Aerogels of hierarchically porous syndiotactic polystyrene with a dielectric constant near to air†

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Herein ultralow density aerogels are developed through a feasible freeze casting technique. Briefly, the syndiotactic polystyrene (sPS) gel was prepared using xylene and subjected to successive steps of solvent exchange using non-solvents like ethanol and water. These samples were freeze-dried to obtain aerogels of the same shape and size as gels. The aerogels obtained exhibited the lowest ever dielectric constant of any polymer aerogel ($\varepsilon = 1.03 \pm 0.02$), which is very close to that of air. Moreover, while analyzing the crystal structure, it was observed that the water derived sPS aerogel existed in the empty $\delta$ ($\delta_0$) form, with microcavities in the crystal lattice in addition to meso and macroporosity. However, annealing at different temperatures yielded aerogels with different polymorphic forms without microporosity leading to slight variations in the dielectric constant. The microporosity in the crystalline state along with the lower density of the material were proven to be the major contributing factors to the lowest ever reported dielectric constant of the sPS aerogel. The sPS aerogels with an ultra low dielectric constant, very high hydrophobicity and adequate mechanical strength can stand as an alternative to conventional brittle inorganic aerogels.

Introduction

The three-dimensional structures of conventional inorganic aerogels, e.g. silica aerogels, prepared by sol–gel techniques are a “pearl necklace” structure, the necks of which are formed by the Si–O–Si bonds. These weak bonds are responsible for their fragility, which is the main bottleneck of this otherwise wonder material. Later organic–inorganic hybrid aerogels and polymer reinforced aerogels were introduced, and aimed to overcome the drawbacks of pure silica-based aerogels. Organic aerogels were prepared for the first time by Pekala via the polycondensation of resorcinol and formaldehyde followed by supercritical drying. The extremely low thermal conductivity and high porosity of these mechanically more stable aerogels paved the way for intense research in the area of polymer-based aerogels.

Later a number of semicrystalline polymers such as syndiotactic polystyrene, isotactic polypropylene, polyethylene, poly(vinylidene fluoride), etc., were found to form thermoreversible gels where the gel network is formed by the crystalline regions (physical bonding) instead of the covalent bonds. Polymeric aerogels with ample mechanical strength whose density and porosity are comparable to the traditional inorganic aerogels promoted the utilization of porous scaffolds in diverse fields like thermal and acoustic insulation, capacitors, oil adsorbents, etc.

Syndiotactic polystyrene (sPS) and polyimide (PI) stand out as the most studied polymer aerogels in the literature, although lots of gel-forming polymers that can be converted into porous structures through supercritical drying or freeze drying are known. sPS is a commercially available semicrystalline engineering thermoplastic polymer which has been proven to form thermoreversible gels using a variety of solvents including chloroform, benzene, toluene, etc. Guerra and co-workers demonstrated the first example of physically bonded aerogels of sPS using a supercritical drying process. Jana and co-workers studied the various structural and morphological aspects of sPS and sulfonated sPS aerogels prepared via a supercritical drying process, and demonstrated their usability in diverse applications like oil adsorption, air filtration etc. Meador and co-workers developed a series of PI-based aerogels whose thermal, mechanical and dielectric properties were investigated systematically. They have also demonstrated the possibility of using the ultra low dielectric constant flexible polyimide aerogels as substrates for the antenna
which can be employed in spacecrafts as an alternative to heavy substrates.\textsuperscript{26}

