Highly Thermally Resistant and Flexible Polyimide Aerogels Containing Rigid-rod Biphenyl, Benzimidazole, and Triphenylpyridine Moieties: Synthesis and Characterization

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Polyimide (PI) aerogels containing rigid-rod biphenyl, benzimidazole, and triphenylpyridine moieties have been developed. The flexible PI aerogels exhibited excellent thermal stability with glass-transition temperatures (T_g) higher than 350 °C. Initial porous structures in the PI aerogels could be maintained even after isothermal aging at 300 °C for 24 h in nitrogen. Furthermore, the weight losses of the aerogels after isothermal aging at 300 and 400 °C for 24 h in nitrogen were below 5 and 10 wt %, respectively.

Organic aerogels have attracted increasing attention in recent years due to their intrinsic low density, low thermal conductivity, high thermal insulation, and low dielectric constants compared to their inorganic counterparts.¹ Various organic aerogels such as polyurethane, polyurea, polystyrene, aramide, and polydicyclopentadiene have been widely investigated in literature and have found applications in high-tech fields.^{2–6} However, common organic aerogels usually suffer from low thermal and dimensional stability at elevated temperatures; therefore, they cannot meet the severe demands of high-temperature applications such as thermal protective coatings or interlayer thermal insulation systems for microelectronic device fabrications.⁷ In order to prevent thermal deformation of the aerogels in the above applications, high-temperature resistant organic aerogels are highly desired.

Polvimides (PIs) represent an important class of hightemperature resistant polymers and have been widely used in the electronic, microelectronic, and optoelectronic industry owing to their excellent combined thermal, mechanical, and dielectric properties.8 Thus, it can be anticipated that PI aerogels might exhibit good comprehensive properties. Some pioneering work on PI aerogels has been reported very recently.9-13 Several PI aerogels based on aromatic dianhydrides, 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 3,3',4,4'-benzophenontetracarboxylic dianhydride (BTDA), aromatic diamines, paraphenylenediamine (PPD), 4,4'-oxydianline (ODA), bisanilinep-xylidene (BAX), 2,2'-dimethylbenzidine (DMBZ), and multifunctional end-cappers, 1,3,5-tris(4-aminophenyl)benzene (TAPB), 1,3,5-tris(4-aminophenoxy)benzene (TAB), octa(aminophenyl)silsesquioxane (OAPS), have been developed. Experimental results obtained in the above-mentioned reports suggest that PI aerogels derived from flexible dianhydride BTDA, flexible diamine ODA, and TAB crosslinker usually exhibited glass-transition temperatures (T_g) below 280 °C, while their volume shrinkages were as low as 20%.9 Conversely, those derived from rigid dianhydride BPDA, rigid diamine PPD or DMBZ, and TAB showed high T_g values up to 346 °C; however, their volume shrinkages were as high as 48%.9 Thus, it is a challenge to achieve a good balance between the thermal and



Scheme 1. Synthesis of PIA aerogels.

dimensional stability of the PI aerogels at elevated temperatures.

In this communication, we report a series of novel flexible PI aerogels with excellent thermal stability at elevated temperatures. The molecular design, synthesis, and effects of their molecular structures on the properties were investigated.

The aerogels were synthesized based on a well-established route for PI aerogel preparation, as shown in Scheme 1. For this purpose, a triphenylpyridine-containing triamine compound, 2,4,6-tris(4-aminophenyl)pyridine (TAPP) was synthesized first, according to the pathway shown in Scheme S1. According to the pathway, TAPP was obtained in good yields via the catalytic reduction of the nitro compound, 4-(4-nitrophenyl)-2,6-bis(4aminophenyl)pyridine (TNPP) with hydrazine monohydrate and palladium catalysts in refluxing ethanol. TNPP was prepared via a modified Chichibabin reaction with 4-nitroacetophene and 4-nitrobenzaldehyde in the presence of ammonium acetate in glacial acid.¹⁴ The structure of TAPP was confirmed using Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (¹H NMR) spectroscopy, and elemental analysis. The obtained pale-brown crystalline TAPP showed high purity and was used as the end-capper for aerogel synthesis. Then, two PI aerogels, PIA-1 (BPDA/4-APBI/TAPP) and PIA-2 (BPDA/ 3-APBI/TAPP) were prepared by the polycondensation of rigid BPDA dianhydride, rigid benzimidazole-containing diamines, and TAPP, respectively, followed by drying in supercritical carbon dioxide (scCO₂). The detailed synthesis procedure is shown in the Supporting Information.¹⁵ Both APBI and TAPP monomers contain rigid components (benzimidazole or triphenylpyridine segments), which are very beneficial for improving the thermal resistance of the derived PI aerogels.

