Available online at www.sciencedirect.com
SCIENCE DIRECT®
Polymer 47 (2006) 6091–6098
polymer
www.elsevier.com/locate/polymer

# New kinds of phenylethynyl-terminated polyimide oligomers with low viscosity and good hydrolytic stability

Xianhua Rao, Hongwei Zhou, Guodong Dang, Chunhai Chen*, Zhongwen Wu

*Alan G. MacDiarmid Institute, Jilin University, Changchun 130012, PR China*

Received 4 March 2006; received in revised form 25 May 2006; accepted 11 June 2006
Available online 7 July 2006

## Abstract

In continuing studies to develop low melt viscosity phenylethynyl end-capped imide oligomers for aerospace applications, new kinds of all-aromatic phenylethynyl-terminated imide oligomers were prepared by the reaction of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) or biphenylenetetracarboxylic dianhydride (s-BPDA) with 2,5-bis(4-aminophenoxy)-biphenyl (*p*-TPEQ) and 4-phenylethynylphthalic anhydride (PEPA) or 4-(1-phenylethynyl)1,8-naphthalic anhydride (PENA). The oligomers bearing pendant phenyl groups exhibit much lower melt viscosities at low temperatures, and thus provide wide processing window. The thermal curing process of the oligomers was investigated with DSC. The tensile and thermal properties of the cured films were evaluated. Oligomers derived from PENA cured at lower temperatures and the corresponding cured polymers show better hydrolytic stability than those of PEPA. Results showed that the utilization of diamine monomer (*p*-TPEQ) can improve the processability and solubility of phenylethynyl-terminated imide oligomers without sacrificing their thermo-oxidative stability.

*Keywords:* Phenylethynyl; Polyimide (PI); Oligomers

## 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: as matrices for high-performance advanced composite materials, as thin films in electronic applications, as structural adhesives and sealants, as high temperature insulators for aircraft wire coatings, and as membranes for gas separation [1–11]. However, a poor processability limited their widespread adoption as matrix resins for structural composites. To improve their processability (melt processing properties or solubility in organic solvents), more and more attention has been focused on the study of various kinds of PETIs (phenylethynyl-terminated polyimide oligomers) [12–22].

Aromatic polyimides prepared from the phenylethynyl-terminated imide oligomers demonstrated many advantages in both favorable processability and good material properties, and could provide high-performance composites with broad potential applications. The advantages of these materials are that (1) no volatiles are formed during the curing reaction, (2) the phenylethynyl group exhibits greater process control over the ethynyl group due to its wider processing window, and (3) improved thermal and thermo-oxidative stability over ethynyl-terminated imide oligomers [4,23]. Ever since 1980s, under the work of many researchers, especially in NASA Langley, more than 100 kinds of PETIs have been prepared and studied. Among them, PETI-5 was the best-evaluated one with a unique combination of excellent mechanical properties and good processability [4,15]. However, it is still necessary to get new kinds of PETIs with much better processability in order to extend the utility of polyimides as high-performance materials.

An effective approach to attain solubilities without decreasing the rigidity of the polymer or oligomer backbone substantially is the incorporation of bulky substituent pendants into the polymer backbone. According to the literature [24], 2,5-bis(4-aminophenoxy)-biphenyl (*p*-TPEQ), an all-aromatic

---

* Corresponding author.
*E-mail address:* cch@jlu.edu.cn (C. Chen).

0032-3861/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2006.06.037

diether–diamine, can form polyimide with higher thermal stability and better solubility than any other bulky substituents, such as the *tert*-butyl-containing one. Besides, comparing properties of polyimides derived from 2,5-biphenyl-linked diamine with those derived from isomeric 4,4′-bis(4-aminophenoxy)biphenyl or 2,2′-bis(4-aminophenoxy)biphenyl, the 2,5-biphenyl-bearing polyimides have far better solubility than the 4,4′-linked one and have a far better tensile property than the 2,2′-linked one [24–28]. Although this phenyl-containing diamine monomer has been used to prepare polyimides by many other researchers [24], only few studies on the phenylethynyl-terminated imide oligomers derived from this diamine could be found in the literature. Herein, we synthesized four series of PETI oligomers by the reaction of 3,3′,4,4′-benzophenonetetracarboxylic dianhydride (BTDA) or biphenylenetetracarboxylic dianhydride (s-BPDA) with *p*-TPEQ and 4-phenylethynylphthalic anhydride (PEPA) or 4-(1-phenylethynyl)1,8-naphthalic anhydride (PENA). It was expected that, for the corresponding cured resins, the incorporation of this unsymmetrical and hindered moiety would disturb the coplanarity of the aromatic unit reducing packing efficiency and crystallizing-ability. This should enhance solubility and maintain high $T_g$s through controlled segmental mobility [24].

As end-capping reagent, PENA gained less attention than PEPA, because the PENA-terminated imide oligomers gave little advantages than the PEPA-based ones and the naphthalic anhydride displays a lower activity [29–31]. However, the lower activity usually leads to a better stability when the naphthalic structures were introduced into the polymer backbone. As we studied, the incorporation of PENA made the cured resins to exhibit better hydrolysis stability than the PEPA-based ones, which makes the PENA-based polyimides applicable in the Fuel Cell system [32–35].

The work reported herein concerns the syntheses, characterizations and preliminary evaluation of some imide oligomers and their corresponding thermally cured polymers.