sPS is well known for the formation of different polymorphic forms in the presence of external stimuli like temperature and solvent environment.\textsuperscript{37–39} sPS gels which contain organic solvent molecules or other guest molecules exist in the (T\textsubscript{C}G\textsubscript{2})\textsubscript{1} helical conformation (the δ form).\textsuperscript{18,31,32} Removal of these guest moieties from the crystalline phase of sPS through supercritical drying results in a porous scaffold with ordered microporosity (less than 2 nm) inside the crystalline cavities along with the disordered mesopores (2–50 nm) and macropores (greater than 50 nm) typical of all aerogels.\textsuperscript{18,33} Generally, sPS aerogels exhibit a fibrillar network morphology with the physical knots of sPS being formed by the microporous crystalline regions,\textsuperscript{34–36} whereas the amorphous tie chains of the semicrystalline polymer help to establish the network structure.\textsuperscript{37,38} Depending on the solvents used for gel formation, the δ form sPS gels can be converted to either the microporous δ form (δ\textsubscript{C}) or the ε form, and by adjusting the temperature and pressure conditions of supercritical drying γ and β form aerogels can also be obtained.\textsuperscript{34,39–42}

Inspired by the above literature, we have attempted to prepare sPS aerogels through a meticulously designed preparation route. Here sPS gels are developed using xylene as the solvent followed by a freeze-drying technique. Freeze-drying has several advantages for the preparation of aerogels over other techniques such as supercritical drying since it is a simple, cost-effective and widely available technique. There is no size limitation for the sample and the use of supercritical fluids is eliminated. We used ethanol and water for the solvent exchange before carrying out the freeze drying and the method is easily scalable and environmentally friendly. The phase formations of the sPS aerogels formed from the gels of different solvents and the phase transformations of the samples annealed at different temperatures were investigated systematically with the help of WAXD. Similarly to supercritical drying, the new procedure adopted here also resulted in the δ type aerogel\textsuperscript{18} and these samples show an impressive and consistent ultra low dielectric constant as low as 1.03 ± 0.02, very close to the value of air.

### Experimental section

#### Materials

The sPS pellets (\(M_\text{w} \sim 272\ 000\) and \(D \sim 2.28\)) used in this study were generously supplied by Idemitsu Petrochemical Co., Ltd (Japan). The xylene (a mixture of isomers) used for the gel preparation was purchased from Merck, India and used without any further purification. Ethanol received from S.D. Fine chemicals and distilled water were used for the solvent exchange.

#### sPS gel and aerogel preparation

For the gel preparation, sPS was first dissolved in xylene above its boiling point until complete dissolution of the polymer. The solution was then cooled to room temperature in suitable plastic moulds. Two sets of samples were made, one with \(C_{\text{pol}} = 0.03\ g\ g^{\text{-1}}\) (polymer to xylene ratio) and the other with \(C_{\text{pol}} = 0.06\ g\ g^{\text{-1}}\). The gels obtained at room temperature were kept for 4 hours for aging followed by a systematic solvent exchange with ethanol and water. In order to exchange xylene with water, the solvent exchange was initially performed with ethanol, then with an ethanol–water mixture of different concentrations and finally with water. The gels with final solvents of either ethanol or water were kept for freezing at \(-60\ °C\) for 12 hours and then volatilized. The different samples developed will be named hereafter as sPS\textsubscript{exh} (aerogel formed from a gel with ethanol as the solvent), sPS\textsubscript{0.03x} (aerogel formed from a gel with a polymer to xylene ratio 0.03 g g\textsuperscript{-1} with water in the porous network after solvent exchange) and sPS\textsubscript{0.06x} (aerogel formed from a gel with a polymer to xylene ratio 0.06 g g\textsuperscript{-1} with water in the porous network after solvent exchange).

#### Characterization

The total porosity of the various samples was estimated using the following equation

\[
P = 100 \left(1 - \frac{\rho_{\text{app}}}{\rho_{\text{poly}}}ight)
\]

