

ORIGINAL ARTICLE

A green and scalable method for producing high-performance polyimide aerogels using low-boiling-point solvents and sublimation drying

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Polymeric aerogels have great potential in numerous fields because of their unique combination of thermal and electrical properties, and lightweight porous structures. However, the laborious supercritical CO₂ drying method required for making these aerogels limits their commercial availability. Here we demonstrate a green and scalable method for preparing high-performance polyimide (PI) aerogels using a low-boiling-point solvent mixture of tetrahydrofuran/methanol, and especially using sublimation drying instead of laborious supercritical CO₂ drying. The monolithic and powder polyamic acid aerogels can be prepared easily; after thermal imidization, PI aerogels with nanofibrous morphology, low density and high thermal stability can be obtained. This green, scalable and cost-effective process will facilitate the application of high-performance PI aerogel materials in many fields, in particular those in which high-temperature resistance is important.

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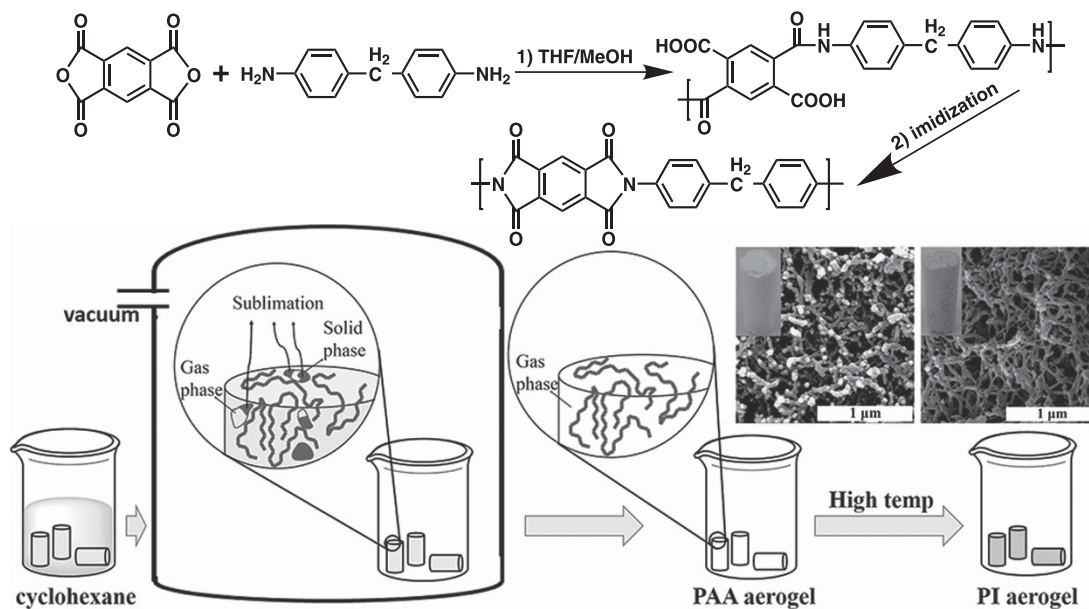
INTRODUCTION

Aerogels are a type of porous materials that are prepared by replacing the solvent in wet gels with air.¹ Organic polymeric aerogels combine low density, high porosity, low thermal conductivity and some other interesting properties, and they have attracted great attention in recent decades.^{2–4} Many researchers have been focused on resorcinol-formaldehyde resin,⁵ polyurethane,⁶ cellulose⁷ and polyimide (PI)⁸ organic polymeric aerogels. In general, polymeric aerogels are prepared from wet gels, which are full of solvent. The preparation of wet gels is generally very easy; however, the drying process is a tough task. If the solvent in the wet gels is evaporated into the air directly, the final aerogels will shrink because of the large capillary forces generated during the drying process at the liquid–vapor interface. The most effective method for solving this problem is supercritical CO₂ drying, which can eliminate these capillary forces. However, the extreme conditions needed to meet the supercritical point of CO₂ make the subsequent drying time consuming, expensive and dangerous;⁹ thus, until now, large-scale commercialized polymeric aerogels have still not been available. Alternative methods such as freeze drying and ambient pressure drying have been explored.^{10,11} The freeze-drying method transforms the liquid–vapor interface into a solid–vapor interface to eliminate the surface tension using a relatively low temperature. However, the ice may destroy the networks and the drying time is usually very long because of the low vapor pressure of ice.^{12,13} Recently, Ren *et al.*¹⁴ proposed a novel strategy for the preparation of inorganic oxide aerogels using tert-butanol as the exchange solvent. Tert-butanol has a low surface tension with a high freezing temperature (25.5 °C) and undergoes sublimation easily, thus allowing the

rapid synthesis of monolithic inorganic oxide aerogels under vacuum conditions. However, until now, this method has been limited to preparing inorganic oxide aerogels and extending this novel strategy to the preparation of organic polymeric aerogels should be of great value.