Table 1. Properties of the PIA aerogels

PI	Porosity ^a	$\sigma^{ m b}$	$ ho_{ m b}{}^{ m c}$	$ ho_{ m s}{}^{ m d}$	d ^e	$T_{5\%}^{f}$	Weight loss after aging for $24 \text{ h}/\%$			
	/% void	$/m^2 g^{-1}$	$/\mathrm{g}\mathrm{cm}^{-3}$	$/\mathrm{g}\mathrm{cm}^{-3}$	/nm	/°C	300 °C	400 °C	450 °C	500 °C
PIA-1	85.9	204	0.21	1.51	18.2	542	2.7	2.9	8.5	21.3
PIA-2	92.3	251	0.11	1.47	40.5	541	3.1	5.2	9.2	29.9

^aCalculated by $1 - (\rho_b/\rho_s)$. ^bBrunauer–Emmett–Teller surface area. ^cBulk density. ^dSkeletal density. ^eAverage pore diameter from the BJH desorption plot. ^fTemperature at 5% weight loss.



Figure 1. SEM images of PI aerogels. (A) PIA-1 and (B) PIA-2.

The chemical structures of the PIA samples were identified by FTIR measurements, illustrated in Figure S1. The characteristic absorption bands due to the vibration of the carbonyl groups in the imide segments are clearly observed at 1776 and 1722 cm⁻¹, which are assigned to the asymmetric and symmetric stretching vibrations, respectively. In addition, the stretching vibration of the C–N bond located at 1375 cm⁻¹ and the imide ring deformation at 721 cm⁻¹ further confirm the formation of polyimide. The absence of an absorption band around 1860 cm⁻¹ indicated the complete reaction of the dianhydride. Similarly, the absence of absorption bands around 3500 (v_{N-H}) and 1640 cm⁻¹($v_{amide,C=0}$) indicated the completion of the reaction of the diamines and the successful conversion from the poly(amic acid) (PAA) precursors to PIs.

Then, the influences of the rigid molecular structures of the PI aerogels on their properties, including density, porosity, surface area, volume shrinkage, and thermal and mechanical properties were investigated in detail. First, a field emission scanning electron microscopy (FESEM) measurement was performed to investigate the morphology of the PI aerogels, as shown in Figure 1. For both the polymers, we observed an openpore structure consisting of three-dimensional networks of tangled nanofibers, with nanoscale diameters. This three-dimensional networked microstructure results from the highly cross-linked molecular chains in the aerogels. The solvents present in the networks were continuously extracted by the solvent-exchange process, followed by supercritical drying procedures, leaving nanopores in the final aerogels.

The porous structures of the current PI aerogels can be further probed by N₂ adsorption and desorption isotherm plots, measured by the Brunauer–Emmett–Teller (BET) method (Figure S2). It can be seen from the plots that both isotherms show a rapid increase in adsorbed volumes at relative pressures above 0.9, which in combination with a narrow desorption loop indicates the existence of both meso- and macroporous structures in the PIAs. Meanwhile, both isotherms showed an early rise in the adsorbed volumes ($P/P_0 < 0.1$), indicating the microporous structure of the aerogels. This porous structure of varying sizes is further confirmed by the pore size distribution



Figure 2. Stress-strain curves of PIA aerogels (Insert: appearance of PIA-1).

measurements according to the Barrett–Joyner–Halenda (BJH) method (Figure S2, insets). According to the BJH plots, both the aerogels had nanopores with sizes in the range of several to one hundred nanometers. The average pore diameters of the aerogels are 18.2 nm for PIA-1 and 40.5 nm for PIA-2 (Table 1). From the BET measurements, the surface areas (σ) of PIA are determined to be 204 m² g⁻¹ for PIA-1 and 251 m² g⁻¹ for PIA-2. The bulk densities (ρ_b) of the PI aerogels, determined by mercury intrusion porosimetry, were 0.21 and 0.11 g cm⁻³, respectively. The porosities of the aerogels calculated from the density values were 85.9% for PIA-1 and 92.3% for PIA-2. Owing to the more bulky molecular packing in PIA-2, caused by the meta-substituted molecular structures, PIA-2 exhibited lower bulky density and higher porosity values.