## 2. Experimental

### 2.1. Materials

The following chemicals were obtained from the indicated sources and used without further purification.

3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA) was obtained from Beijing Jiaohua Company, 97%, m.p. 221 °C, biphenylenetetracarboxylic dianhydride (s-BPDA) from Chriskev Company Inc., m.p. 305–308 °C, 4-phenylethynylphthalic anhydride (PEPA) from MANAC Corp., Japan, m.p. 152 °C and *N*-methyl-2-pyrrolidinone (NMP) and *D*,*N*-dimethyl formamide (DMF) were purchased from Tianjin Chemical Agent Factory. *N*,*N*-Dimethylacetamide (DMAc) was distilled under reduced pressure before use.

Dinitro compound (2,5-bis(4-nitrophenoxy)biphenyl) was synthesized according to the literature [24], the diamine monomer was obtained by the catalytic hydrogenation of dinitro compound with Fe/HCl in ethanol/water. The overall yield was 60%. Mass spectroscopy: (*m*/*e*) 368, calculated molecular weight: 368.43 g mol$^{-1}$, m.p. (d.s.c., 20 °C min$^{-1}$) peak at 58–61 °C. PENA was synthesized according to the literature [31]. Mass spectroscopy: (*m*/*e*) 298, calculated molecular weight: 298.29 g mol$^{-1}$, m.p. (d.s.c., 20 °C min$^{-1}$) peak at 233 °C (sharp).

### 2.2. Polyimide synthesis

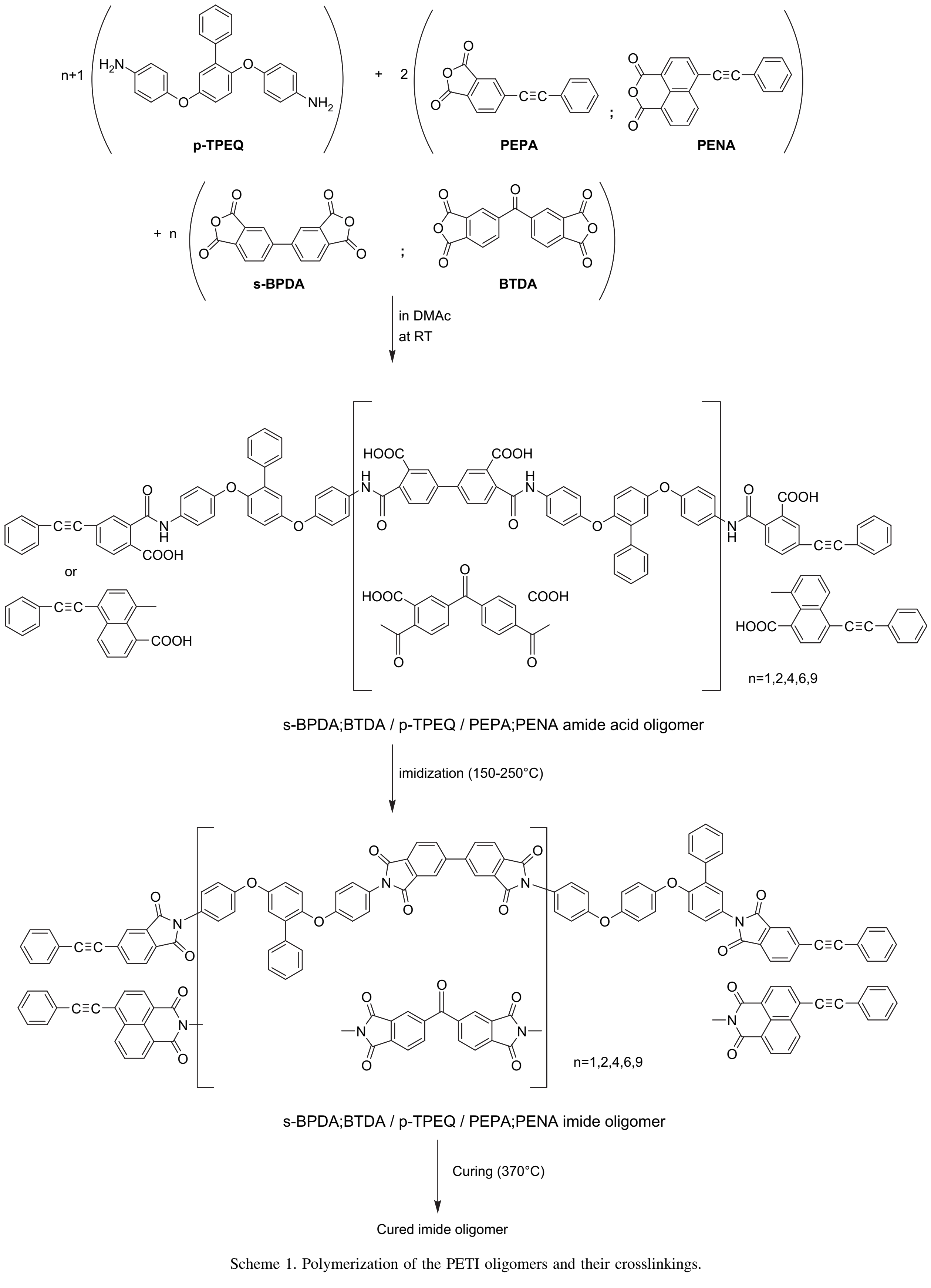
Scheme 1 represents the experimental procedure used to prepare the oligomers and their cured polymers. Because the oligomers were synthesized with the same diamine, they were denominated as the dianhydrides and the end-caps can be divided into four series. For convenience, in this paper, all the samples are denominated in shortened forms of the monomer, dianhydride: "s" represents s-BPDA, "bt" represents BTDA; end-cap agent: "a" represents PEPA, "b" represents PENA; the oligomer-degree nos. 1, 2, 4, 9 represent the number of the dianhydride molecules in the oligomer. For example, "s–a1" means the sample made from s-BPDA with *p*-TPEQ and PEPA with an oligomer degree of 1.