In addition to the laborious and tedious drying process, another weakness of polymeric aerogels is that most of them show relatively low thermal and dimensional stability at high temperatures. Thus, they cannot be used for some high-temperature applications such as entry, descent and landing systems.¹⁵ In these cases, high-temperature-resistant organic polymeric aerogels are needed. PI is a type of high-performance polymer with excellent thermal stability and some PI aerogels have been reported.^{8,16,17} In general, high-boiling-point solvents such as *N,N*-dimethylformamide, *N,N*-dimethylacetamide and *N*-methyl-2-pyrrolidone are commonly used to prepare the polyamic acid (PAA) precursor, followed by chemical imidization using acetic anhydride and pyridine to transform into PI gels. Most of these high-boiling-point solvents are very difficult to recycle and thus become an environmental pollution. In addition, all PI aerogels are obtained through dangerous and laborious supercritical CO₂ drying. Very recently, Han reported the fabrication of PI aerogel microparticles via a simple method that did not use the CO₂ supercritical extraction method.¹⁸ However, during this solvothermal process, high-pressure autoclaves are needed. Thus, the development of a new drying technique to shorten the aerogel production time and reduce its production costs would be highly valuable for the commercialization of high-performance PI aerogels.

Here we report on the green and scalable fabrication of high-performance PI aerogels using low-boiling-point solvents and novel



Scheme 1 The preparation of PAA aerogel and PI aerogels using low-boiling-point solvents and a novel sublimation drying process. A full color version of this figure is available at *Polymer Journal* online.

sublimation drying. This novel process is based on a unique phenomenon that we observed during our research. We found that a PAA precursor prepared from pyromellitic dianhydride (PMDA) and 4,4'-diaminodiphenyl methane (DDM) can gelate easily in mixed solvents composed of tetrahydrofuran (THF) and methanol with a mass ratio of 4:1, and result in a transparent and tough PAA wet gel, whereas monomer components other than PMDA–DDM do not gelate and only result in a viscous solution.¹⁹ When the transparent PAA wet gel is immersed in acetone to exchange the solvents, phase separation occurs and results in an opaque white PAA gel. To avoid laborious supercritical CO₂ drying after solvent exchange by acetone, the PAA gel is further subjected to solvent exchange by cyclohexane. Cyclohexane was chosen, primarily because it has a relatively high freezing temperature (6 °C) and high vapor pressure (13 kPa at 25.0 °C), which makes it easy to freeze and sublimate rapidly under vacuum conditions.^{20,21} PAA aerogels are obtained through the novel vacuum sublimation drying method. Finally, monolithic and powder-like PI aerogels were easily prepared through high-temperature imidization without obvious collapse. Thus, it is possible to create a green, scalable and cost-effective process for the preparation of high-performance PI aerogel materials that have great potential applications in many fields in which high-temperature resistance is of essential importance.

EXPERIMENTAL PROCEDURE

Materials

PMDA and DDM were purchased from Aladdin Chemical Corporation (Shanghai, China) and were used as received. Methanol, THF, acetone, hexane and other solvents were all purchased from Chengdu Kelong Chemical Reagent Co. (Chengdu, China) and were used without further purification.

Preparation of PI aerogel

A typical process for preparing PAA precursor aerogel and PI aerogels is shown in Scheme 1. DDM was dissolved in the 80/20 wt% THF and methanol mixture, a stoichiometric amount of PMDA was added and the total weight of the precursors in solution was formulated to be 10 wt%. The mixture was stirred for 2 h and yielded a transparent homogeneous PAA solution. The PAA solution was then poured into plastic molds and sealed, and the solutions were allowed to stand for 1–4 days, during which time the viscous solution gradually gelled

and formed tough and transparent PAA wet gels. Next, the PAA wet gels were taken out and soaked in acetone for 1 day and they became white and opaque. The wet gels were exchanged with acetone every 6 h for 1 day to remove the THF and methanol. Solvent exchange was continued with cyclohexane every 6 h for 2 days, to fill the PAA wet gels with cyclohexane. The wet gels were then placed in a beaker and dried at ~10 °C under a vacuum to yield white PAA aerogels. The PAA aerogels were heated at 100 °C for 2 h, 200 °C for 2 h and finally 300 °C for 1 h, to complete the imidization and create yellow PI aerogels.