where \(\rho_{\text{app}}\) is the apparent density calculated from the mass/volume ratio of the porous aerogels with a definite shape and \(\rho_{\text{poly}}\) is the density of the bulk polymer. The morphologies of the various samples were determined using scanning electron microscopy (using a Zeiss EVO 18 cryo-SEM and JEOL-JSM 5600 LV). Thermogravimetric analysis (TGA) was carried out using a thermogravimetric analyzer TA Q50 under a nitrogen gas atmosphere at a heating rate of 10 °C min\textsuperscript{-1} to check the thermal stability of the samples and to understand the complete solvent removal after freeze drying. The contact angle of the samples was measured under ambient conditions using an Automated Goniometer/Tensiometer, Model 290, Ramé-Hart Instrument Co., USA. WAXD measurements were carried out to confirm the phase formations and phase transformations of the various aerogel samples on a XEUS SXS/WAXS system using a Genixmicrosource from Xenocs operated at 50 kV and 0.6 mA. The Cu K\textsubscript{α} radiation (\(\lambda = 1.54\ \text{Å}\)) was collimated with a FOX2D mirror and two pairs of scatterless slits from Xenocs. The 2D-patterns were recorded on a Mar345 image plate and processed using the Fit2D software. All measurements were made in the transmission mode. The dielectric properties were measured using a vector network analyzer (E5071C ENA Vector Network Analyzer, 300 kHz–20 GHz, Agilent Technologies, CA) by a waveguide method. The sample dimensions used were 22.86 × 10.8 mm for X band (8.2–12.4 GHz). The mechanical properties of the aerogel specimens were investigated by compressive strength analysis using a Universal Testing Machine (Hounsfield, H5KS UTM, Redhill, UK) with a crosshead speed of 1.3 mm min\textsuperscript{-1}, where cylindrical samples of an approximately 1.5 : 1 diameter to height ratio were used. The Brunauer–Emmett–Teller (BET) surface area and pore size of the samples were measured, after degassing the samples at room temperature for 12 hours, using a nitrogen adsorption-desorption isotherm (Gemini 2375, Micromeritics, Norcross, USA). The pore size distributions of the aerogels were measured using the Barrett–Joyner–Halenda (BJH) method.
Results and discussion

The preparation of aerogels started with the dissolution of sPS granules in xylene. Fig. 1 depicts the schematic representation of the different steps involved in aerogel preparation. Xylene is known to be a good solvent for dissolving sPS at elevated temperatures and when cooled it forms the gel structure. It has been reported that any solvent with a molecular volume between 69 and 153 Å³ and a solubility parameter value between 8.8 and 12.3 (cal cm⁻³)¹/² is able to form stable gels of sPS. The volume of the two identical cavities formed by the organization of ten phenyl groups in the helical sPS δ form is calculated to be around 0.12 nm³, and these cavities are supposed to be capable of holding the smaller sized xylene molecules in them to form the co-crystals. The polymer to xylene concentrations were adjusted to 0.03 g g⁻¹ and 0.06 g g⁻¹ to obtain samples of varying porosity. Appreciably stable gels were formed in a short period, usually less than 10 minutes. The semi-transparent physical gel of sPS with xylene as the solvent was further subjected to a systematic solvent exchange process before carrying out the facile freeze-drying. The solvent exchange was started with ethanol for the 0.03 g g⁻¹ samples since it can remove the xylene completely and fill up all the pores. In addition, ethanol, being a non-solvent for the sPS-xylene system induces liquid–liquid phase separation in the gel system as indicated by the opaqueness developed in the gel (see Fig. 1). These ethanol containing sPS gels were further frozen to −60 °C, followed by sublimation of the solvents. Since the freezing point of ethanol is around −114 °C, we assume that the ethanol present in the sPS gel might not solidify completely. This means that some amount of ethanol might still have existed in the liquid form, and instead of undergoing sublimation this might have just evaporated leaving behind porous sPS samples with visibly distorted shapes (see the photograph shown in Fig. S1, ESI†). The density measured for the samples was only 0.35 g cm⁻³ with an apparent porosity of 65%.

