

Synthesis and Properties of Soluble Phenylethynyl-Terminated Imide Oligomers Bearing *N*-Phenylated Melamine Units

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ABSTRACT: Novel soluble aromatic phenylethynyl end-capped imide oligomers were prepared by the reaction of 2,4-bis(4-aminoanilino)-6-anilino-1,3,5-triazine and 4,4'-oxydianiline with 3,3',4,4'-biphenyltetracarboxylic dianhydride and 4-phenylethynylphthalic anhydride. The imide oligomers exhibited good solubility in amide-type polar solvents and good thermal processability with increasing the content of *N*-phenylated melamine unit. The oligomers cured at 370°C possessed high glass transition temperatures of around 300°C and 5% weight loss temperatures around 500°C, maintaining good mechanical properties.

Introduction

Aromatic phenylethynyl-terminated imide oligomers have been demonstrated as polymer matrixes for advanced composite materials.¹⁻⁴ Carbon fiber/imide resin composites have been fabricated from the wet prepreg using an amic acid oligomer solution because the solubility of the imide oligomer is generally poor. When the composite is prepared from the amic acid wet prepreg, by-products such as water in the curing process must be removed to obtain the void-free composite. The handling of the amic acid wet prepreg is complicated and the curing process should be carefully controlled. On the other hand, an imide oligomer wet prepreg generates no by-products during the curing process due to the usage of the fully imidized oligomer. A poor processability of imide oligomers limited their wide-spread adoption as matrix resins for advanced composites. To improve their processability such as solubility in organic solvents or melt processing properties, many efforts have been focused on the synthesis of various kinds of aromatic phenylethynyl-terminated imide oligomers.^{5,6} An effective approach to attain solubility without sacrificing their thermal stability is the incorporation of asymmetric, kinked, or bulky structures into the imide backbone. The soluble imide oligomers were successfully developed from asymmetrically kinked 2,3,3',4'-biphenyltetracarboxylic dianhydride, or bulky and rigid 9,9-bis(4-aminophenyl)fluorene and 9,9-bis(4-aminophenoxy-phenyl)fluorene.⁷⁻⁹ The objective of this study is to synthesize soluble imide oligomers through introducing a bulky *N*-phenylated melamine unit into the phenylethynyl-terminated imide oligomer. The imide oligomers were cured to give crosslinked resins, which were also characterized in respect of thermal and mechanical properties.

Experimental Section

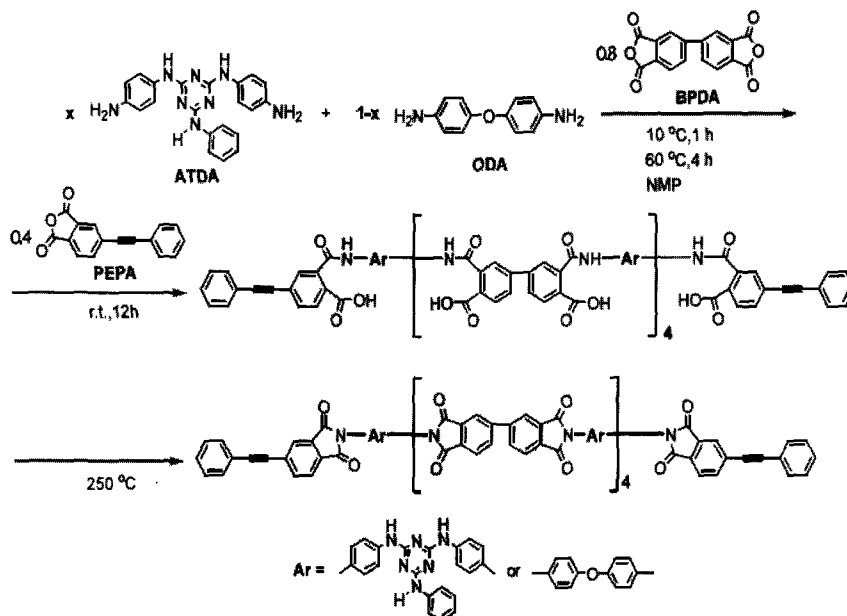
Materials. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA), 4,4'-oxydianiline (ODA), and 4-phenylethynylphthalic anhydride (PEPA) which was supplied by Manac Inc. were purified by sublimation under reduced pressure. 2,4-Bis(4-aminoanilino)-6-anilino-1,3,5-triazine (ATDA) was synthesized by the reaction of 6-anilino-2,4-dichloro-1,3,5-triazine with excess *p*-phenylenediamine. *N*-Methyl-2-pyrrolidone (NMP) was purified by distillation over calcium hydride.

