BUILDING BLOCKS AND THEIR EFFECTS ON POLYMER AEROGEL PROPERTIES

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BUILDING BLOCKS AND THEIR EFFECTS ON POLYMER AEROGEL PROPERTIES

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ABSTRACT

We investigated the effects of polymerization conditions, such as temperature, the polarity of the solvents, and microscale confinement during sol-gel transition, on the microstructure and physical properties of the resultant polymer aerogels. This work includes two main parts. (1) Studies of properties and formation mechanism of polybenzoxazine aerogels showing spherical and cylindrical building blocks; (2) Evaluation of properties of the aerogels obtained from the gel precursors synthesized in an oil-in-oil emulsion and a macroporous polymer host.

In the first part (Chapter III & IV), p-toluenesulfonic acid (TSA) was used as the catalyst for cationic ring opening polymerization of benzoxazine to produce polybenzoxazine (PBZ) aerogels. The PBZ aerogel building blocks (spheres vs. strands) and pore surface area show strong dependence on the solvent and the gelation temperature. The use of dimethyl sulfoxide (DMSO) and dimethylacetamide (DMA) led to spherical particle networks while fibrillar networks were obtained using N-methyl-2-pyrrolidone (NMP). A combination of dynamic light scattering (DLS) and static light scattering (SLS) was used to monitor the growth of polymer networks during polymerization. The light scattering results revealed that polymer networks formed via nucleation and growth mechanism. In addition, the shape of building blocks was found to be associated with the concentration of the nuclei and the gelation time. In DMSO, a higher concentration of nuclei resulted in a fast crowding of the building blocks that constituted the gel network.
However, at low concentration of the nuclei and at long gelation times, the spherical building blocks evolved into cylinders by self-assembly and formed a fibrillar network when NMP was used as the solvent. Originally, the differences in the concentration of nuclei were due to the differences in dissociation constant of TSA in DMSO and NMP.

In the second part, the preparation and characterization of aerogel microparticles and aerogel foams were presented respectively in Chapter V and Chapter VI. In this regards, polyurea open cell aerogel foams (PUA OCAFs) were created by the sol-gel process inside a macroporous PEO template. The microstructure of PUA OCAFs were found to be a combination of interconnected large pores (pore size ~ 10 µm) and intercellular skins composed of mesoporous aerogel domains. The unique hierarchical structures of OCAFs offered higher sorption kinetics and air permeability than the regular PUA aerogel monoliths, which are helpful for applications, such as airborne nanoparticles filtration and oil-spill cleanup.

PBZ and polyimide (PI) aerogel microparticles were prepared via sol–gel reactions inside micrometer size droplets created in an oil-in-oil emulsion system. The oil-in-oil emulsion system was obtained by dispersing in cyclohexane the droplets of the sols of PBZ or PI prepared in dimethylformamide (DMF). The sol droplets transformed into harder gel microparticles due to sol–gel reactions.
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CHAPTER I

INTRODUCTION

Aerogels are highly porous materials well-known for their excellent characteristics, such as low bulk density (reaching as low as 0.002 g/cm$^3$), low thermal conductivity (10 – 30 mW/m·K), high specific surface area (reaching more than 1000 m$^2$/g), and high porosity. Since Kistler$^1$ reported the use of supercritical drying of organic liquids in synthesis of shrinkage-free silica aerogels, supercritical drying was successfully used in synthesis of organic aerogels from chemically reacting systems such as resorcinol and formaldehyde (RF),$^2$ polyurea,$^3$–$^5$ and polybenzoxazine.$^6$–$^8$ Aerogels were also synthesized from syndiotactic polystryrene via thermoreversible gelation process$^9$ and from layered silicate clay via freeze-drying process.$^{10}$ Aerogels find applications in thermal insulation,$^{11}$ energy storage,$^{12}$ waste treatment,$^{13}$ and drug delivery.$^{14}$ The application of aerogels essentially depends on the nature of the precursor materials, synthesis method, and the relevant highly porous structures. Therefore, proper selection of materials, strategies to tailor the network structure of aerogels, and the specific structure-property relationships play a vital role in determining the nature of specific applications of aerogels.

Considering the fragility of neat silica aerogels, a host of chemical means were used in reinforcement of pearl-necklace structures of silica aerogels, e.g., via flexible silanes,$^{15}$–$^{16}$ diisocyanates,$^{17}$–$^{18}$ free-radical polymerization,$^{19}$ organic–inorganic hybrid nanoparticles,
epoxies, polyurethaneurea, and fluorosilanes. Moreover, properties of organic aerogels such as RF aerogels, polyimide aerogels, and polyurea aerogels were tuned focusing on the control of the precursor materials and processing conditions.

