



## Novel thermally stable and organosoluble aromatic polyamides with main chain phenyl-1,3,5-triazine moieties

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### ABSTRACT

The syntheses and properties of phenyl-1,3,5-triazine functional aromatic polyamides are described. From 2,4,6-trichloro-1,3,5-triazine (1), an aromatic diacid, namely 4-(4,6-diphenyl-1,3,5-triazin-2-yl) benzoic acid (6), was prepared by a three-step reaction in satisfactory yields. A model reaction of 6 with aniline (7) was carried out to determine feasibility of amidization. Aromatic poly(phenyl-1,3,5-triazine amide)s (10a–10e) with inherent viscosities ranging from 0.28 to 1.26 dL/g were synthesized from Yamazaki phosphorylation polycondensation of 6 with aromatic diamines (9a–9e). The reactions were conducted in *N*-methyl-2-pyrrolidone (NMP) to yield high-molecular-weight amorphous polymers in essentially high yields. All polymers are readily soluble in NMP and *N,N*-dimethylacetamide (DMAC) at room temperature, and formed transparent films from their solution. The films exhibit good mechanical properties with tensile strengths of 71.5–94.7 MPa, elongations at break of 6.1–10.0%, and initial moduli of 2.3–2.8 GPa except that of 10a is slightly brittle. These polymers have high glass transitions from 311 to 330 °C, depending on the aromatic diamines used in the polycondensation, and they demonstrate excellent thermal stabilities in excess of 440 °C (5% weight loss in air). Isothermal TGA measurements reveal that the obtained benzene-1,3-diamine-based poly(phenyl-1,3,5-triazine amide) (10b) belongs to the most superior class of heat resistant polymers such as polyamide<sup>®</sup>.

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### 1. Introduction

Poly(phenyl-1,3,5-triazine)s (PPTs) and related structures comprise a novel class of polymers exhibiting many attracting characteristics which include excellent thermo-oxidative stability, high glass transition temperature ( $T_g$ ) and module, good flame retardancy and low dielectric constant [1]. Such polymers have recently attracted a great deal of academic interests due to their potential utilities in a wide variety of applications such as advanced performance composites, catalyst supports, flat-panel displays as well as fuel cells [2–5].

PPT networks are generally synthesized by the trimerization of aromatic dinitriles, where the cyano cyclization is the polymer-forming reaction. Harsh reaction conditions including high

temperature and pressure were frequently required for this chemistry. A notable example is the trimerization of 4,4'-biphenyldicarbonitrile to PPT networks which is conducted at a temperature of 200–500 °C under a pressure of 30–50,000 atm [6,7]. Although linear full aromatic PPTs can be readily prepared by the reaction of aromatic diethyl acetimidate with benzaldehyde, the obtained polymers are often of low molecular weight. Additionally, the most obvious disadvantage of carrying out polycondensation in organic solvents is the extremely poor solubility of the PPTs [8,9]. Therefore, rather rigorous synthetic reaction conditions and unacceptable low molecular weights for PPTs strictly hamper their applications as composite matrix resins, membranes or adhesives.

To tackle these problems, much effort has been devoted to the improvement of linear PPTs' solubility or their melt processability via structural modification of the polymer chains [10,11]. The introduction of flexible groups including ether, ethynylene and ester into the thermally stable PPT backbones has been employed to achieve good solubility, and the subsequent polymers are of high-molecular-weight [12,13]. This change in molecular structure is accompanied by variation of the crystallinity, mechanical properties, glass transition temperatures ( $T_g$ s) and solubility in organic