#### 2.2.1. The synthesis of PEPA end-capped oligomers

Two series of PEPA end-capped oligomers from s-BPDA or BTDA were synthesized according to a published method [12,20,21] as illustrated by oligo-s–a4. *p*-TPEQ (3.68 g, 0.01 mol) and 15 ml DMAc were placed in a flame-dried 100 ml three necked round-bottom flask which was equipped with nitrogen inlet, mechanical stirrer and drying tube. After the diamine was dissolved completely, s-BPDA (2.352 g, 0.008 mol) was added and the reaction mixture was stirred at room temperature for ~3 h under a nitrogen atmosphere. Then PEPA (0.992 g, 0.004 mol) was added with additional DMAc to adjust the solids' concentration to ~30% (w/w). The mixture was stirred at room temperature for another 2 h. The oligoamide acid solution was cast on a glass plate and dried in an air oven at 80 °C and 150 °C for 1 h each, then the material was imidized at 200 °C for 1 h and 250 °C for 1.5 h in a vacuum oven, finally ground to obtain oligo-s–a4 powder which has the polymerization degree of 4 (as described before, 4 represents the number of the dianhydride molecules in the oligomer). All other PEPA terminated oligomers were synthesized with an analogous procedure as described.

#### 2.2.2. The synthesis of PENA end-capped oligomers

Two series of PENA end-capped oligomers from s-BPDA or BTDA were prepared as follows. The first step for the amide acid solution was just the same as that of PEPA. While PENA was added, because of its poor activity at ambient temperature, the mixture was heated to keep the end-cap reaction going on. Finally imide oligomer was prepared by subsequently adding toluene and refluxing the solution under a Dean Stark trap for 5 h under nitrogen atmosphere. The solution was then



Scheme 1. Polymerization of the PETI oligomers and their crosslinkings.

cast on a glass plate and dried at 150 °C in an air oven to remove the solvent, then in a vacuum oven at 250 °C for 1 h to get the entirely imidized oligomer and finally ground to obtain the PENA end-capped imide oligomer powder.

#### 2.2.3. Films

The obtained imide oligomers were molded by using $6 \times 6 \times 0.005\ \mathrm{cm}^3$ polyimide film frame on a $15 \times 15\ \mathrm{cm}^2$ stainless steel plate with UPILEX-S separator films under 1.4 MPa by heating initially to $T_g + 60\ °C$ for 20 min and subsequently to 370 °C for 1 h. The dark red or yellow film-like specimens of $6 \times 6 \times 0.005\ \mathrm{cm}^3$ were obtained.

#### 2.2.4. Hydrolysis stability in base and acid environments

The hydrolysis stability tests of the polyimide films were performed by immersing the films into 10% NaOH or 10% $H_2SO_4$ aqueous solution, and refluxing for 24 h. Then, the mechanical properties of the treated films were compared with the unsettled ones.

### 2.3. Characterization and measurements

*Differential scanning calorimetry (DSC)* of the imide oligomers was performed using a Mettler Toledo DSC 821e series analysis system at a heating rate of $20\ °C\ \mathrm{min}^{-1}$ under a nitrogen atmosphere at a flow rate of $100\ \mathrm{cm}^3\ \mathrm{min}^{-1}$. Each oligomer was scanned twice. The glass transition temperature ($T_g$) was taken at the mid-point of the heat flow versus temperature curve. *Infrared spectroscopy (IR)* of oligomer powder sample deposited onto KBr plates was performed with OPUS FTIR spectrometer. *Melt viscosity* measurements were performed on a Physica MCR300 dynamic rheometer at a ramp rate of $4\ °C\ \mathrm{min}^{-1}$ in a nitrogen flow. Sample specimen discs of 2.54 cm diameter and 1.5 mm thickness were prepared by press molding with 0.5 g of the powder-like imide oligomer at $T_g - 20\ °C$. After loading, specimens were heated to 200 °C for bonding to the paralled plates. The lower plate was oscillated at a fixed strain of 5% and at a fixed angular frequency of $10\ \mathrm{rad\ s}^{-1}$, while the upper plate was attached to a transducer that recorded the resultant torque. Melt viscosity ($\eta^*$, complex viscosity as a function of time) was measured from 200 °C to 380 °C. *Dynamic mechanical analysis (DMA)* was performed on thin film specimen ($3 \times 0.65 \times 0.05\ \mathrm{cm}^3$) on a TA instrument DMA Q800 at a heating rate of $5\ °C\ \mathrm{min}^{-1}$ and at a load frequency of 1 Hz in an air atmosphere. The peak on the tan $\delta$ as a function of temperature curves was regarded as $T_g$ of the cured film. *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 Daojing AG-I tensile apparatus. Sample size: $3 \times 0.3 \times 0.005\ \mathrm{cm}^3$, strain rate: $8\ \mathrm{mm\ s}^{-1}$. *Thermogravimetric analysis (TGA)* was performed using a Perkin–Elmer (TGA-7) thermogravimetric analyzer with Pyris data collection and analysis software for Windows. Film samples were heated at a constant rate of $5\ °C\ \mathrm{min}^{-1}$ in air or nitrogen ($25\ \mathrm{cm}^3\ \mathrm{min}^{-1}$) atmosphere.