The stress-strain curves obtained from the compression tests for the PI aerogels are shown in Figure 2. The appearance of a thin sheet of PIA-1 is shown in the inset. The curves exhibited linear elastic regions below 10% strain and yielded in a relatively low slope. Young's modulus of PI aerogels is 9.32 MPa for PIA-1 and 2.38 MPa for PIA-2, indicating good flexibility and tough nature of the polymers. The inset picture shows that PIA-1 aerogel can be folded without visible cracks. The good flexibility of the current PI aerogels is very beneficial for their utility in high-tech applications.

Thermal properties of the PI aerogels were evaluated by thermogravimetric analyses (TGA), thermomechanical analyses (TMA), and isothermal aging measurements. TGA measurements of the PI aerogels were performed in nitrogen from 50 to 750 °C, and the results are shown in Figure S3. From the plots, it can be observed that both aerogels showed good thermal stability up to 400 °C, and they began decomposing at temperatures greater than 450 °C. The smooth plots around 300 °C indicated the complete removal of residual NMP solvent by the supercritical drying procedure and the complete imidization in the systems. The 5% weight loss temperatures ($T_{5\%}$) are 542 °C for PIA-1 and 541 °C for PIA-2. The char yields of both aerogels



Figure 3. TMA curves of PIA aerogels.

exceed 70% in nitrogen, which indicated the good thermal stability of PIAs.

Changes in aerogel dimensions are investigated by TMA measurements, as depicted in Figure 3. The aerogels showed different dimension change behaviors at elevated temperatures. PIA-2 shrunk sharply when the temperature exceeded its glass-transition temperature (T_g); however, PIA-1 showed expansion behavior beyond the T_g . The plots revealed the T_g values to be 360 °C for PIA-1 and 356 °C for PIA-2. Owing to the more symmetric molecular structure of PIA-1, it exhibited a slightly higher T_g value, compared to PIA-2. Nonetheless, both PI aerogels showed good dimensional stability and thermal stability. This is mainly due to the presence of rigid-rod substituents in the aerogels.

The thermal stability of the PI aerogels was further determined by isothermal aging measurements carried out at four different temperatures (300, 400, 450, and 500 °C) in nitrogen for 24 h. Graphs of weight retention versus aging time of both aerogels are shown in Figure 4, and the data are tabulated in Table 1. PIA-1 showed weight loss values of 2.7% at 300 °C, 2.9% at 400 °C, 8.5% at 450 °C, and 21.3% at 500 °C. indicating good thermal stability of the polymer below 400 °C. However, the corresponding thermal loss data of PIA-2 at those specific aging temperatures are all greater than those observed for PIA-1. This is mainly due to the more rigid molecular structure of PIA-1. The SEM images of PIA-1 and PIA-2 after heating at 300 °C for 24 h showed little change. However, after aging for 24 h at 450 °C, the mesoporous structures of the PIA-1 aerogel partly collapsed; in contrast, the porous structure of PIA-2 was completely destroyed. This also reflects the higher thermal stability of PIA-1 compared to its analog PIA-2.

In Table 1, we summarize the properties of PIA aerogels.

In summary, rigid-rod biphenyl, benzimidazole, and triphenylpyridine moieties endow polyimide aerogels with excellent thermal stability ($T_g > 350$ °C). The mesoporous structures could retain their initial morphology even after heating at 300 °C for 24 h, and the weight losses for both aerogels after aging for 24 h at 450 °C were lower than 10 wt %.

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References and Notes

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Figure 4. Isothermal thermal aging plots of PIA aerogels. (a) PIA-1; (b) PIA-2 (Inset: SEM images of PIA aerogels after aging at 300 and 400 °C for 24 h. The scale number is 200 nm).

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