



Influence of crystalline polyimide hard block on the properties of poly(imide siloxane) copolymers



Xueliang Pei, Guofei Chen, Jiangtao Liu, Xingzhong Fang*

Ningbo Key Laboratory of Polymer Materials, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, China

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ABSTRACT

Comparative study was carried out regarding the properties of poly(imide siloxane) copolymers (PISs) with crystalline polyimide hard block and PISs with amorphous polyimide hard block. The crystalline polyimide hard block was synthesized from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 1,3-bis(4-aminophenoxy)benzene (TPER), and the amorphous polyimide hard block was synthesized from 2,2-bis(4-(3,4-dicarboxyphenoxy)phenyl)propane dianhydride (BPADA) and meta-phenylenediamine (*m*-PDA). The polysiloxane soft block based on bis(γ -aminopropyl)polydimethylsiloxane (APPS) had a molecular weight of 995 g/mol, and the APPS content in monomers varied from 32.6 to 53.0 wt%. The crystallization of PISs with crystalline polyimide hard block was investigated by differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WXR) and polarized optical microscope (POM). It was found that the crystalline polyimide hard block was more effective in retaining storage modulus and improving solvent resistance and elastic property of the PISs than the amorphous polyimide hard block.

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1. Introduction

Copolymerization is one of the most general and successful ways for preparation of new materials with specifically desired properties, due to the incorporation of two structures with different chemical or physical properties in the same polymer chain [1]. It has been established that polyimides modified with polysiloxane exhibit a number of beneficial properties, such as good solubility, high hydrophobicity, ease of processability, resistance to degradation in aggressive oxygen environment, excellent adhesion, low dielectric constant, low stress, high flexibility and impact resistance [2–9]. These particular advantages render poly(imide siloxane) copolymers (PISs) attractive for aerospace, microelectronic, adhesive, printed circuit and thermoplastic elastomer applications [2–11].

In the PISs, the polyimide hard block plays a role of physical crosslink at service temperature. However, after high polysiloxane soft block content was incorporated, the polyimide hard block of PISs always exhibits much lower glass transition temperature (T_g) compared with the corresponding homopolyimide, which in turn

affects the thermal stability of PISs [7,12–14]. For example, the T_g of homopolyimide synthesized from 4,4'-oxydiphthalic anhydride and 2,6-bis(3-aminophenoxy)benzotrile was 219 °C, while the T_g of the polyimide hard block decreased to 149 °C after 41 wt% polysiloxane soft block was incorporated [7]. In addition, Saudi Arabian Basic Industries Company (SABIC) has commercialized a kind of PIS having 40 wt% polysiloxane soft block under the registered trademark of Siltem STM-1500, which is an excellent choice for wire and cable coatings and high heat powder coating [15,16]. However, the T_g of its polyimide hard block is 168 °C, which is 49 °C lower than the T_g of corresponding homopolyimide [15]. According to Fitzgerald et al., the reduction in the T_g of polyimide hard block after incorporating polysiloxane was because the length of the polyimide hard block in PISs was shorter than the length of homopolyimide and the polysiloxane increased the free volume of PIS system [17].

It is known that several methods were used to increase the T_g of polyimide hard block or thermal stability of PISs. McGrath et al. found, for PISs with the same length of polyimide hard block, the T_g of polyimide hard block increased with increasing the length of polysiloxane soft block [18]. McGrath et al. explained it was because the extent of phase mixing between the polyimide hard block and the polysiloxane soft block decreased with increasing the length of

* Corresponding author. Tel.: +86 574 86685185; fax: +86 574 86685186.

E-mail address: fxzhong@nimte.ac.cn (X. Fang).

polysiloxane soft block. In Banerjee et al.'s studies and our previous study, two or more amino-terminated polysiloxanes were first linked together by dianhydride and then further reacted with polyimide hard block or non-siloxane diamine and dianhydride [19–21]. This method could increase the length of polyimide hard block in PIS for a given polysiloxane content. As a result, the T_g of polyimide hard block was increased. Ghosh et al. indicated the polysiloxane grafted PIS had much higher T_g of the polyimide hard block than PIS with the polysiloxane moiety in the main chain [22]. SiO₂ and TiO₂ were also used for the reinforcement of PISs, and the obtained composites had higher thermal stability than bare PISs [23,24]. In addition, crosslinking could increase the thermal stability of PISs at high temperature [25,26].