Synthesis of imide oligomer (ATDA/ODA=50/50 mol%). In a three-necked flask equipped with a stirrer shaft and nitrogen inlets were placed ATDA (0.481 g, 1.25 mmol), ODA (0.251 g, 1.25 mmol), and NMP (5.5 mL). Diamines were dissolved under nitrogen atmosphere. After BPDA (0.588 g, 2.00 mmol) was added to the solution, the mixture was stirred at 10°C for 1 h and then 60°C for 4 h. PEPA (0.248 g, 1.00 mmol) was added to the solution at room temperature, and then stirred for 12 h, resulting in phenylethynyl end-capped amic acid oligomer solution. The amic acid oligomer had inherent viscosity of 0.23 dL/g, measured at a concentration of 0.5 g/dL in NMP at 30°C. The amic acid solution was cast onto a dry glass plate and heated in a vacuum oven at 80, 100, 150, 200, and 250°C for 1 h each to yield an off-white powder in 96% yield (1.42 g). The imide oligomer had

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inherent viscosity of 0.28 dL/g, measured at a concentration of 0.5 g/dL in NMP, and number-average molecular weight of 3000 and weight-average molecular weight of 7100, determined by gel permeation chromatography (GPC) on the basis of polystyrene calibration in NMP with 0.01 M LiBr. IR (KBr, cm^{-1}): 3054 (aryl C-H str), 2211 (ethynyl str), 1774 (imide C=O asym str), 1717 (imide C=O sym str), 1576 (triazine C=N str), 1371 (imide C-N str), 738 (imide C=O bend). Anal. Calcd for $\text{C}_{178.5}\text{H}_{100}\text{N}_{25}\text{O}_{22.5}$: C, 72.55%; H, 3.42%; N, 11.85%. Found: C, 71.96%; H, 3.51%; N, 11.76%.

Preparation of cured imide resins. The imide oligomer powder (0.6 g) was placed in a UPILEX-75S polyimide film frame (80 mm length, 50 mm wide, 75 μm thickness). The powder was heated at 320°C for 20 min on a hot-press machine, and then cured at 370°C for 1 h under 3 MPa, giving brown, transparent, and flexible cured films. IR (film, cm^{-1}): 3056 (aryl C-H str), 1774 (imide C=O asym str), 1721 (imide C=O sym str), 1577 (triazine C=N str), 1374 (imide C-N str), 740 (imide C=O bend).



Scheme 1. Synthesis of imide oligomers having *N*-phenylated melamine units.

Results and Discussion

Synthesis of imide oligomers. Phenylethynyl-terminated imide oligomers consisting of 40, 50, and 60 mol% melamine content were synthesized quantitatively by the polymerization of BPDA, diamines (ATDA and ODA), and PEPA as shown in Scheme 1. The respective molar ratios of BPDA, diamines, and PEPA were fixed at 4:5:2. The degree of polymerization of each imide oligomer was $n = 4$, and calculated average molecular weights were 2900-3000. The obtained amic acid oligomers with inherent viscosities of 0.23-0.26 dL/g were successfully converted at 250°C for 1 h to imide oligomers. They had inherent viscosities of 0.28-0.31 dL/g and number-average molecular weights (M_n) of 3000-3400 determined by GPC (Table 1). Polydispersities (M_w/M_n) were 2.2-2.9. The inherent viscosities of the oligomers are what may be expected on the basis of molecular weights of about 3000 and fall in the range of 0.28-0.31 dL/g. The M_n s agree well with the calculated molecular weights. The structure of imide oligomers was confirmed by FT-IR spectroscopy and elemental analysis.

Table 1. Synthesis of Amic Acid Oligomers (AAOs) and Imide Oligomers

| diamine (mol%) | | AAO | | imide oligomer | | |
|----------------|-----|---------------------------------|---------------------------------|----------------------|--------------------|-------------|
| ATDA | ODA | η_{inh}^a (dL/g) | η_{inh}^a (dL/g) | $M_n \times 10^{-3}$ | | M_w/M_n^b |
| | | | | Calcd. | Found ^b | |
| 40 | 60 | 0.25 | 0.31 | 2.9 | 3.3 | 2.9 |
| 50 | 50 | 0.23 | 0.28 | 3.0 | 3.0 | 2.3 |
| 60 | 40 | 0.26 | 0.28 | 3.0 | 3.4 | 2.2 |

^a Measured at a concentration of 0.5 dL/g in NMP at 30°C.

^b Determined by GPC on the basis of polystyrene calibration in NMP.

The incorporation of bulky substituent pendants into the polymer backbone is an effective way to improve the solubility of the polymer. The solubility of the imide oligomers is summarized in Table 2. With the content of melamine-containing diamine ATDA increasing, the solubility of the imide oligomers increased. All the oligomers had better solubility in NMP up to 20 wt% than in DMAc.