## 3. Results and discussion

### 3.1. Oligomer synthesis

Four series of imide oligomers with different molecular weights were prepared as in the method outlined in Scheme 1. The amide acid oligomers were synthesized by the reaction of calculated stoichiometric ratios of anhydride (BTDA or s-BPDA) and diamine (*p*-TPEQ) with phenylethynyl end-capping agent (PEPA or PENA) in DMAc and subsequently cyclodehydrated by thermal imidization to obtain four series of phenylethyl terminated imide oligomers. PENA failed to react at ambient temperature, as a six-membered ring in PENA is more stable than a five-membered ring in PEPA.

Many works showed that reducing average molecular weight by changing the stoichiometry and diamine composition of oligomers has a profound effect on the processability of the uncured oligomers and on the $T_g$ value after crosslink [4,20,21,36]. In this article, the monomers used for synthesizing the polyimide oligomers were varied systematically within the series to study the influence of both molecular structure and molecular weight on the physical and film-forming properties. Four series of imide oligomers which had the polymer degrees of 1, 2, 4, 9 (as listed in Table 1) were prepared. They are denominated in a way as discussed before in Section 2.2.

### 3.2. Properties of imide oligomers

#### 3.2.1. Thermal properties of the imide oligomers

The thermal properties of all uncured oligomer powder with different molecular weights were measured by DSC. Fig. 1 shows the DSC curves of oligo-s–a4 powder in the first and second scan. All other oligomers had similar thermal behavior. As expected, only one glass transition was observed in the first heating run, which represents the $T_g$ of uncured imide oligomer. A higher glass transition temperature was observed in the second heating run as a result of phenylethynyl crosslinking. Glass transition temperature of the oligomers ($T_g^1$) and glass transition temperature of the cured polymers ($T_g^2$), the onset curing temperatures ($T_{\mathrm{onset}}$), exothermic peaks ($T_{\mathrm{exo}}^1$ and $T_{\mathrm{exo}}^2$) and normalized heat enthalpy ($\Delta H$) are all listed in Table 1.

The exothermic peak due to the crosslinking reaction appeared at 330–405 °C in the first heating run of DSC. Exothermic enthalpy ($\Delta H$) decreased as the content of phenylethynyl decreased. The onset curing temperatures of oligo-s–a1–9 were in the range of 389–405 °C, about 50 °C higher than those of the other 12 oligomers in the range of 330–360 °C, we consider that was because oligo-s–a1–9 had neither carbonyl group nor naphthyl group, which can accelerate the crosslinking of phenylethyl. Similar phenomena have been discussed in the literature [31].

The $T_g$ determined in the second heating run showed higher $T_g$, ranging from 256 °C to 327 °C, as a result of a complex reaction of the C≡C in the course of the first heating run. $\Delta T_g$ ($\Delta T_g = T_g^2 - T_g^1$) varied from 56 °C to 179.5 °C according to the molecular weight and the content of phenylethynyl.

Table 1
Properties of the oligomers from *p*-TPEQ

| Samples | Uncured powder | | | | | | | | | Cured DSC $T_g^2$ (°C) | $\Delta T_g$ (°C) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $n$ | Calcd. $M_n$ (g mol$^{-1}$) | Solubility[a] | | DSC first run | | | | | | |
| | | | DMF | NMP | $T_g^1$ (°C) | $T_{onset}$ (°C) | $T_{exo}^1$ (°C) | $T_{exo}^2$ (°C) | $\Delta H$ (J/g) | | |
| s–a1 | 1 | 1400 | + | ++ | 161.5 | 389 | 418 | – | 166 | 300 | 138.5 |
| s–a2 | 2 | 2100 | + | + | 175 | 391 | 418 | – | 133 | 288 | 113 |
| s–a4 | 4 | 3300 | + | + | 190 | 400 | 438 | – | 72 | 277 | 87 |
| s–a9 | 9 | 5500 | – | + | 207 | 405 | 417 | – | 24 | 263 | 56 |
| bt–a1 | 1 | 1500 | + | ++ | 160 | 340 | 417 | 440 | 173 | 306 | 146 |
| bt–a2 | 2 | 2100 | + | + | 176 | 361 | 416 | 439 | 116 | 292 | 116 |
| bt–a4 | 4 | 3400 | + | ++ | 172 | 346 | 402 | 441 | 98 | 264 | 92 |
| bt–a9 | 9 | 5700 | ± | + | 199 | 348 | 399 | – | 56 | 259 | 60 |
| s–b1 | 1 | 1600 | + | ++ | 147.5 | 330 | 355 | – | 156 | 327 | 179.5 |
| s–b2 | 2 | 2200 | + | + | 163 | 337 | 366 | – | 108 | 297 | 134 |
| s–b4 | 4 | 3400 | + | + | 187 | 346 | 380 | – | 56 | 285 | 98 |
| s–b9 | 9 | 5600 | ± | + | 183 | 350 | 390 | – | 27 | 256 | 73 |
| bt–b1 | 1 | 1600 | + | + | 197 | 340 | 400 | 422 | 160 | 295 | 98 |
| bt–b2 | 2 | 2200 | + | + | 196 | 340 | 410 | – | 114 | 323 | 127 |
| bt–b4 | 4 | 3500 | + | ± | 195 | 330 | 408 | 422 | 77 | 290 | 95 |
| bt–b9 | 9 | 5800 | ± | – | 188 | 348 | 400 | 430 | 20 | 266 | 78 |