Characterizations

Fourier transform–infrared spectra were measured using a Nicolet 560 spectrometer (Nicolet Instrument Technologies, Madison, WI, USA). Solid-state nuclear magnetic resonance (¹³C-NMR) spectra were recorded on a Bruker Avance III 500 MHz (Bruker, Ettlingen, Germany) with a standard 4-mm Bruker MAS Probe (Bruker Biospin GmbH, Rheinstetten, Germany) at a sample spinning rate of 8.0 KHz. Scanning electron microscopy (SEM) was conducted with an Inspect F SEM (FEI, Eindhoven, The Netherlands) at an accelerating voltage of 20 kV. Nitrogen adsorption and desorption isotherms were measured at 77 K using a Tristar system (Micromeritics, Norcross, GA, USA). The sample was degassed at 150 °C for 10 h before the measurement. The surface area was calculated from the adsorption data by Brunauer–Emmett–Teller (BET) method. The thermal properties were measured using thermo gravimetric analysis instruments (SDT Q600) (TA Instruments, Melbourne, VIC, Australia) over a temperature range of 30 °C to 800 °C with a heating rate of 10 °C min⁻¹.

RESULTS AND DISCUSSION

Figure 1 shows the preparation of PI aerogels. The dianhydride PMDA was reacted with diamine DDM in a THF/methanol mixture of solvents and formed a homogeneous viscous PAA precursor solution. After standing for a dozen hours, the viscous solution gradually transformed into a faint yellow, transparent PAA wet gel that could stand by itself, indicating that the PAA wet gel is strong (Figure 1a). We found that PAA precursors that are prepared from monomer components other than PMDA–DDM do not gelate but only result in a viscous solution. This unusual PAA wet gel may be attributed to the delicate balance between the interchain PAA hydrogen-bonding interaction and PAA–solvent interaction. When the THF and methanol in the wet gel are exchanged for acetone and cyclohexane, the

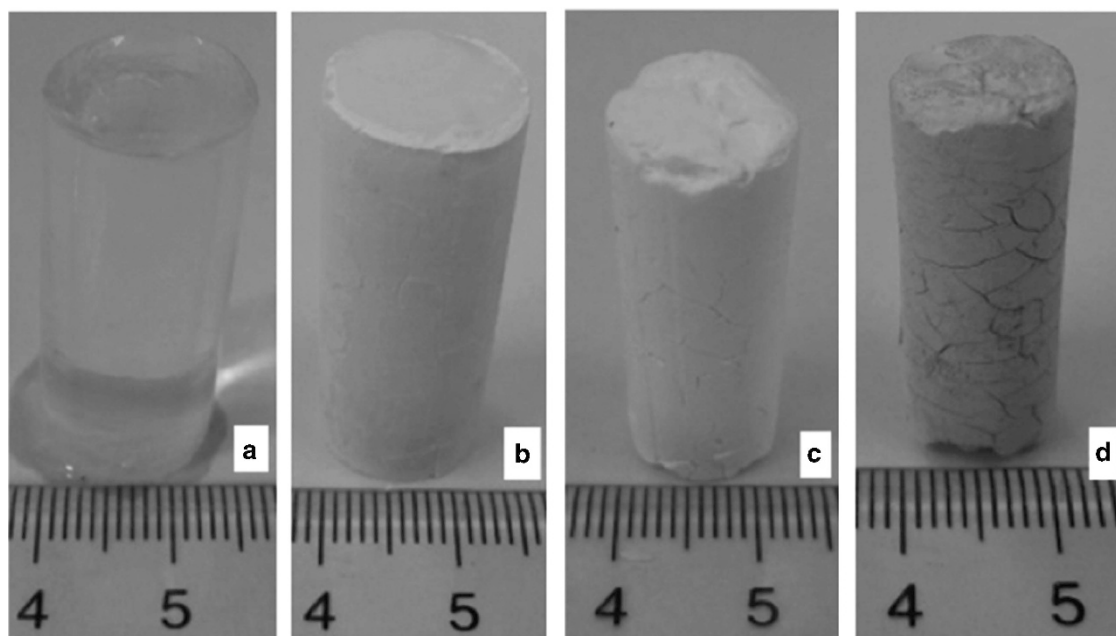


Figure 1 (a) PAA wet gel containing THF and methanol; (b) PAA wet gel exchanged by cyclohexane, (c) PAA aerogel and (d) PI aerogel. A full color version of this figure is available at *Polymer Journal* online.