In the studies of designing the properties of aerogels, an interesting phenomenon was observed that particulate and fibrous aerogel networks can be obtained by varying the reactants, catalysts, surfactants, as well as drying conditions in different polymer systems. For example, Kanamori and co-workers synthesized silica aerogel using methyltrimethoxysilane (MTMS) as the precursor material dissolved in aqueous acetic acid with urea and surfactant. Urea was used to accelerate the polymerization reaction and the surfactant, cetyltrimethylammonium bromide (CTAB) or F127, was used to promote the mixing of MTMS-derived species and the solvent. The results revealed that silica aerogels synthesized with F127 exhibited continuous fibrous network, whereas CTAB promoted the formation of a globular-aggregated network. The authors proposed that both morphologies were obtained from spinodal decomposition (SD). The globular-aggregated network formed at the early stage of SD, and the fibrous network formed at the later stage where the structural coarsening proceeded to lower the surface energy. Meador and co-workers reported a similar observation in the study of polyimide aerogels. Aerogels derived from p-phenylenediamine (PDA) and benzophenone-3,3,4’4’-tetracarboxylic dianhydride (BTDA) appeared as collections of polymer strands with diameters ranging from 30 to 50 nm in thickness. However, the combination of 4,4’-oxydianiline (ODA) and BTDA produced aerogels with aggregation of clusters of 50 to 100 nm particles. According to the N2-sorption analysis, the fibrous network exhibited a sharp pore size distribution with the predominant pore diameter around 20 nm. In comparison, the pore size distribution
of the particulate network was broader and bimodal ranging from 10 nm to almost 100 nm.

The first objective of this research was to optimize the production and properties of polybenzoxazine (PBZ) aerogels. It included shortening the gelation time by catalysts and tailoring the pore structures and surface area using different solvents and temperatures. Interestingly, we also obtained PBZ aerogels exhibiting fibrous and particulate networks produced from N-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO), respectively. Our second goal was to investigate the formation of these two types of PBZ network. Laser light scattering (LLS) technique was employed to probe the growth path of the nanoparticles during the sol-gel process. Third, we explored the applicability of the theory established based on the LLS results within two specific situations, sol-gel process in micrometer-sized droplets and in a macroporous polymer template. The details of our studies are organized in this thesis as follows.

Chapter III presents a time-efficient synthesis of PBZ aerogels using p-toluenesulfonic acid (TSA) as the catalyst for cationic ring opening polymerization of benzoxazine (BZ). At a concentration of 0.275 g/mL, the solution of BZ with TSA (2% w/w of BZ) in DMSO gelled in 5 min whereas the gelation time of pure BZ solution was more than 6 h. Furthermore, the PBZ aerogel building blocks (sphere vs. strand) and pore surface area show strong dependence on the solvent and the gelation temperature. The use of dimethyl sulfoxide (DMSO) and dimethylacetamide (DMA) led to spherical particle network while fibrillar networks were obtained using N-methyl-2-pyrrolidone (NMP). The aerogel derived in DMSO showed a sharp pore size distribution while the distribution curve of the aerogel from NMP at 130 °C was broader and bimodal. The influence of gelation
temperature was also studied. It was indicated that gelation of DMSO at 90 °C took longer time than that at 130 °C. In terms of properties, aerogel synthesized at 90 °C provided higher surface area but lower mesopore volume than the ones prepared at 130 °C.

In Chapter IV, our purpose was to develop a thorough understanding of the formation of the networks from spheres and strands as the building blocks. A combination of dynamic light scattering (DLS) and static light scattering (LLS) was used to monitor the growth of polymer networks due to polymerization induced nucleation and growth. The light scattering results revealed that the shape of building blocks was governed by with the concentration of the nuclei and the gelation time. In DMSO, a higher concentration of nuclei resulted in a fast crowding of the elements. However, a lower concentration of nuclei and longer gelation time in NMP allowed the globules to evolve and connected as cylinders by self-assembly and eventually to form a fibrillar network in NMP. Overall, the formation of both networks took place via nucleation and growth mechanism. The final morphology of the 3Ds network was determined by the growth mode of the nuclei in the solution which could be influenced by many factors, such as the polarity of the solvents, the concentration of the catalyst, and the temperature.