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

Note: all the samples are denominated in shortened forms of the monomer, dianhydride: "s" represents s-BPDA, "bt" represents BTDA; end-cap agent: "a" represents PEPA, "b" represents PENA; the oligomer-degree nos. 1, 2, 4, 9 represent the number of the dianhydride molecules in the oligomer. For example, "s–a1" means the sample made from s-BPDA with *p*-TPEQ and PEPA with an oligomer degree of 1. The same is seen in Tables 2 and 3.

[a] Solubility: +, measured at a polymer concentration of 1% w/w; ++, soluble more than 5% at room temperature; ±, partially soluble on heating; –, insoluble.

Oligo-s–b1 demonstrated the highest $T_g$ and the highest $\Delta T_g$ after curing among the 16 samples. The glass transition temperatures of the cured imide oligomers are related to not only crosslink density, but also to the oligomer chain conformation.

### 3.2.2. *Processability of the imide oligomers*

The incorporation of bulky substituent pendants into the polymer backbone is an effective way to improve the solubility of the polymer [24]. The solubilities of the imide oligomers in NMP and DMF were investigated, and the results are summarized in Table 1. With the molecular weight increasing, the solubility decreases. The PEPA imide oligomers had higher solubilities than those of PENA due to the steric hindrance of the naphthyl groups. All the oligomers have better solubilities in NMP than in DMF because the polarity of NMP is higher.

As mentioned before, the purpose of our work was to find a kind of phenylethynyl-terminated oligomer that can meet the RTM (resin transfer molding) requirements. Low viscosity is the most important character. The melt viscosity measurement of the oligomers was carried out, and the different melt viscosities as a function of curing temperature are displayed in Fig. 2 which was illustrated with the s-BPDA/*p*-TPEQ/PEPA series.

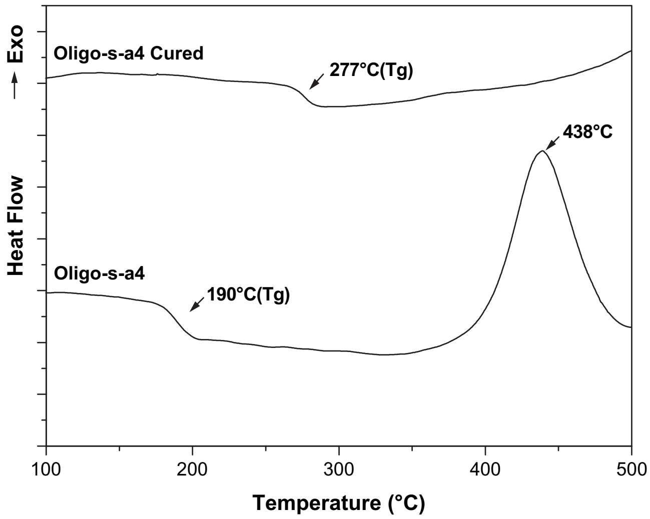


Fig. 1. Typical DSC curves of the oligo-s–a4 powder.

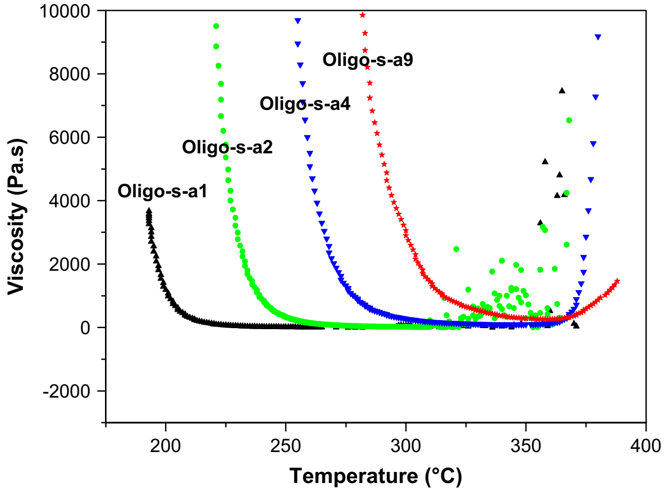


Fig. 2. Complex melt viscosity behaviors of oligo-s–a1–9.

Oligo-s–a1, oligo-s–a2, oligo-s–a4, oligo-s–a9 exhibited minimum melt viscosity as low as 5 Pa s (260 °C), 6 Pa s (320 °C), 93 Pa s (343 °C) and 266 Pa s (345 °C), respectively. All the minimum melt viscosities were lower than the reported oligomers (PETI-5 exhibited its minimum melt viscosity at 60 000 Pa s (371 °C) and TriA-PI had a lower minimum melt viscosity at 1000 Pa s (320 °C)) [4,20]. The lower minimum melt viscosities of the oligomers were the contribution of the pendant phenyl group and the diether group in the diamine monomer (*p*-TPEQ). 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.

