxian. Progress in Ploymer Science [J], 2007, 32: 623-628

[5] J. W. Park, M. Lee, M.-H. Lee, J. W. Liu, S. D. Kim, J. Y. Chang, S. B. Rhee. Macromolecules [J], 1994, 13: 3459-3463

[6] Yanfeng Liu, Zhen Wang, Huili Yang, Lianxun Gao, Gao Li, Mengxian Ding. Journal of Polymer Science: Part A: Polymer Chemistry [J], 2008, 46: 4227–4235

[7] Hongjie Sun, Haitao Huo, Hao Nie, Shiyong Yang, Lin Fan. European Polymer Journa [J], 2009, 45: 1169–1178

[8] P. M. Hergenrother, J. W. Connell, J. G. Smith Jr. Polymer[J], 2000, 41: 5073–5081

[9] Smith J G, Connell J W, Hergenrother P M, Gardner S. Polymer [J], 1997, 18: 4657

[10] Robert G. Bryant, Brian J. Jensen, Paul M. Hergenrother. Journal of Applied Polymer Science [J], 1996, 59: 1249-1254

[11] Hongbo Liu, Christopher D. Simone, Parag S. Katiyar, Daniel A. Scola. International Journal of Adhesion & Adhesives, 2005, 25: 219–226

[12] Takeshi Sasaki, Hiroyuki Moriuchi, Shoichiro Yano, Rikio Yokota. Polymer [J], 2005, 46: 6968–6975

[13] Xianhua Rao, Hongwei Zhou, Guodong Dang, Chunhai Chen, Zhongwen Wu. Polymer, 2006, 47: 6091-6098

[14] Y. J. Tong, S. L. Liu, H. M. Guan, M. X. Ding. Polymer Engineering and Science [J], 2002, 42: 101-110

[15] Hongwei Zhou, Chunhai Chen, Reito Kanbara, Takeshi Sasaki, Rikio Yokota. High Performance Polymers [J], 2005, 17: 193-212

(continuing fromp157)

[33] Drew HDK, Hatt HH. Chemiluminescent organic compounds. Part I. Isomeric simple and complex hydrazides of phthalic acid and mode of formation of phthalazine and isoindole rings. J Chem Soc 1937; 16-26.

[34] Drew HDK, Hatt HH. Chemiluminescent organic compounds. Part II. The effect of substituents on the closure of phthalhydrazides to 5- and 6-membered rings. J Chem Soc 1937; 26-33.

[35] Gao JP, Wang ZY. Synthesis and properties of polyimides from 4,4'-binaphthyl-1,1'-8,8'-tetracarboxylic dianhydride. J Polym Sci Part A: Polym Chem 1995; 33: 1627-35.

(contiune from p169)

[1] K. Takizawa, J. Wakita, M. Kakiage, H. Masunaga, S. Ando, *Macromolecues*, **43**(5), 2115– 2117 (2010).

[2] J. Wakita, S. Ando et al., *J. Phys. Chem. B*, **113**(26), 8835–8846 (2009).

[3] J. Wakita, S. Ando et al., *J. Phys. Chem. B*, **113**(46), 15212–15224 (2009), *Macromolecues*, **43**(8), 3594–3605 (2010).