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solvents and as a consequence synthetic conditions and applications. Essentially, such polymers are generally synthesized by solution polycondensation of phenyl-1,3,5-triazine functional bisphenols or dihalides under milder conditions relative to the traditional PPTs. Experimentally, these synthetic approaches demonstrated that the phenyl-1,3,5-triazine linkage survived in typical polycondensation conditions [14,15]. The etherification and esterification transformation occurred with high selectivity and were judged suitable as a polymer-forming reaction. Although in some cases, the synthesis and application of PPT polymers, higher boiling point solvents such as diphenyl sulfone or sulfolane are still required to keep the polymer in solution and drive it to high-molecular-weight [16,17]. The obtained amorphous or semi-crystalline polymers are featured by improved solubility compared to the known PPTs since the flexible groups facilitate the segmental motions, while other attracting properties namely mechanical property and stability are more or less sacrificed. Our laboratory has recently attempted to synthesize phthalazinone-based poly(phenyl-1,3,5-triazine ether)s that maintains good thermal and mechanical properties of PPT, but with increased solubility. High molecular weight polymers can be obtained in common polar solvents with high yields, and they can be cast into flexible and tough films simply from their organic solution [18,19].

As part of our ongoing project dealing with high performance polymeric materials, we investigate a new kind of PPTs system with amide moiety in this article. This new series of poly(phenyl-1,3,5-triazine amide)s that are capable of solution processing through the incorporation of ether, sulfone or methylene groups can be synthesized and cast into films from common polar organic solvents, has good mechanical properties. Therefore, they could be of great potential commercial importance if they are used as high performance membrane or coatings. This paper studies the effects of monomer composition on the solubility, thermal properties as well as mechanical properties of the obtained polymers.

## 2. Experimental

### 2.1. Experimental materials

2,4,6-Trichloro-1,3,5-triazine (1) was purchased from Alfa Aesar Chemical Inc. and used as received. 1-Bromobenzene (2), 1-bromo-4-methylbenzene (4), benzene-1,4-diamine (9a), benzene-1,3-diamine (9b), 4,4'-oxydianiline (9c), 4,4'-methylenedianiline (9d) and 4,4'-sulfonyldianiline (9e) were purchased from Aldrich–Sigma Chemical Inc. and used as received. Tetrahydrofuran (THF) was refluxed over calcium hydride and distilled under reduced pressure. *N*-methyl-2-pyrrolidone (NMP) was vacuum-distilled over calcium hydride, and stored over molecular sieves (type 4A<sup>o</sup>) before use. Pyridine (Py) was refluxed over KOH pellets and distilled. Triphenyl phosphite (TPP) was distilled under vacuum. Anhydrous calcium chloride (CaCl<sub>2</sub>) was dried for 4 h at 180 °C under vacuum just before use. Unless otherwise specified, all other solvents and reagents were purchased from Shanghai Sino-pharm Chemical Inc. and used as received.

### 2.2. Instruments

Inherent viscosities ( $\eta_{inh}$ ) of the polymers were measured by Ubbelohde capillary viscometer at a concentration of 0.5 g/dL in *N*-methylpyrrolidone (NMP) at 25 °C. Infrared measurements were performed on a Thermo Nicolet Nexus 470 Fourier transform infrared (FT-IR) spectrometer using KBr pellets of monomers and thin films of polymers. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100 MHz) were obtained with a Varian Unity Inova 400 spectrometer at an operating temperature of 25 °C using CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> as solvents

according to solubility of samples, and the data were listed in parts per million downfield from tetramethylsilane (TMS). For polymers, their <sup>1</sup>H NMR (400 MHz) were obtained by using H<sub>2</sub>SO<sub>4</sub>-*d*<sub>2</sub> as solvent. High performance liquid chromatogram (HPLC) was performed on a Hewlett–Packard (HP) 1100 liquid chromatography using a mixture of acetic acid (0.1 wt%) and methanol (*v/v* = 90:10) as eluting solvent and a 2.0 × 150 mm Microbore column (Waters Spherisorb<sup>®</sup>S5 ODS2) as column. Matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF/MS) analyses were performed on a Micromass GC-TOF CA 156 MALDI-TOF/MS. Elemental analysis was measured on a Vario ELIII CHNOS Elementaranalysator from Elementaranalysesysteme GmbH. Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were performed on a Mettler TGA/SDTA851 thermogravimetric analysis instrument in a nitrogen atmosphere and in an air atmosphere at 20 °C min<sup>-1</sup> from 100 to 800 °C on 8–9 mg samples. Decomposition temperatures of 1% and 5% weight loss, temperatures for the maximum weight loss rate ( $T_{max5}$ ) and char yields ( $C_y$ s) were recorded.  $C_y$  was calculated as the percentage of solid residue after heating from 100 to 800 °C in nitrogen atmosphere. Differential scanning calorimetry (DSC) was measured on a Mettler DSC822 DSC in flowing nitrogen (20 mL/min) at a heating rate of 10 °C min<sup>-1</sup>. Wide-angle X-ray diffraction (WAXD) was performed at room temperature on a Rigaku D/max 2400 automatic X-ray diffractometer with Ni-filtered Cu K $\alpha$  radiation (40 kV, 100 mA).