The processability was improved by decreasing the molecular weight of the oligomers, which can be seen in Fig. 2. Furthermore, the PEPA end-capped ones exhibited higher potential for RTM (resin transfer molding) use.

### 3.2.3. Crosslink characterization

The crosslink reaction of phenylethynyl end group was monitored by IR spectroscopy as illustrated by oligo-bt–a2. As can be seen in Fig. 3, oligo-bt–a2 showed an absorption of the terminated phenylethynyl C≡C at 2210 $cm^{-1}$ and the imide carbonyls C=O at 1780 $cm^{-1}$, 1720 $cm^{-1}$, and characteristic imide bands at 1370 $cm^{-1}$, 1110 $cm^{-1}$, and 740 $cm^{-1}$. When cured at 370 °C, the absorption at 2210 $cm^{-1}$ decreased gradually and almost vanished after 70 min, but the imide and carbonyl absorptions remained constant during the thermal cure process, which indicated that the C≡C bonds of phenylethynyl reacted during 370 °C curing.

## 3.3. Films

The cured imide oligomer films were prepared by molding the oligomer powder at 370 °C for 1 h under pressure. Thermal curing of imide oligomers leads to the phenylethynyl group undergoing a complex reaction involving chain extension, branching and crosslinking without the evolution of volatile by-products. The color of the films made from oligo-s–a1–9 was lighter than the others.

Table 2
Properties of the cured films from the oligomers

| Samples | Cured film properties | | | | | | |
|---|---|---|---|---|---|---|---|
| | DMA | TGA ($N_2$) | | TGA (air) | Tensile properties | | |
| | $T_g^3$ (°C) | $T_{d_5}$ (°C) | Retain (%) | $T_{d_5}$ (°C) | Strength (MPa) | Modulus (GPa) | Elongation (%) |
| s–a1 | 305 | 506 | 62.5 | 494 | 53 | 2.6 | 2.4 |
| s–a2 | 289 | 521 | 64 | 514 | 116 | 3.0 | 7.1 |
| s–a4 | 272 | 530 | 63 | 535 | 140 | 3.4 | 8.8 |
| s–a9 | 253 | 535 | 63.8 | 535 | 103 | 3.2 | 5.4 |
| bt–a1 | 307 | 549 | 67.5 | 534 | 55 | 2.8 | 4.0 |
| bt–a2 | 288 | 526 | 65.5 | 504 | 114 | 3.1 | 6.3 |
| bt–a4 | 265 | 524 | 64.1 | 504 | 109 | 3.2 | 4.7 |
| bt–a9 | 251 | 529 | 65.5 | 517 | 130 | 2.9 | 8.0 |
| s–b1 | 319 | 508 | 62.5 | 511 | 57 | 2.5 | 3 |
| s–b2 | 294 | 531 | 67.8 | 490 | 93 | 2.7 | 4.7 |
| s–b4 | 274 | 532 | 70.6 | 500 | 122 | 2.7 | 13 |
| s–b9 | 242 | 548 | 67.9 | 501 | 31 | 0.9 | 7 |
| bt–b1 | 295 | 531 | 68.8 | 534 | 62 | 2.8 | 3 |
| bt–b2 | 327 | 542 | 66.9 | 510 | 40 | 2.5 | 2.6 |
| bt–b4 | 262 | 534 | 70.2 | 507 | 67 | 2.8 | 3.6 |
| bt–b9 | 250 | 539 | 64.5 | 505 | 57 | 1.5 | 5.8 |

$T_g^3$: glass transition temperature of the oligomers determined on cured film by DMA at a heating rate of 5 °C $min^{-1}$; $T_{d_5}$: 5% weight loss temperatures in $N_2$ or air atmosphere; retain: weight% at 700 °C in $N_2$ atmosphere.

### 3.3.1. Dynamical mechanical properties

The $T_g$ values of cured imide oligomer films were determined by DMA. The peak on the tan $\delta$ as a function of temperature curves was considered as the $T_g$ of the cured film, and the data are listed in Table 2. Fig. 4 shows the DMA curves (modulus as a function of temperature) of cured PI oligomers ($n = 1, 2, 4, 9$) films based on s-BPDA/*p*-TPEQ/PEPA. $T_g$ exhibited an obvious reduction with the increasing molecular weight because of lower crosslink density.

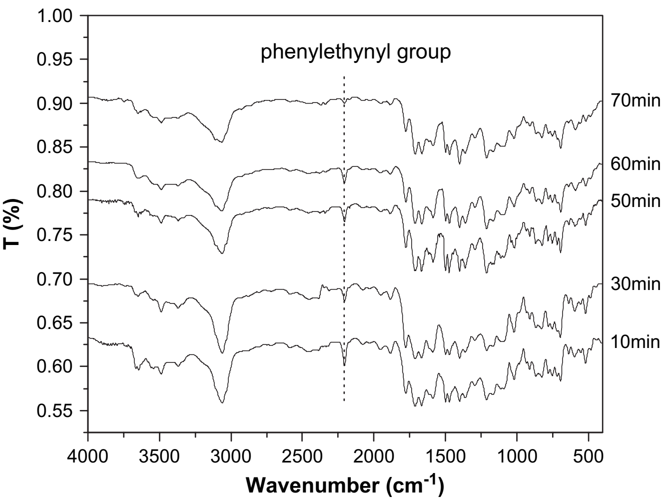


Fig. 3. Variations of FTIR spectra of oligo-s–b2 heat-treated at 370 °C.

