

Synthesis and characterization of semi-crystalline poly(decamethylene terephthalamide) thermosets



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ABSTRACT

We have explored the synthesis of semi-crystalline polyamide (PA) thermosets via a reactive PA oligomer precursor route. Poly(decamethylene terephthalamide) (PA 10T) oligomers with a target M_n of 1 K and 3 K $\text{g} \cdot \text{mol}^{-1}$ were synthesized via solution polymerization and end-capped with reactive phenylethynyl (PE) groups. The reactive oligomers could be cured in a stepwise manner using successive high temperature treatment steps. Depending on the concentration of PE end-groups, the degree of crystallinity of the final thermosets can be controlled and depressed by 60% for the crosslinked 3 K precursor and completely eliminated for the crosslinked 1 K precursor. From the calculated molecular weight between crosslinks, we estimated that 35–41% of the PE end-groups form crosslinking functionalities and the remainder of the PE end-groups contribute to chain extension. All thermoset films are stable up to ~ 400 °C in DMTA experiments due to network formation, effectively increase the maximum use temperature of PA 10T by 100 °C.

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1. Introduction

Semi-aromatic and aliphatic polyamides (PAs) have been widely used in demanding engineering applications because of their excellent heat resistance, fluid stability and thermo-mechanical properties [1]. To access PAs with better dimensional stability at elevated temperatures, researchers have explored the possibility of crosslinking PAs. Ionizing irradiation and thermal curing protocols have been used to prepare semi-aromatic and aliphatic PA thermosets. Ionizing irradiation, especially electron beam irradiation, was used to crosslink aliphatic PAs, such as PA 66 and PA 6 [2–4]. The ionizing irradiation initiates crosslinking in the amorphous phase and the crystallite interface of the PAs [3]. An increase in yield strength and Young's modulus was observed for electron beam crosslinked PA 66 [4]. The downside of this method is that degradation may take place, especially when high irradiation doses are used. Also, this method is only suitable for thin film applications due to the limited penetrating depth of the radiation. Little research has been reported on crosslinked semi-aromatic PAs. One example

is based on the thermal cure of a PA precursor with benzoxazine groups placed in the polymer backbone [5]. This route requires complicated synthetic procedures and results in an amorphous thermoset ($T_g = 169$ °C) due to the high crosslinking density.

Crosslinked semi-aromatic PAs are of scientific and engineering interest because crosslinking can be used to control the degree of crystallinity of the final product, which in turn controls mechanical properties such as storage modulus (E') and stress-strain behavior. Crosslinked semi-crystalline polymers have also attracted interest as functional polymers as they can be used in shape-memory applications [6–8]. As a model system for this study we have selected poly(decamethylene terephthalamide) or PA 10T. This semi-aromatic PA is of special interest because the 10- CH_2 diamine has a bio-based origin and improves the hydrophobicity of the polymer [9,10]. Typically, PA 10T is prepared via a 3-stage high-temperature polycondensation procedure [11,12]. The hydrogen-bonded terephthalamide units provide a relatively stiff backbone with a T_g of 127 °C and a high T_m of ~ 315 °C. The main difference with the aliphatic PAs is the high melting temperature and this in turn will limit our selection of reactive functionalities, i.e. the reactive functionalities have to remain latent during the polymerization and successive processing step. These constraining conditions limit our options to phenylethynyl-based reactive functionalities. This reactive functionality is well-known and used as chain extender/

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crosslinker in a variety of all-aromatic high-performance polymers [13–17]. Phenylethynyl (PE) is known for its excellent thermal stability, volatile-free polymerization and high cure temperature. When placed at both polymer chain-ends, a reactive oligomer or macro-monomer can be obtained, which has the additional advantage of a low melt viscosity (ease of processing). Considering the melting point of PA 10T (~315 °C) selecting the PE end-group (cure temperature ~310–400 °C) provides a proper melt processing window [13]. As stated earlier, PA 10T is typically prepared using melt polymerization methods. The high temperatures employed during melt condensation will not be compatible with the reactive PE end-groups as they will start to react prematurely. For this reason we will adopt a solution polymerization method in which we utilize a reactive diacyl chloride, in our case terephthaloyl chloride, and couple this under moderate heating conditions with the aliphatic 1,10-decanediamine monomer.

In this paper we will discuss the synthesis and properties of a semi-aromatic crosslinked PA model system PA 10T. Thermosets were prepared from reactive 1 K and 3 K $\text{g}\cdot\text{mol}^{-1}$ PA 10T oligomers with PE end-groups and the reactive oligomers were synthesized using a solution polymerization method. The cure behavior, the thermo-mechanical and morphological properties of the final semi-crystalline thermosets were investigated and will be discussed in detail in this paper.