Table 2. Solubility of Imide Oligomers^a

| diamine (mol%) | | solvent | | | |
|----------------|-----|-----------------|------|-----|---------|
| ATDA | ODA | NMP | DMAc | THF | dioxane |
| 40 | 60 | + | ± | - | - |
| 50 | 50 | ++ (20 wt%*) | + | - | - |
| 60 | 40 | ++ (20 wt%*) | ++ | - | - |

^a ++, soluble at room temperature; +, soluble after heating; ±, partially soluble on heating; -, insoluble; *, solubility on heating.

The influence of the *N*-phenylated melamine structure on the thermal properties of the oligomer was elucidated by DSC and TGA measurements. Table 3 shows that the T_g s of imide oligomers were in the range of 203–212°C. The T_g s increase with increasing ATDA contents due to the bulky and polar *N*-phenylated melamine units. The oligomers had good thermal stability with 5% weight loss temperatures above 500°C in both air and nitrogen.

Table 3. Thermal Properties of Imide Oligomers

| diamine (mol%) | | T_g^a (°C) | T_{d5}^b (°C) | | T_{d10}^c (°C) | |
|----------------|-----|--------------|-----------------|----------------|------------------|----------------|
| ATDA | ODA | | Air | N ₂ | Air | N ₂ |
| 40 | 60 | 203 | 510 | 510 | 540 | 540 |
| 50 | 50 | 211 | 505 | 505 | 530 | 530 |
| 60 | 40 | 212 | 505 | 500 | 525 | 525 |

^a Determined by DSC in nitrogen at a heating rate of 20°C/min.

^b 5% weight loss temperature, determined by TG in air or nitrogen at a heating rate of 10°C/min.

^c 10% weight loss temperature by TGA in air or nitrogen at a heating rate of 10°C/min.

The crosslinking reaction of phenylethynyl end group was monitored by FT-IR spectroscopy. The imide oligomers showed an absorption of the terminated phenylethynyl at 2211 cm⁻¹ and the imide carbonyls at 1774 and 1717 cm⁻¹, triazine C=N bonds at 1576 cm⁻¹ and characteristic imide bands at 1371 and 738 cm⁻¹. When cured at 370°C, the absorption at 2211 cm⁻¹ disappeared gradually and almost vanished after 1 h, but the imide carbonyls and characteristic absorptions remained during the thermal curing process. This result indicates that phenylethynyl groups reacted during 370°C curing.

The cured imide oligomer films were prepared by molding the oligomer powder in a polyimide frame at 370°C for 1 h under pressure. The phenylethynyl groups in the thermal curing undergo a complex reaction involving chain extension, branching, and crosslinking without the evolution of volatile by-products. The brown, transparent, and flexible cured films were obtained from the imide oligomers. Thermal and mechanical properties of thermosetting imide resins are shown in Table 4. The cured resins had high glass transition temperatures of 295–306°C and relatively lower thermal coefficient of thermal expansion of 50 ppm/°C. The temperatures at which 5% weight loss occurred were recorded as 490–510°C in air and nitrogen along with the char yield of 60% at 800°C in nitrogen.

Table 4. Thermal and Mechanical Properties of Cured Resins Derived from Imide Oligomers

| diamine (mol%) | | T_g^a (°C) | T^b (MPa) | E^c (%) | M^d (GPa) |
|----------------|-----|--------------|----------------|--------------|----------------|
| ATDA | ODA | | | | |
| 40 | 60 | 306 | 127 | 5.0 | 4.5 |
| 50 | 50 | 295 | 147 | 5.0 | 4.8 |
| 60 | 40 | 300 | 149 | 3.6 | 5.7 |

^a Determined by TMA in nitrogen at a heating rate of 10°C/min.

^b Tensile strength. ^c Elongation at break. ^d Tensile modulus.

The cured imide oligomer films exhibited excellent tensile properties with the tensile strength a break in the range of 127-149 MPa, the elongation at break of 3.6-5.0%, and the tensile modulus of 4.5-5.7 GPa.

Conclusion

Novel soluble phenylethynyl-terminated imide oligomers containing *N*-phenylated melamine unit were readily synthesized by the polymerization of aromatic diamine having a melamine unit, aromatic tetracarboxylic dianhydride, and phenylethynylphthalic anhydride. The incorporation of *N*-phenylated melamine units increased the solubility and processability of the imide oligomers without sacrificing their thermo-oxidative stability. The imide oligomers were soluble in aprotic polar solvents and had glass transition temperatures of around 210°C along with good thermal stability up to 500°C. The imide oligomers were compressed into cured films, which exhibited excellent thermal stability and mechanical properties.

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