In Chapter V, a class of novel materials, called polyurea open cell aerogel foams (PUA OCAFs), were created by the sol-gel process in a macroporous PEO template. After removal of PEO and supercritical drying, microstructure of PUA OCAFs were found to be a combination of interconnected large pores (pore size ~ 10 µm) and the intercellular skins composed of mesoporous aerogel domains. The skin layers of the aerogel domains appeared as globular-aggregated networks while the internal network was fibrillar. We confirmed that polyurea networks were also formed due to nucleation and growth.
However, in this specific case, the heterogeneous nucleation and growth played an important role in interpreting the unique morphology of OCAFs. Heterogeneous nucleation induced by the PEO template resulted in a higher local concentration of the nuclei on the surface of PEO, leading to a fast crowding to form the particulate network. In the middle of the cavities, the spherical nuclei of lower concentration assembled into cylinders and formed interconnected fibrillar networks. The unique hierarchical structure of OCAFs offered higher sorption kinetics and air permeability than the normal PUA aerogels.

Chapter VI presents results on the preparation of PBZ and polyimide (PI) aerogel microparticles via sol–gel reactions inside the micrometer size droplets created in an oil-in-oil emulsion system. The oil-in-oil emulsion system was obtained by dispersing in cyclohexane the droplets of the sols of PBZ or PI prepared in dimethylformamide (DMF). The sol droplets transformed into harder gel microparticles due to sol–gel reactions. Finally, the aerogel microparticles were recovered using supercritical drying of the gel microparticles. It was observed in SEM images that the surfaces of the aerogel microparticles exhibited denser structures than the internal domains. We propose that the interfaces between two oil phases promoted nucleation so that more nuclei formed first on the outside of the gel particles. Interfacial stress was another possible factor that could deform the polymer networks near the interfaces in the emulsion droplets. The PBZ and PI aerogel microparticles prepared in this manner showed mean diameter 32.7 and 40.0 μm, respectively, mesoporous internal structures, and surface area 55.4 and 512.0 m²/g, respectively. Carbonization of PBZ aerogel microparticles maintained the mesoporous internal structures but yielded narrower pore size distribution.
CHAPTER II

BACKGROUND

2.1 Overview of aerogels

Aerogels are a class of highly porous, structural solid with all the pores filled by air. Aerogels have many excellent characteristics, for example, low bulk density (reaching as low as 0.16 mg/cm$^3$),\textsuperscript{45} low thermal conductivity (10-30 mW/m$\cdot$K),\textsuperscript{15} high specific surface area (reaching more than 1000 m$^2$/g),\textsuperscript{45} and high porosity.\textsuperscript{15} In addition, aerogels are an important member in the family of nanomaterials as the solid building blocks are of the scale of a few tens of nanometers. Aerogels prepared with different raw materials were found to show microporosity (pore sizes in the range of 0-2 nm) and mesoporosity (pore sizes in the range of 2-50 nm). The small pores enable aerogels to be applicable in many areas related to energy and environment.\textsuperscript{46-52}

Aerogels were first produced by Kistler in 1931.\textsuperscript{1} Initially, he intended to remove the liquid, typically water and alcohol, from a gel without any volume shrinkage. In his research, a wet silica gel was synthesized when the colloidal silica particles connected with each other by condensation reactions of the silanol groups. However, the evaporation of the liquid inside the pores of the silica gel under ambient conditions destroyed the gel due to the capillary stress generated during evaporation. To eliminate this concern, the supercritical drying process was used to remove the solvent from the gel and to retain the
same internal structures. For this purpose, first, the gel precursor was soaked in alcohol to replace the liquid in the gel. Subsequently, the temperature and pressure were raised to the critical point of the alcohol. In this process, the effect of interfacial tension was removed. The alcohol under supercritical condition easily escaped the gel without affecting the internal structures.