In order to avoid the undesirable formation of distorted shapes of the prepared aerogel, we have chosen water as a medium of solvent exchange which can freeze under the selected conditions. Since xylene and water are immiscible solvents the solvent exchange was started with ethanol followed by ethanol–water mixtures of varying concentrations and finally pure water. As already stated, we have chosen two combinations of sPS to xylene solvent ratios to prepare the aerogels. To our surprise, we obtained an ultra low-density material with extremely high porosity for both the gels after freeze-drying, in spite of the fact that the highly hydrophilic water is not a good solvent for nonpolar sPS. The density calculated for sPS_{0.03g g⁻¹} was only ~0.04 g cm⁻³, corresponding to an ~96% porosity. The shape and size of the aerogel remained the same as that of the gel with negligible shrinkage as depicted in Fig. 1 and Fig. S2 (ESI†). The density and porosity of the various samples are summarized in Table 1.

The surface morphology of the various samples was studied by SEM, and the images are shown in Fig. 2. There is an understandable change in the macroporous structure of the sPS aerogels prepared under different solvent conditions even though the mesoporous structure reveals an entangled fibrous network structure in all cases. The fibers possess diameters of a few tens of nanometers, as observed in Fig. 2. The porous sPS formed from ethanol based gels exhibited a comparatively dense macroporous structure (Fig. 2a and d) with a seemingly rough fibrous surface. The macroporous structures show some differences depending on the concentration of polymer in the initial solvent for gelation and the lower polymer concentration (sPS_{0.03g g⁻¹}) led to a flake-like macroporous structure in comparison to the aggregated sphere-like morphology exhibited by the aerogels formed from polymers with a higher concentration (sPS_{0.06g g⁻¹}) in xylene (Fig. 2b and c, respectively). The microporous structures obtained for water-based aerogels formed via freeze casting are quite similar to the reported microporous structures of sPS aerogels formed under supercritical drying of physical gels with solvents like THF, chloroform, etc.⁵ Even though the fibrous network structure exists for all the aerogels prepared (see Fig. 2d–f), a highly porous structure was achieved for the water-based aerogels with a lower initial concentration of the

![Fig. 1](image-url) Photographs and schematic representation of the different stages involved in the preparation of sPS aerogels possessing macroporosity, mesoporosity and ordered microporosity.
Table 1  Density and porosity of the sPS aerogel samples obtained after freeze drying

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g cm$^{-3}$)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent exchange with ethanol</td>
<td>0.35</td>
<td>65</td>
</tr>
<tr>
<td>Solvent exchange with water (sPS$0.03\text{g g}^{-1}$)</td>
<td>0.04</td>
<td>96</td>
</tr>
<tr>
<td>Solvent exchange with water (sPS$0.06\text{g g}^{-1}$)</td>
<td>0.15</td>
<td>85</td>
</tr>
</tbody>
</table>

polymer in solution. A more aggregated structure was obtained for the sPS aerogels with 85% porosity obtained from the gels of sPS$0.06\text{g g}^{-1}$. The difference in the morphology of the samples might have originated from the different possible solvent escape rates from the gels (sublimation of crystals during freeze-drying) of varying polymer concentrations. The porous structures visible in the surface morphological analysis of the sPS aerogels are contributed to by the macro and mesopores, whereas the microporous structure can be investigated further with the help of X-ray diffraction techniques which will be discussed in the forthcoming section.

Aerogels which contain more than 90% air in their matrix are well known for their lower dielectric constant. Hrubesh et al. reported the linear relationship between the dielectric properties and density of silica aerogels/resorcinol formaldehyde aerogels. They reported dielectric constants of between 1.0 and 2.0 for aerogels with densities ranging from 10 to 500 kg m$^{-3}$. Polymide aerogels fabricated with different precursors and crosslinking agents also exhibited a very low dielectric constant, as low as 1.16, in the X band region of the electromagnetic spectrum. Compared to the radio frequency range, the dielectric property measurement in the microwave frequency range is more accurate since the influence of interfacial and dipolar polarisation is insignificant where ionic and electronic contributions dominate. However, there is a scarcity of microwave dielectric measurement data available for polymer aerogels. With the help of a microwave transmission waveguide technique, we could measure the dielectric constants of the various sPS aerogels in the X band frequency range (8–12 GHz) coming under the microwave frequency region of the electromagnetic spectra where most wireless communications take place.