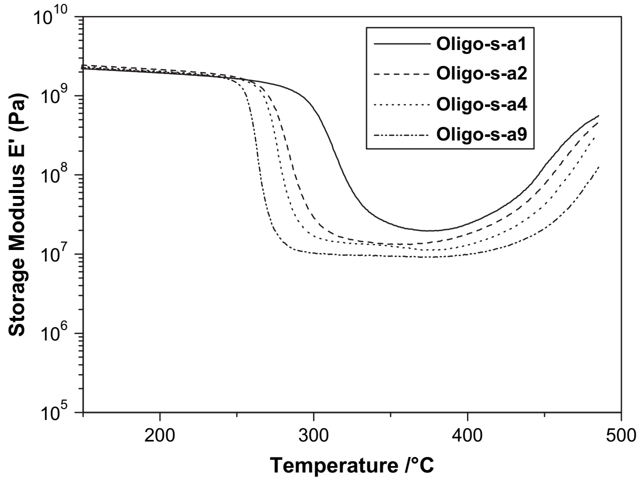


Fig. 4. DMA curves of cured PI oligomer ($n = 1, 2, 4, 9$) films based on s-BPDA.

### 3.3.2. Tensile properties

The room temperature tensile properties of cured oligomer films are presented in Table 2. The films of cured imide oligomers with lower molecular weight were easy to break due to higher crosslink density. All cured PEPA end-capped imide oligomer films exhibited better tensile properties, which had the strength at break more than 110 MPa, the modulus more than 2 GPa, and the PENA end-capped ones exhibited relatively lower tensile strength and modulus except that of oligo-s–b4. The oligo-s–b4 showed excellent tensile properties, with a strength at break of 122 MPa and a modulus of 2.7 GPa, and 13% elongation. Comparing their tensile properties, the four series of polymers showed the same trend that the cured imide oligomers with a calculated molecular weight of 3300 g $mol^{-1}$ exhibited the best strength and modulus and higher elongation to break. In all, oligo-s–a4 offered the best tensile properties after crosslinking.

### 3.3.3. Thermal stability

The thermal stability of films obtained from oligomers cured at 370 °C was evaluated by TGA in $N_2$ and air atmospheres at a heating rate of 5 °C $min^{-1}$. All cured films with different molecular weights exhibited excellent thermal stability. The data are listed in Table 2 and the thermal stability behavior was illustrated by bt–b9 in Fig. 5. The temperatures of 5% weight loss were all above 506 °C in $N_2$, the char yields reported at 700 °C in $N_2$ is above 62.5%.

### 3.3.4. Hydrolysis stability in base and acid solutions

The hydrolysis stability tests of the polyimide films were performed by immersing the films (as illustrated by oligo-s–a4 and oligo-s–b4, which were just different from the end-capping agent with the same molecular weight) into 10% NaOH or 10% $H_2SO_4$ aqueous solution, and refluxing for 24 h. The mechanical properties of the membranes before and after hydration are listed in Table 3.

As can be seen from Table 3, the film from oligo-s–a4 showed 30% reduction in tensile strength to failure and a 6% reduction in tensile modulus after boiling in 10% NaOH aqueous solution for 24 h, while oligo-s–b4 showed just 10% reduction in strength to failure and nearly no reduction in modulus, from which we can see that PENA is better than PEPA as the end-capping agent according to the hydrolysis stability. The reason is that naphthalene group has participated in the crosslink reaction and thus leads to a more dense network of the membrane, so the water molecule cannot easily move into the network to break the bond of the imide ring.

Table 3
Mechanical properties of the membranes before and after hydration

| Sample | Treatment[a] | Tensile properties | | |
|---|---|---|---|---|
| | | Strength (MPa) | Modulus (GPa) | Elongation (%) |
| s–a4 | 1 | 140 | 3.4 | 8.8 |
| | 2 | 97 | 3.2 | 12 |
| | 3 | 120 | 2.6 | 9 |
| s–b4 | 1 | 122 | 2.7 | 13 |
| | 2 | 110 | 2.7 | 7 |
| | 3 | 120 | 2.7 | 7 |

[a] Treatment 1: without any treatment; 2: refluxing in 10% NaOH aqueous solution for 24 h; 3: refluxing in 10% $H_2SO_4$ aqueous solution for 24 h.

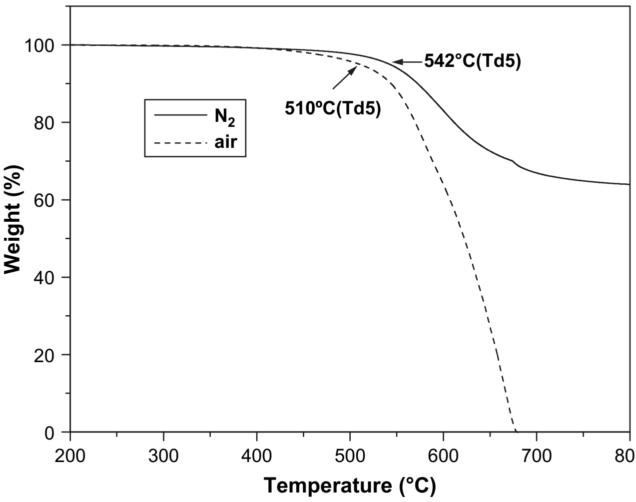


Fig. 5. TGA curves of the fully cured bt–b9 film in air and $N_2$ atmospheres.