Table 1 Physical properties of PAA and PI aerogel

Gel Time (days)	1	2	3	4
PAA wet gel (cm ³)	1.39	1.37	1.47	1.46
PAA aerogel (cm ³)	0.97	0.96	1.03	0.99
PAA aerogel (g cm ⁻³)	0.130	0.130	0.125	0.131
PI aerogel (cm ³)	0.61	0.59	0.58	0.55
PI aerogel (mg)	107	106	107	109
PI aerogel (g cm ⁻³)	0.175	0.180	0.184	0.198
BET of PI aerogel (m ² g ⁻¹)	22	44	84	116

Abbreviations: BET, Brunauer–Emmett–Teller; PAA, polyamic acid; PI, polyimide.

transparent wet gel becomes opaque and rigid. The rapid evaporation of cyclohexane in the air makes the wet gel whiten slightly on the surface (Figure 1b). Next, the wet gel is placed in a beaker and dried under a vacuum. The freezing point of cyclohexane is $\sim 6^\circ\text{C}$ and the saturated vapor pressure is 13 kPa (at 25.0°C). Under vacuum drying, the cyclohexane evaporates quickly and the rapid endothermic evaporation of the solvent leads to a dramatic decrease in the temperature and causes a portion of the cyclohexane to become solid. The solidified solvent sublimates to gas and the endothermic sublimation makes more cyclohexane become solid. The continuous changes in the three phases prevent capillary force, which is the primary culprit in the collapse of micropores during the liquid–gas conversion during the traditional drying processes, and a white PAA aerogel was obtained (Figure 1c). The volume shrinkage of the aerogel is not obvious and the aerogel does not break into pieces during the drying process. Finally, the PAA aerogel was put into a high-temperature oven under an N_2 atmosphere to yield PI aerogel. Figure 1d shows that the yellow PI aerogel yields an intact shape and little shrinkage.

As shown in Table 1, some degree of shrinkage occurred when the wet gels were vacuum dried, to afford PAA aerogel, and after imidization, to afford PI aerogels. The densities of the PAA aerogels

are $\sim 0.13\text{ g cm}^{-3}$; these densities are relatively low, because the cyclohexane sublimation drying process prevents the collapse caused by capillary force, accounting for the fact that the PAA aerogels were prepared by direct vacuum sublimation drying instead of laborious supercritical CO_2 drying; such low density is rarely reported. After imidization, the densities of the PI aerogels slightly increase to $\sim 0.175\text{ g cm}^{-3}$.

The successful preparation of PAA precursor and PI aerogels was confirmed by Fourier transform–infrared and solid-state ^{13}C -NMR. The Fourier transform–infrared spectra of PAA and PI aerogels are shown in Figure 2. The stretching vibration of N–H in PAA aerogels can be observed at 3428 cm^{-1} . The broad peak at $3300\text{--}2600\text{ cm}^{-1}$ is the stretching vibration of O–H in the carboxyl group and the stretching vibration of C=O can be observed at 1715 cm^{-1} . The absorption peak at 2916 cm^{-1} belongs to the methylene groups in DDM. The characteristic band at 1651 cm^{-1} belongs to the C=O in $-\text{NH}-\text{CO}-$. After high-temperature imidization, the aerogels exhibit characteristic peaks at 1777 and 1724 cm^{-1} , which are attributed to the symmetric and asymmetric vibrations of the C=O group in the five-membered imide ring. The stretching vibration of N–C–N can be observed at 1371 cm^{-1} . In solid-state ^{13}C -NMR spectra, this aerogel exhibits an apparent peak at $\sim 168\text{ p.p.m.}$, which is the characteristic peak of the carbonyl carbon in the five-membered imide ring. A series of peaks from 122 to 140 p.p.m. belong to the aromatic carbons in PMDA and DDM. In addition, the characteristic peak of the methylene carbon in DDM can be seen at 45 p.p.m.

This novel process is based on the unique gelation phenomenon of PMDA/DDM PAA precursors in THF/methanol solvent, and thus the gelling time might be an important issue for the properties of the final aerogel. As shown in Figure 3, the SEM image revealed that the aerogel morphology for PAA aerogel that gelled over 1 day yields some short and thick irregular sticks that are composed of agglomerated nanoparticles (Figure 3a). When extending the gelling time to 2–4 days (Figure 3b–d), the morphology becomes remarkably different. The SEM image clearly revealed many nanofibers tangled