It is observed from Fig. 3a that the porous sPS formed by the freeze-drying of sPS gels of ethanol possessed a dielectric constant of $\kappa \approx 1.6$ in the X band frequency region (10 GHz), which is comparatively less than that of bulk sPS ($\kappa \approx 2.5$). The dielectric constant was decreased to near 1.1 for the sPS aerogels which possessed about 85% porosity (sPS$0.06\text{g g}^{-1}$). In the case of the sPS aerogels with almost 96% porosity, we could achieve the lowest reported dielectric constant for any polymer aerogel ($\kappa = 1.03 \pm 0.02$), which is very close to the dielectric constant of air ($\kappa = 1$). This remarkably low dielectric constant is much less than that of many of the silica derived aerogels, other inorganic aerogels and polymer aerogels reported in literature as shown in Fig. 3b. Here it is quite logical to correlate the dielectric constant of the sPS aerogels with the density of the material, as these parameters were found to have a linear relationship. For example, sPS$\text{eth}$ possessed a higher density than the sPS$\text{water}$ aerogels and lower than the bulk sPS, and hence its dielectric constant is found to be less than sPS$\text{bulk}$ and higher than sPS$\text{water}$. In the case of the water derived aerogels, the slight difference in dielectric constant can be attributed to the marginal changes in density which directly contribute to the changes in porosity. In other words, the dielectric constant increases with density as a general rule in all the prepared aerogels. However, for sPS aerogels, along with density, changes in the polymorphic forms can also play a vital role in determining the dielectric constant. We have also tried to fit the measured dielectric constant values for the various sPS aerogels possessing different amounts of porosity with well-known theoretical models. Here, we used different equations like the Maxwell equation of volume averaging theory, Lichtnecker’s rule, the Maxwell–Garnet equation, the serial model, the parallel model, etc., in order to predict the effective dielectric constant of porous sPS aerogels, assuming the aerogels are composites of the low polarizable polymer and air. It is found that the calculated dielectric constants match well with the measured values in most of the cases. Table 2 summarizes the measured and predicted dielectric constants for sPS aerogels with different amounts of porosity and the model equations used for the calculations are given in the ESL.

![Fig. 2](image-url)  
Fig. 2  SEM images of the aerogels of (a and d) sPS$\text{eth}$, (b and e) sPS$0.03\text{g g}^{-1}$, and (c and f) sPS$0.06\text{g g}^{-1}$ at different magnifications.
When the developed highly porous and low dielectric constant sPS aerogels are intended for use in practical applications, it is very much essential to check the reliability of the dielectric constant upon loading weight on the material. With this intention, we loaded different weights on top of a 0.04 g sample with 96% porosity, and the dielectric constant was measured in the frequency range of 8.2 GHz to 12.4 GHz (Fig. 3c). It is seen that there is not much variation in the dielectric constant in the specified frequency range, and the values lie between 1.03 and 1.07. The dielectric loss values measured for the sPS aerogel samples are given in Fig. S3 (ESI†). The dielectric loss of sPS0.06g g−1 at 10 GHz is around 0.004 ± 0.002, which is comparable to other polyimide-based aerogels.26 The lower dielectric constant which is very near to that of air and comparable to other reported aerogels, and the low dielectric loss of this stable porous monolith, make the material appropriate for wide use in high-performance electronic devices and the material can out-perform conventional silica aerogels in many aspects including its stable dielectric properties and mechanical strength.