In general, presence of high-melting crystalline hard block in block copolymers can further improve their thermal stability above their upper T_g s [27–30]. This strategy has been well recognized and widely used in block copolymer chemistry [28–30]. However, as far as we know, the strategy was seldom used in PIS. Therefore, in this study, a direct comparison of thermal, mechanical and solubility properties was carried out between PISs with crystalline polyimide hard block and PISs with amorphous polyimide hard block. The crystalline polyimide hard block was based on polyimide from 1,3-bis(4-aminophenoxy)benzene (TPER) and 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), which displays a T_g at 210 °C and a high melting temperature at 395 °C and has a very fast crystallization rate [31]. The amorphous polyimide hard block was based on polyimide from 2,2-bis(4-(3,4-dicarboxyphenoxy)phenyl)propane dianhydride (BPADA) and meta-phenylenediamine (*m*-PDA), which displays a T_g at 217 °C [32]. The two polyimides have nearly the same T_g , which is helpful in understanding the influence of crystalline polyimide hard block on the properties of PISs. In addition, the effect of polysiloxane soft block on the crystallization of PISs with crystalline polyimide hard block was also investigated.

2. Experimental

2.1. Materials

Bis(γ -aminopropyl)polydimethylsiloxane (APPS) was synthesized as reported in the literature [7], and the numerical average molecular weight of it determined by means of ¹H NMR spectrum was 995 g/mol. 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA) was purified by sublimation in vacuum. 2,2-Bis(4-(3,4-dicarboxyphenoxy)phenyl) propane dianhydride (BPADA), 1,3-bis(4-aminophenoxy)benzene (TPER) and meta-phenylenediamine (*m*-PDA) were recrystallized from 9/1 ratio of acetic anhydride/toluene, toluene and 9/1 ratio of toluene/cyclohexane, respectively, before use. *N*-Methyl-2-pyrrolidone (NMP) and 1,2-dichlorobenzene (ODCB) were distilled under vacuum over phosphorus pentoxide and stored over 4 Å molecular sieves. Tetrahydrofuran (THF) was refluxed with sodium and benzophenone until the blue color of the ketyl of benzophenone was well established and then was distilled. All other reagents were guaranteed grade and used as received without further purification.

2.2. Measurements

Inherent viscosities of the PISs were measured with an Ubbelohde viscometer at 30 ± 0.1 °C in *m*-cresol at a concentration of 0.5 g/dL. ¹H NMR spectra were performed at 400 MHz on a Bruker 400 AVANCE III in deuterated chloroform (CDCl₃). Fourier transform infrared (FT-IR) spectra of the PIS films were recorded with a Thermo Nicolet 6700 FT-IR spectrometer. The wide-angle X-ray diffraction (WAXRD) measurement of the PIS films was undertaken on a Bruker D8 Advance with Cu K α radiation (40 kV, 40 mA) at a

scanning rate of 5°/min from 5 to 50°. Differential scanning calorimetry (DSC) study was performed on a Mettler Toledo-DSC I under nitrogen atmosphere. The amount of PIS powder utilized in a given thermal scan was kept at 8 ± 0.2 mg. Dynamic mechanical thermal analysis (DMTA) of PIS films (5 mm × 2 cm × 0.05 mm) was conducted with a Mettler Toledo DMA in a tensile mode at a heating rate of 5 °C/min and a frequency of 1 Hz. Thermogravimetric analysis (TGA) was performed in both nitrogen and air atmospheres (flow rate of 50 mL/min) at a heating rate of 10 °C/min from 50 °C to 800 °C with a Mettler Toledo-TGA/DSC I instrument. The morphology of the PIS films were performed on an Olympus BX51 polarized optical microscope (POM). Mechanical properties were measured and averaged on at least six film specimens by an Instron model 5567 tensile tester at room temperature. The specimen gauge length was 50 mm and the specimen width was 10 mm.