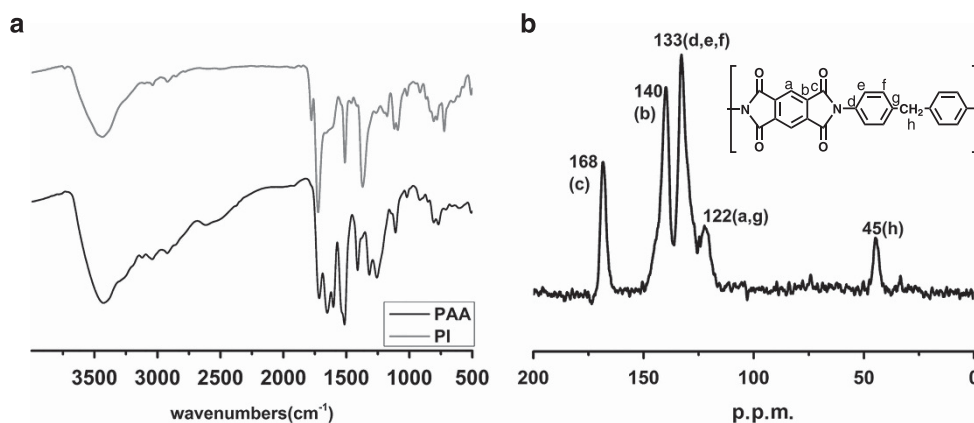


Figure 2 (a) Fourier transform–infrared spectra of PAA and PI aerogel and (b) solid-state ^{13}C -NMR spectra of the PI aerogel. A full color version of this figure is available at *Polymer Journal* online.

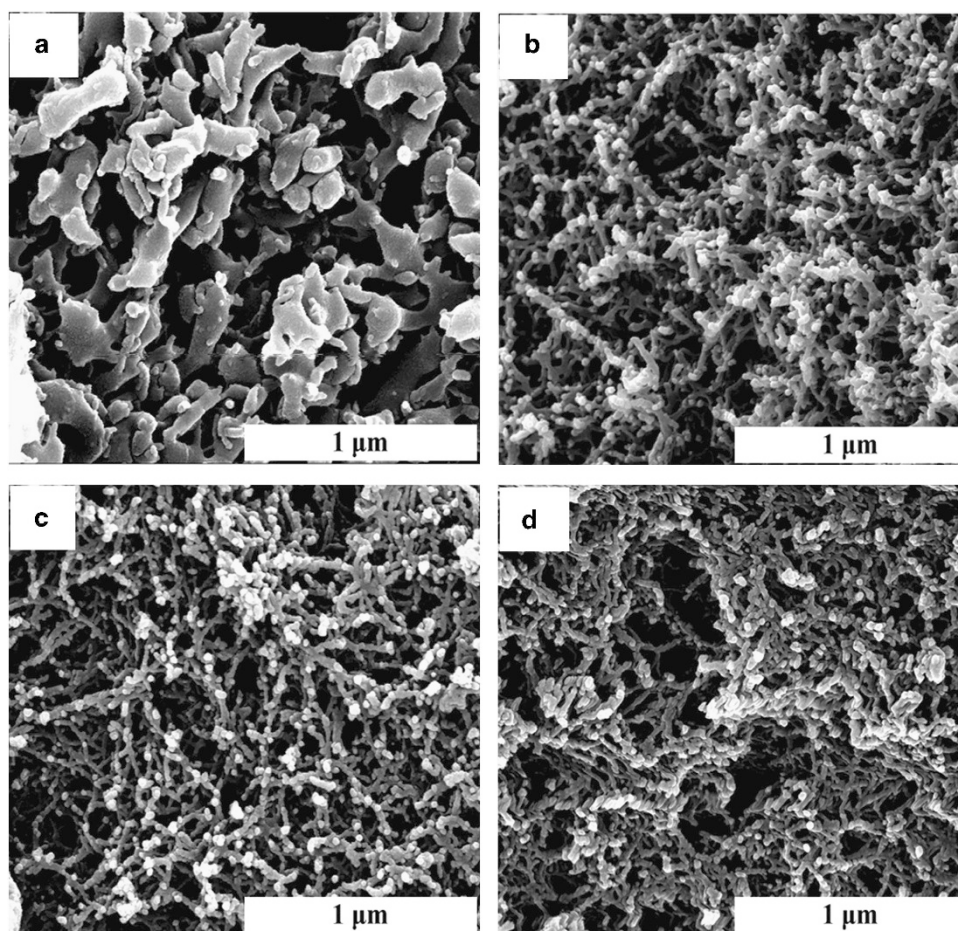


Figure 3 SEM images of PAA aerogels after sublimation drying of the gels for periods of (a) 1, (b) 2, (c) 3 and (d) 4 days.

together, which is a typical morphology for polymeric aerogels. The distribution of the nanofibers is homogeneous with abundant pores among them. These characteristics indicate that the morphology tends to involve nanofibers and the cyclohexane sublimation dry process with increasing gelling time, and these factors prevent the capillary force that maintains homogeneous nanofiber distribution.