To gain more information about the relation between the dielectric constant and the spatial arrangement of the polymer chains, dielectric and WAXD measurements of the sPS aerogels were carried out for the samples annealed at 30 °C, 120 °C and 200 °C after cooling to room temperature. It is a known fact that sPS is capable of forming different polymorphic forms in the presence of solvents and solvent-crystallized sPS further undergoes phase transitions upon heating or annealing at higher temperatures.27,41,42,58 Among the major crystalline forms of sPS, g, d and e are obtained by solvent-induced crystallization, with d being favored in most of the solvent complexes and physical gels.27,41,59,60 The monoclinic d form of sPS contains isolated cavities which can hold guest solvent molecules of appropriate dimensions within them.61 Removal of the guest molecules from the cavities by any means leads to the formation of the kinetically stable microporous crystalline sPS (d,e) form as shown in the schematic representation in Fig. 1, which has a density even lower than the amorphous phase of sPS.58,62

![Fig. 3](image)

**Fig. 3** (a) Dielectric constants of sPSbulk and various aerogels in the X-band, (b) comparison of the dielectric constant obtained in the present work with those of other reported aerogels (the reference number is provided near the data point), (c) reliability of the dielectric constant of sPS0.03g g−1 on loading various weights, and (d) the effect of the annealing temperature on the dielectric constant of sPS0.03g g−1.

<table>
<thead>
<tr>
<th>Table 2</th>
<th>The measured and modeled dielectric constants for sPS aerogels with different porosity</th>
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</thead>
<tbody>
<tr>
<td>Model</td>
<td>Dielectric constants of the aerogels</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------------------</td>
</tr>
<tr>
<td>Measured</td>
<td>1.03</td>
</tr>
<tr>
<td>Maxwell’s equation</td>
<td>1.06</td>
</tr>
<tr>
<td>Lichtenecker’s rule</td>
<td>1.04</td>
</tr>
<tr>
<td>Maxwell–Garnet equation</td>
<td>1.04</td>
</tr>
<tr>
<td>Parallel model</td>
<td>1.06</td>
</tr>
<tr>
<td>Serial model</td>
<td>1.02</td>
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helped in the removal of the solvent molecules not only from the fibril network, but also from the crystalline cavities of the sPS molecules. The sPS aerogels in the $\delta$ ($\delta_{c}$) form with the microporous cavities inside the helices and the macro and mesopores originating from the solvent removal from its fibrous network showed the lowest dielectric constant very close to air ($\kappa = 1.03 \pm 0.02$).

Further to be noted from Fig. 4b is that instead of the diffused peaks near $2\theta = 8.4^\circ$ corresponding to $d_{010} \approx 1.06$ nm of the $\delta$ form, the peak at 9.2° in the case of the sPS aerogels annealed at 120 °C indicates the transition of sPS from the $\delta$ ($\delta_{c}$) form to the $\gamma$ form. Here the helical chain conformation of sPS is still retained, but without the cavities in the crystal lattice. The $\gamma$ form sPS aerogels obtained after annealing at 120 °C, which still possessed macroporosity as evidenced from the lower density (see Table 3) but without the cavities in the crystal lattice of the sPS fibrils, exhibited a higher dielectric constant of 1.37 at 10 GHz. It should be noted that this value is higher than that of sPS_0.06g g$^{-1}$ at room temperature, which possessed a higher density than sPS_0.03g g$^{-1}$ annealed at 120 °C. Also, the central diffused scattering observed in the WAXD pattern of the sPS aerogel at room temperature (Fig. 4a) can be related to its inherent microporosity. It is quite evident from Fig. 4a that the intensity of the diffused scattering decreased significantly when the annealing temperature was raised to 120 °C, indicating the collapse of the crystalline porosity. So the increase in dielectric constant of the annealed aerogel can be an indirect proof of the absence of microporosity inside the crystalline region of sPS.