### 2.3. Synthesis of 2,4-dichloro-6-phenyl-1,3,5-triazine (3)

6.05 g of magnesium turnings (250 mmol) was heated to reflux in 100 mL of THF for 30 min. 15.71 g of bromobenzene (2, 100 mmol) in 20 mL of THF was added dropwise through an addition funnel. The reaction was then heated to reflux for 2 h and cooled. The Grignard solution was then added dropwise over 2 h to 18.45 g of 2,4,6-trichloro-1,3,5-triazine (1, 100 mmol) in 100 mL of THF. The mixture was stirred overnight in an ice/salt bath. 100 mL of toluene was added, followed by 80 mL of 12% HCl. The resulting slurry was extracted twice by using ethyl acetate, and a pale orange solid was collected by vacuum filtration. The product was dried in a vacuum oven at 100 °C to give 19.21 g (85.1%) of product in high purity. Selected data of 3: M.p.: 121.2–123.5 °C. FT-IR (KBr, cm<sup>-1</sup>): 3066 (=C–H), 2222 (C≡N), 1595, 1492 (C=C), 1251 (C–O), 1170, 867, 840 (w,  $\gamma_{C-H}$ ). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$ : 7.85~7.90 (d, 4H), 7.75~7.81 (d, 4H), 7.22~7.27 (d, 4H), 7.14~7.19 (d, 4H). TOF/MS. GC/MS (M + Calcd. as C<sub>9</sub>H<sub>5</sub>Cl<sub>2</sub>N<sub>3</sub>, 226.0646) *m/z*: 226.0608 (M+). Elem. Anal. Calcd. for C<sub>9</sub>H<sub>5</sub>Cl<sub>2</sub>N<sub>3</sub>: C, 47.82; H, 2.23; N, 18.59%. Found: C, 47.76; H, 2.34; N, 18.33%.

### 2.4. Synthesis of 2-phenyl-4,6-dip-tolyl-1,3,5-triazine (5)

In a way similar to phenylmagnesium bromide, 33.21 g of 4-tolylmagnesium bromide (170 mmol) in 150 mL of THF was prepared starting from 1-bromo-4-methylbenzene (4, 170 mmol). 18.08 g of compound 3 (80 mmol) in 100 mL THF was added dropwise into the Grignard solution, and the mixture was gradually heated to reflux overnight. The reaction mixture was cooled, and then rinsed with 5% HCl (2×) and water. The precipitated products were collected, and further purified by recrystallization from toluene (2×). After drying under vacuum at 100 °C, a white solid (22.75 g) was obtained with a yield of 84.3%. Selected data of 4: M.p.: 223.2–224.5 °C. FT-IR (KBr, cm<sup>-1</sup>): 3066 (w, =C–H), 2982 (w, –CH<sub>3</sub>), 1614, 1582, 1516 (s, C=C/N), 1370 (m, C–N), 803 (w,  $\gamma_{C-H}$ ). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>, ppm)  $\delta$ : 2.47(6H, s), 7.32–7.37(4H, d), 7.52–7.64(3H, m), 8.60–8.71(2H, d), 8.74–8.80(2H, d). TOF/MS. GC/MS (M + Calcd. as C<sub>23</sub>H<sub>19</sub>N<sub>3</sub>,

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