PAA precursor aerogels were transformed into PI aerogels through high-temperature imidization. Figure 4 shows the SEM images of the

PI aerogels. The morphology is similar to that of the PAA aerogels after undergoing extended high-temperature imidization and it is clear that this high temperature has little effect on the gel morphology. This finding indicates great thermal resistance. The thin nanofiber morphology is the same as that reported for PI aerogels that were prepared by the laborious supercritical CO_2 drying process.^{8,16,17,22,23}

The pore structures of the resulting PI aerogels were determined by N_2 adsorption–desorption isotherms. All the isotherms of the PI

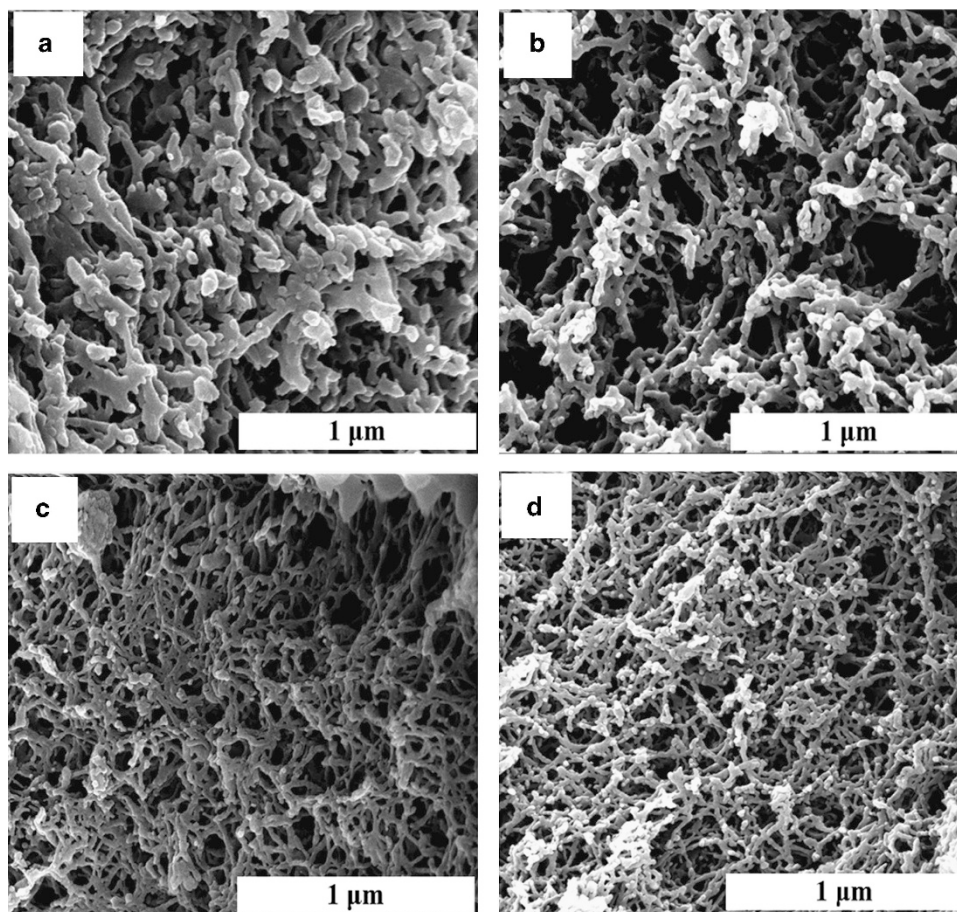


Figure 4 SEM images of fully imidized PI aerogels with precursors that were gelled for periods of (a) 1, (b) 2, (c) 3 and (d) 4 days.

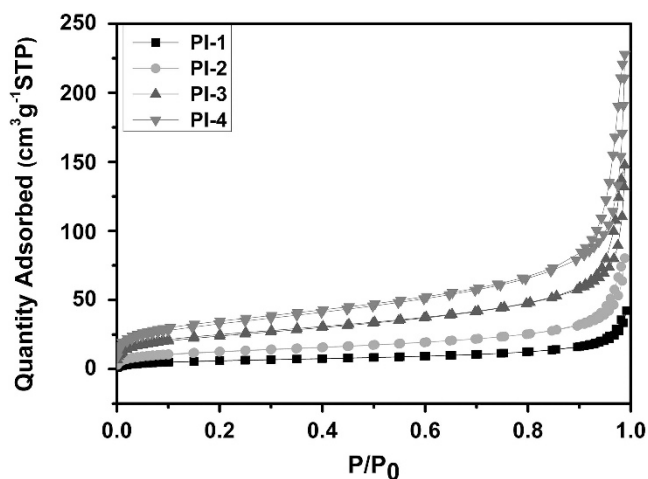


Figure 5 N_2 adsorption-desorption isotherms of fully imidized PI aerogels with precursors gelled for periods of (PI-1) 1, (PI-2) 2, (PI-3) 3 and (PI-4) 4 days. A full color version of this figure is available at *Polymer Journal* online.