On the other hand, when the aerogels were annealed at 200 °C, the structure was transformed into the $\alpha''$ form with a planar all-trans conformation, which is shown by the appearance of the characteristic peak at $2\theta = 6.8^\circ$. Here, the dielectric constant increased slightly, probably due to the transition of the helical $\gamma$ form to the all-trans planar $\alpha''$ form along with a slight increase in density as given in Table 3. At this point, we assume that the dielectric constants of the sPS aerogels are not only decided by the density alone, but that they are a result of the collective contributions of the density of the porous monoliths along with the spatial organization of the sPS chains.

The phase transformations of the sPS aerogels upon annealing were further understood with the help of DSC analysis and are given in Fig. S5a (ESI†). An exothermic peak near 110 °C is observed in both the isotherms, just after the glass transition temperature at $\sim$ 100 °C, which can be assigned to the transition of the $\delta_c$ form to the $\gamma$ form.58 Meanwhile, the exotherm corresponding to the transition to the $\alpha''$ form appearing at $\sim$ 180 °C is correlated to the phase transition of sPS from its helical TTGG conformation (the $\gamma$ form) to the all-trans planar $\alpha''$ form.27 More importantly, TGA [Fig. S5b, ESI†] revealed that the highly porous aerogels possessed sufficient thermal stability, to higher than 300 °C, to be employed for diverse industrial applications. Thermogravimetric analysis conducted for the aerogels also confirms the complete solvent removal with freeze-drying. The thermograms given in Fig. S5b (ESI†) do not show any weight loss corresponding to the solvents in the lower temperature regions (less than 200 °C) indicating the complete removal of the solvents after the freeze-drying process.

Nitrogen adsorption isotherms were utilized to measure the BET surface area and the pore size distribution of the various sPS aerogels, and the results are given in Fig. 5a. The surface areas of the samples are 301 m$^2$ g$^{-1}$, 261 m$^2$ g$^{-1}$ and 198 m$^2$ g$^{-1}$ for sPS_0.03g g$^{-1}$, sPS_0.06g g$^{-1}$ and sPS_{sth} respectively, with a remarkable decrease in value with the increase in the density of the porous scaffolds. All the isotherms were typical type IV adsorption isotherms arising from a monolith of continuous 3D macro pores or mesopores.60 The hysteresis loop that appeared at higher $P/P_0$ values (0.75–0.90) can be attributed to the capillary condensation and evaporation of nitrogen in the mesopores of the sPS aerogel, whereas the low slope region in the middle of the isotherm indicates the multilayer adsorption on external surfaces including mesopores and macropores.21 At the lower end of the isotherms, Table 3 Comparison of the dielectric constants of the various aerogels with their density and polymorphic forms

<table>
<thead>
<tr>
<th>Material</th>
<th>Dielectric constant at 10 GHz</th>
<th>Density (g cm$^{-3}$)</th>
<th>Polymorphic form of sPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>sPS_{bulk}</td>
<td>2.6 ± 0.05</td>
<td>1.03</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>sPS_{sth}</td>
<td>1.55 ± 0.02</td>
<td>0.35</td>
<td>$\delta_c$</td>
</tr>
<tr>
<td>sPS_{0.06g g$^{-1}$}</td>
<td>1.12 ± 0.02</td>
<td>0.15</td>
<td>$\delta_e$</td>
</tr>
<tr>
<td>sPS_{0.03g g$^{-1}$}</td>
<td>1.03 ± 0.02</td>
<td>0.04</td>
<td>$\delta_e$</td>
</tr>
<tr>
<td>sPS_{0.03g g$^{-1}$ annealed at 120 °C}</td>
<td>1.37 ± 0.02</td>
<td>0.06</td>
<td>$\gamma$</td>
</tr>
<tr>
<td>sPS_{0.03g g$^{-1}$ annealed at 200 °C}</td>
<td>1.47 ± 0.02</td>
<td>0.08</td>
<td>$\alpha''$</td>
</tr>
</tbody>
</table>

Fig. 4 WAXD patterns of (a) sPS_0.03g g$^{-1}$ annealed at different temperatures and (b) the magnified view of the region from $2\theta = 5$–35°.
the overlapping of the adsorption and desorption curves represents the formation of monolayer and multilayer adsorption.\(^{13}\)