2.3. Synthesis of PISs

The synthesis of PIS **I-c** is used below as an example to illustrate the general synthetic route for the preparation of the PISs.

To a solution of BPDA (3.5306 g, 12 mmol) in 30 mL of NMP/THF (1:1), APPS (5.9700 g, 6.0 mmol) and TPER (1.7540 g, 6.0 mmol) were added sequentially under nitrogen flow. The mixture was stirred at room temperature for 12 h to yield a viscous poly(amic acid siloxane) solution. Then ODCB (5 mL) was added and the reaction temperature was raised to 185 °C. After 8 h, the viscous solution was cooled to room temperature, diluted with NMP and trickled into excess ethanol with stirring to afford a precipitate. The precipitate was collected, washed thoroughly with hot ethanol and dried under vacuum at 120 °C for 12 h to give the PIS **I-c**.

The preparation of other PISs was the same as the PIS **I-c**, and their structures were identified by FT-IR and ¹H NMR spectroscopies.

PIS I-a: FT-IR (thin film, cm⁻¹): 2962 (aliphatic C–H stretching), 1774 (asym C=O stretching), 1717 (sym C=O stretching), 1089 (asym Si–O–Si stretching), 1024 (sym Si–O–Si stretching), 801 (Si–C stretching).

PIS I-b: FT-IR (thin film, cm⁻¹): 2962 (aliphatic C–H stretching), 1773 (asym C=O stretching), 1717 (sym C=O stretching), 1089 (asym Si–O–Si stretching), 1027 (sym Si–O–Si stretching), 801 (Si–C stretching).

PIS I-c: FT-IR (thin film, cm⁻¹): 2962 (aliphatic C–H stretching), 1772 (asym C=O stretching), 1716 (sym C=O stretching), 1090 (asym Si–O–Si stretching), 1024 (sym Si–O–Si stretching), 801 (Si–C stretching). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.191 (s, 0.43H), 8.111–8.028 (m, 1.40H), 7.982–7.956 (m, 1.07H), 7.459–7.438 (d, 0.94H, *J* = 8.4 Hz), 7.360–7.320 (t, 0.27H, *J* = 8.0 Hz), 7.186–7.165 (d, 1.0H, *J* = 8.4 Hz), 6.852–6.831 (m, 0.77H), 3.697 (s, 1.0H), 1.715 (s, 1.02H), 0.604–0.563 (m, 0.97H), 0.20–0 (m, 15.48H).

PIS II-a: FT-IR (thin film, cm⁻¹): 2963 (aliphatic C–H stretching), 1776 (asym C=O stretching), 1716 (sym C=O stretching), 1092 (asym Si–O–Si stretching), 1011 (sym Si–O–Si stretching), 801 (Si–C stretching). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 7.915–7.894 (d, 1.14H, *J* = 8.4 Hz), 7.795–7.760 (t, 0.57H, *J* = 7.6 Hz), 7.664 (s, 0.52H), 7.645–7.604 (t, 0.61H, *J* = 8.0 Hz), 7.530–7.510 (d, 1.19H, *J* = 8.0 Hz), 7.447 (s, 1.13H), 7.379–7.314 (m, 4.76H), 7.065–7.010 (m, 3.26H), 3.662–3.627 (m, 1.0H), 1.765 (s, 4.76H), 1.685–1.666 (m, 1.05H), 0.595–0.514 (m, 0.94H), 0.241–0 (m, 15.06H).

PIS II-b: FT-IR (thin film, cm⁻¹): 2963 (aliphatic C–H stretching), 1775 (asym C=O stretching), 1709 (sym C=O stretching), 1090 (asym Si–O–Si stretching), 1020 (sym Si–O–Si stretching), 800 (Si–C stretching). ¹H NMR (400 MHz, CDCl₃, δ , ppm): 7.915–7.895 (d, 0.74H, *J* = 8.0 Hz), 7.796–7.777 (m, 0.57H), 7.668

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