aerogels are type IV curves, which indicate that they were mesoporous. When the relative pressure is high ($P/P_0 > 0.8$), the isotherms rise sharply because of the capillary condensation of N_2 in the mesopores. The hysteresis loops in the isotherms of PI-3 and PI-4 are a consequence of the different pressures at which capillary condensation

and capillary evaporation take place.²⁴ BET surface areas seem to depend on the gelling time. With increasing time, the BET surface areas increase from 22 to 116 g cm^{-3} . As shown in Figure 3e-h, and consistent with the last BET surface areas, the nanofibers tangled with one another to make the pores much smaller than the result for short and thick irregular sticks, and thus the BET surface areas increase. However, the numbers are still relatively low, primarily because there are few micropores in the aerogels, which contributes the most to the BET surface areas.

In addition to monolithic aerogels, aerogel powders may be more suitable for thermal insulation applications. Thus, we extended this novel strategy further to the preparation of high-performance PI aerogel powders. Figure 5 shows the process for preparing PI aerogel powders, which is similar to the process used for the monoliths. Homogeneous viscous PAA solution (Figure 6) would gradually become wet gel and then acetone was added to the wet gel with strong stirring to make the gel into powder; phase separation occurred and led to a white and opaque PAA wet gel. After further exchange with cyclohexane and vacuum drying, PAA aerogel powders were easily obtained. Thermal treatment at $300 \text{ }^\circ\text{C}$ resulted in fully imidized PI aerogel powders. The SEM images of the PAA and PI aerogels show the same homogeneous nanofibers as the monolith aerogels.

Along with the severe demands of some special applications, the thermal stability of the aerogels has become one of the most important indexes. PI is a high-performance material with great thermal properties. The thermal stability of the PI aerogels is measured from