The pore size distribution curves of the various samples depicted in Fig. 5b display a broad range of pore diameters in all cases ranging from mesopores to macropores. The distribution was found to be more ordered in the water-based aerogel sample which possessed maximum porosity (a lower initial polymer concentration), with a maximum pore volume centered near to 80 nm. The peak maximum was shifted to a higher pore diameter in both the ethanol-based porous scaffolds (sPS\(_{0.06 g/g}\)) and sPS\(_{0.06 g/g}\).

The water contact angle measurements were carried out on sPS\(_{0.03 g/g}\) and sPS\(_{0.06 g/g}\) and are given in Fig. 6 and Fig. S6 (ESI†), respectively. The image of the water droplet on the surface of the highly porous sPS aerogel is shown in Fig. 6. The measurement was not carried out on the ethanol derived porous scaffold since in this case it was difficult to obtain smoothly surfaced samples of bigger dimensions. Even though the material contained very high porosity, it was found that the water contact angle is very high, indicating its highly hydrophobic nature. The aerogel with the highest porosity of 96% (sPS\(_{0.03 g/g}\)) possessed the highest contact angle of 135\(^{\circ}\), and the one with 85% porosity (sPS\(_{0.06 g/g}\)) exhibited a slightly lower contact angle of 126\(^{\circ}\). It is evident from Fig. 6a that the water droplet, colored with rhodamine dye, retains its sphericity on the aerogel surface without any wetting. The combined effect of the macro, meso and microporosity of the aerogel, along with the inherent hydrophobicity of the entangled sPS fibers might have led to this extreme moisture resistant nature in the freeze-dried aerogels, which helps to extend its versatility.\(^{21}\) In order to verify the moisture absorption of the samples experimentally, aerogel samples were dipped in water for five days, and the weight of the sample was measured before immersion and at specific intervals after immersion. No considerable weight gain was observed for the samples even after three days of immersion in water, indicating the highly hydrophobic nature of these porous scaffolds. After three days a slight increase in weight (less than 2%) was observed as seen in Fig. 6c.

The stress–strain curve obtained for the ultra-low density sPS aerogel is given in Fig. 7. sPS aerogels underwent buckling...
as reported by Jana and co-workers and were converted to a dense solid at a relatively low compressive stress, without any shattering of the specimen. The aerogel exhibited a linear behavior in the low strain region, corresponding to elastic behavior, and at higher strain the material exhibited plastic deformation as indicated by the nonlinear behavior in the stress–strain graph. In the elastic region, the aerogel pores get deformed, whereas after plastic deformation the pores completely collapse leading to a dense solid. The Young’s modulus calculated from the linear portion of the stress–strain graph was nearly 0.45 MPa for the aerogels with 96% porosity. However, it should be noted that the mechanical strength of this polymer derived ultra-low dielectric aerogel is comparable with some of the sPS and sPS–silica aerogels. As can be seen from the inset in Fig. 7, sPS aerogels with 96% porosity have sufficient mechanical strength to hold more than 1500 times their original weight.

Conclusions

In summary, we have developed a mechanically strong sPS aerogel via a simple freeze-drying technique in the presence of water as a medium of solvent exchange. The ultra-low density β-form aerogels, which exhibited a low dielectric constant (1.03 ± 0.02 at 10 GHz) and had 96% porosity and a very hydrophobic nature, can be tailored for wide applications in microelectronics. It is also understood that there occurs a phase transformation of the polymer upon annealing at different temperatures, which was confirmed by WAXD and DSC, and this transition affects the dielectric constant of the aerogels due to the variation of the amount of crystalline porosity. It can be concluded that the polymorphic state of the polymer and the density of the aerogel together contribute to the low dielectric constant of the developed aerogels.

Conflicts of interest

The authors declare no competing financial interest.

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