2. Experimental

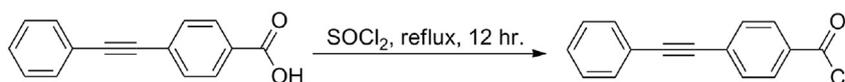
2.1. Materials

Terephthaloyl chloride was purchased from Sigma-Aldrich and purified via sublimation prior to use. 1,10-Decanediamine was generously supplied by DSM and dried under vacuum. CaCl_2 (96%) was purchased from Acros Organic and dried at 200 °C under vacuum. Triethylamine (99%) was purchased from Sigma-Aldrich and distilled over CaH_2 before use. Extra dry *N*-methyl-2-pyrrolidone (NMP, water content <0.005%) and concentrated sulfuric acid (96%) were purchased from Acros Organic and used as received. Trifluoroacetic acid (TFA, 99%), thionyl chloride (99%), anhydrous chloroform (99%) and anhydrous *N,N*-dimethylformamide (99.8%) were purchased from Sigma-Aldrich. 4-Phenylethynyl benzoic acid was purchased from Fluorochem and recrystallized from ethanol.

2.2. Synthesis

2.2.1. Reactive end-cap 4-phenylethynyl benzoyl chloride (PE-COCl)

The title compound was prepared from 4-phenylethynyl benzoic acid as illustrated in Scheme 1. A mixture of 4-phenylethynyl benzoic acid (10 g, 45 mmol) in 25 mL SOCl_2 with two drops of *N,N*-dimethylformamide was refluxed at 80 °C for 12 h with argon purge before the SOCl_2 was distilled off. The solid was purified via recrystallization in dry hexane, yielding 8.1 g (75%). mp = 85 °C. ^1H NMR (400 MHz, CDCl_3 , δ): 7.37–7.38 (m, 3H), 7.54–7.56 (m, 2H), 7.62–7.64 (d, $J = 8.0$ Hz, 2H), 8.08–8.10 (d, $J = 8.0$ Hz, 2H). ^{13}C NMR (400 MHz, CDCl_3 , δ): 88.0, 94.6, 122.2, 128.5, 129.2, 130.7, 131.3, 131.8, 131.9, 132.1, 167.7. MS m/z (%): 240.00 (26.9) [M^+], 205.05 (100.0), 176.00 (53.0), 151.10 (27.3), 88.10 (48.2).



Scheme 1. Synthetic route towards PE-COCl.

2.2.2. PE model compound

A well-defined PE model compound was prepared to determine the thermal cure range. The preparation procedure is depicted in Scheme 2. In a 100 mL dry flask with argon purge, 30 mL of NMP was placed followed by 1,10-decanediamine 0.431 g (2.5 mmol). The mixture was stirred and heated to 70 °C to allow the 1,10-decanediamine to dissolve completely, and then cooled to 0 °C in an ice-bath. Triethylamine (1 mL) was added into the flask, followed by PE-COCl (1.203 g, 5 mmol). The reaction was stirred at 0 °C for 30 min and at 55 °C for another 3 h. A cloudy mixture was formed, which was precipitated in water and the collected solids were washed 3 times with water. The title compound was obtained after drying under vacuum at 60 °C overnight.

2.2.3. PE end-capped PA 10T oligomers

Carothers theory was used to calculate the monomer to reactive PE end-cap ratio [18,19]. Oligomers with an M_n of 1 K and 3 K $\text{g}\cdot\text{mol}^{-1}$ were prepared according to the procedure shown in Scheme 3 and denoted as PA 10T-PE-1K and PA 10T-PE-3K, respectively. The synthetic procedure of PA 10T-PE-3K is described as an example:

In a dry 100 mL three-neck flask equipped with a mechanical stirrer, an argon inlet and a vacuum connection, 30 mL of NMP, 2.4 g of CaCl_2 and 1.785 g (10.36 mmol) of 1,10-decanediamine was placed. The mixture was warmed to 70 °C to allow the 1,10-decanediamine to dissolve completely, and then cooled to 0 °C in an ice-bath. Triethylamine (4 mL) was added into the flask followed by 10 mL NMP solution of terephthaloyl chloride (1.900 g, 9.36 mmol) and PE-COCl (0.481 g, 2 mmol). The mixture was stirred at 350 rpm for 30 min at 0 °C and for another 3 h at 55 °C to obtain a viscous slurry. This slurry was precipitated into demineralized water and the solids were washed 3 times with water in a heavy-duty blender before being collected by filtration. The oligomer was obtained after drying under vacuum at 60 °C overnight. A PA 10T homopolymer was synthesized using equal molar amount of both monomers under the same conditions. This polymer was used as our high molecular weight reference sample and denoted as PA 10T-ref.

2.3. Characterization

^1H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker WM-400 at 25 °C. WAXD studies were performed using a PANalytical X'Pert Pro PW3040/60 diffractometer with $\text{CuK}\alpha$ -radiation. Data was collected in an angular 2θ range of 3–30° at a rate of $2^\circ\cdot\text{min}^{-1}$ and a step size of 0.008° .

The density of the thermoset films was measured using a Mettler Toledo AG204 Delta-Range scale equipped with a density measurement kit (gravimetric method according to Archimedean principle). The gel fraction of the thermoset films was determined according to Equation (1).

$$\text{gel fraction} = \frac{W_g}{W_0} \times 100\% \quad (1)$$

where W_g and W_0 are the sample weight before and after extraction with TFA, respectively.

The rheological behavior of the oligomers was investigated

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