## 4. Conclusions

Four series of phenylethynyl-terminated imide oligomers consisting of s-BPDA or BTDA with *p*-TPEQ were prepared. The incorporation of *p*-TPEQ increased the solubility and processability of the oligomers compared with the other reported PETI oligomers. The oligomers have low $T_g$s and low minimum melt viscosities at low temperature, which was contributed by the pendant phenyl groups. The $T_g$s of cured imide oligomers were related not only to crosslink density, but also to the oligomer chain conformation. All the oligomers can be compressed into films and the films exhibited excellent thermal stability and good mechanical properties. Films obtained from PEPA showed higher tensile strength and modulus at break than PENA. The films of cured imide oligomers with $M_w$ 1500 g $mol^{-1}$ have higher $T_g$ but poorer tensile properties due to higher crosslink densities and branching. Oligo-s–a4 offered the best combination of properties among all the 16 different oligomers. PENA is better than PEPA as the end-capping agent to get more hydrolysis stable polymer in alkali or acid environment.

## Acknowledgement

The Financial support from the National Nature Science Foundation of China (National 973 program No. G2003CB615604) and Jilin Province Prominent Youth Foundation of China is gratefully acknowledged.

## References

[1] Sroog CE. J Polym Sci Macromol Rev 1976;161.
[2] Hergenrother PM. High Perform Polym 2003;15:3.

[3] Hergenrother PM, Watson KA, Smith Jr JG, Connell JW. Polymer 2002;43:5079.
[4] Connell JW, Smith Jr JG, Hergenrother PM. JMS Rev Macromol Chem Phys 2000;C40(2&3):207–30.
[5] Lee YJ, Huang JM, Kuo SW, Chang FC. Polymer 2005;46:10056.
[6] Jiang X, Bin Y, Matsuo M. Polymer 2005;46:7418.
[7] Yang CP, Su YY. Polymer 2005;46:5797.
[8] Watson KA, Ghose S, Delozier DM, Smith Jr JG, Connell JW. Polymer 2005;46:2076.
[9] Hergenrother PM, Watson KA, Smith Jr JG, Connell JW, Yokota R. Polymer 2004;45:5441.
[10] Fang X, Yang Z, Zhang S, Gao L, Ding M. Polymer 2004;45:2539.
[11] Smith Jr JG, Connell JW, Delozier DM, Lillehei PT, Watson KA, Lin Y, et al. Polymer 2004;45:825.
[12] Hergenrother PM, Connell JW, Smith Jr JG. Polymer 2000;41:5073.
[13] Holland TV, Glass TE, McGrath JE. Polymer 2000;41:4965.
[14] Smith Jr JG, Connell JW, Hergenrother PM. Polymer 1997;38:4657.
[15] Fang X, Rogers DF, Scola DA, Stevens MP. J Polym Sci Part A Polym Chem 1998;36:461.
[16] Tan B, Vasudevan V, Lee YJ, Gardner S, Davis RM, Bullions T, et al. J Polym Sci Part A Polym Chem 1997;35:2943.
[17] Hergenrother PM, Smith Jr JG. Polymer 1994;35:4857.
[18] Simone CD, Scola DA. Macromolecules 2003;36:6780.
[19] Chuang KC, Bowman CL, Tsotsis TK, Arendt CP. High Perform Polym 2003;15:459.
[20] Yokota R, Yamamoto S, Yano S, Sawaguchi T, Hasegawa M, Yamaguchi H, et al. High Perform Polym 2001;13:S61.
[21] Zhou H, Chen C, Kanbara R, Sasaki T, Yokota R. High Perform Polym 2005;17:193.
[22] Sasaki T, Moriuchi H, Yano S, Yokota R. Polymer 2005;46:6968.
[23] Wang DH, Baek JB, Nishino SF, Spain JC, Tan LS. Polymer 2006; 47:1197.
[24] Yang CP, Chen RS. J Polym Sci Part A Polym Chem 2002;40:429–38.
[25] Liaw DJ, Liaw BY. Polym J 1996;28:970.
[26] Yang CP, Yang HW. J Appl Polym Sci 2000;75:87.
[27] Liaw DJ, Liaw BY. J Polym Sci Part A Polym Chem 1997;35:1527.
[28] Hsiao SH, Yang CP, Lin CK. J Polym Res 1995;2:1.
[29] Wright ME, Schorzman DA, Pence LE. Macromolecules 2000;33:8611.
[30] Wright ME, Schorzman DA. Macromolecules 2001;34:4768.
[31] Thompson CM, Hergenrother PM. Macromolecules 2002;35:5835–9.
[32] Chen S, Yin Y, Tanaka K, Kita H, Okamoto K. Polymer 2006; 47:2660.
[33] Genies C, Mercier R, Sillion B, Petiaud R, Cornet N, Gebel G, et al. Polymer 2001;42:5097.
[34] Fang J, Guo X, Harada S, Watari T, Tanaka K, Kita H, et al. Macromolecules 2002;35:9022.
[35] Miyatake K, Zhou H, Matsuo T, Uchidia H, Watanabe M. Macromolecules 2004;37:4961.
[36] Yudin VE, Divoux GM, Otaigbe JU, Svetlichnyi VM. Polymer 2005;46:10866.