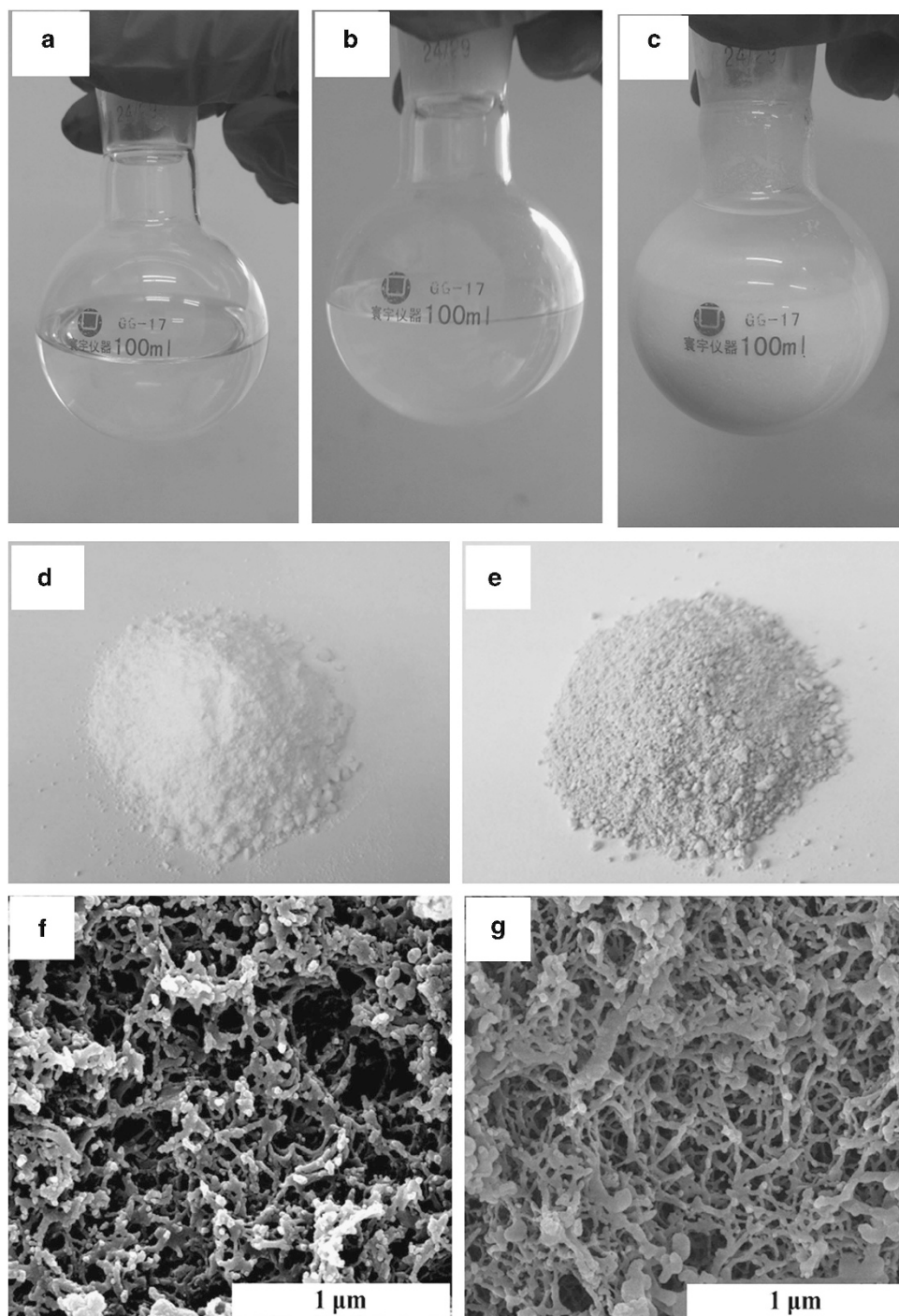


Figure 6 (a) PAA solution in THF/methanol mixture. (b) PAA wet gel full of THF/methanol mixture. (c) PAA wet gel exchanged by acetone and cyclohexane. (d) PAA aerogel. (e) PI aerogel. (f) SEM image of PAA aerogel. (g) SEM image of PI aerogel. A full color version of this figure is available at *Polymer Journal* online.

room temperature to 800 °C and the curves are shown in Figure 7. The decomposition temperatures of the aerogels are all above 500 °C, indicating that the imidization is complete and they all have excellent thermal resistance. The PI aerogel is maintained under an N₂ atmosphere at 300 °C for 3 h; the nanofibers of the gel remain intact and the morphology is the same as that of the original. The PI aerogels can clearly meet stringent demands and they have great potential for use in various applications.

CONCLUSIONS

In conclusion, high-performance PI aerogels were prepared easily in a THF/methanol solvent mixture through vacuum sublimation drying. The THF/methanol mixture makes it easy to perform solvent exchange and the relatively high freezing point and vapor pressure of cyclohexane led to fast solidification and sublimation under vacuum conditions, which can prevent the widely used laborious and dangerous supercritical CO₂ drying process. Using a similar

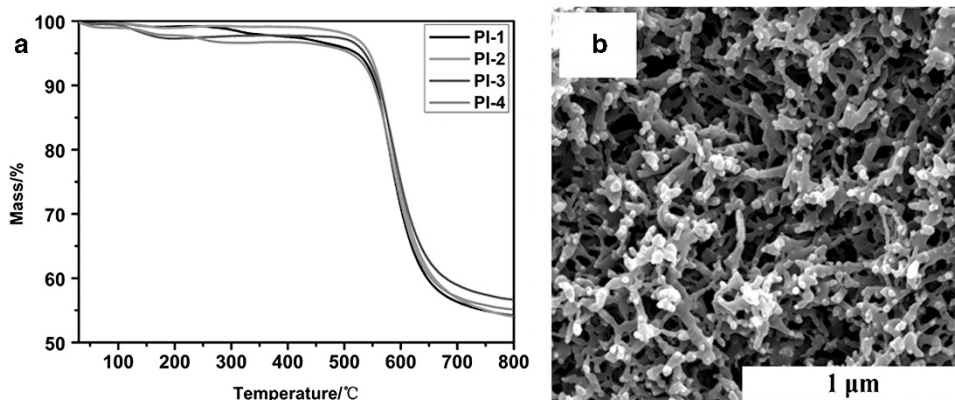


Figure 7 (a) Thermo gravimetric analysis curves of the PI aerogels over a temperature range from 30 °C to 800 °C. (b) An SEM image of the PI aerogel after treatment at 300 °C for 3 h. A full color version of this figure is available at *Polymer Journal* online.

technology, PI aerogel powders can also be prepared. This green, scalable and cost-effective process for preparing monolithic and powder PI aerogels with nanofibrous morphology, low density and high thermal stability will certainly facilitate their applications in many fields, especially in those in which high-temperature resistance is of essential importance.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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