However, the procedure invented by Kistler was costly and lengthy to prepare aerogels. A number of attempts were made by scientists to optimize the aerogel production process. In 1960’s, Teichner et al.\textsuperscript{53} developed a methodology using tetramethoxysilane (TMOS) as the silica precursor to produce silica aerogels via a synthesis path which is now well-known as the sol-gel process. The advantage of Teichner’s method was to shorten the aerogel production process from days to several hours. Twenty years later, Tillotson et al.\textsuperscript{54} reported an advanced two-step sol-gel preparation method for silica gel, including acid-catalyzed hydrolysis and base-catalyzed condensation. This method opened a window for researchers to precisely control the properties and the morphology of silica aerogels by process engineering. In the above studies, the use of methanol or ethanol as supercritical fluid caused safety concerns due to the high critical temperature of the liquids. In 1985, Tewari\textsuperscript{55} and Gowda\textsuperscript{56} proposed a safer supercritical drying step by using liquid CO$_2$, which has a much lower critical temperature (31 °C). This, however, introduced an additional step. The solvents in the gels should be exchanged with liquid CO$_2$ before the temperature and pressure are raised to the critical point. The use of liquid CO$_2$ in supercritical drying was also important for the development of organic polymer aerogels because the structure of some polymer aerogel are not stable at the critical temperature of methanol (240 °C).
In recent two decades, the theme of aerogel studies changed from “how to simply and safely produce aerogels” to “how to create aerogels with expected properties”. Using the well-developed aerogel production method, a variety of aerogels were synthesized from different organic and inorganic materials. As shown in Figure 2.1, most of the aerogels were presented as the monoliths which were dried from the gel precursors formed in a cylindrical mold, such as syringe and scintillation vial. It is convenient to measure the dimensions of aerogel cylinders to calculate the volume and then bulk density. Also, the cylinder is an ideal geometry for measuring the properties, such as compression modulus and air permeability.

Figure 2.1 Photograph of (a) polyurea aerogels with different solid contents (b) reduced graphene oxide aerogel, (c) silica aerogel monoliths with different crosslinkers\textsuperscript{57}, (d) syndiotactic polystyrene aerogel with multi-wall carbon nanotubes (Reprinted with permission from ref. 4, 45, 57, and 158).
Aerogels in the form of thin films were also studied considering that some important applications require the aerogels to be used as thin layers.\textsuperscript{52} For example, electronic applications require micrometer thin aerogel film bonded to a substrate. The first study on silica aerogel film was reported by Mulders et al. in 1995.\textsuperscript{58} The silica aerogel was cut to sub-centimeter size and used for helium uptake in the porous film. Since then, a number of aerogel films with thickness larger than 1 \( \mu \)m were reported. The aerogel films were generally deposited by dip coating, spin coating, and spray coating. For example, Budunoglu et al.\textsuperscript{59} produced the method of preparing highly transparent superhydrophobic organically modified silica (ORMOSIL) aerogel thin films by spin coating the silica colloidal dispersions. The silica gel was synthesized by two step sol-gel process using methyltrimethoxysilane (MTMS) precursor. The gel was then homogenized in ethanol by ultrasonication. Subsequently, the resulting suspension was spin-coated on a glass slide and dried at room temperature. The aerogel thin films showed both micrometer- and nanometer-scale surface roughness resulting in superhydrophobicity. Kim and Hyun developed window glazing coated with silica aerogel film.\textsuperscript{60} The aerogel film was manufactured by dip- or spin-coating of silica sol on the glass slide. The solvent was exchanged with n-heptane in order to minimize the shrinkage during ambient drying. The window glazing showed the transmittance of 90\% and the optimal thermal conductivity of the window could be as low as 0.2 W/(m·K). In addition to the coating methods, a fixture made by two glass flats (Figure 2.2) were also used as the sealed mold for preparing gel thin films. The gel layer was synthesized and aged in the mold so that no solvent evaporation took place to cause the shrinkage. The gel was then exfoliated and immediately soaked into solvent, e.g. methanol or ethanol. Finally, the aerogel film was obtained by
supercritical drying. This method was used by Mezza et al.\textsuperscript{61} and Shen et al.\textsuperscript{62} to produce silica aerogel film and resorcinol formaldehyde (RF) aerogel film, respectively. Films prepared by this method normally show diameters in the range of 5 to 200 µm.

Moreover, aerogels of the configuration of microparticles are preferred in many cases, such as bioadsorption\textsuperscript{63, 64}, catalysis\textsuperscript{65-68}, and water purification\textsuperscript{69-71}. Emulsion polymerization is the most common system for producing aerogel microparticles. Horikawa et al.\textsuperscript{64} synthesized RF hydrogel particles by dispersing the RF aqueous sol in cyclohexane containing a surface-active agent. The diameter of the RF gel was significantly influenced by the viscosity of the RF sol. The scanning electron microscope (SEM) images of the supercritically dried RF aerogel particles reveals that the particles show a spherical shape and the diameter ranges from 10 to 500 µm. Alnaief et al.\textsuperscript{72} used water-in-oil emulsion to prepare the biodegradable nanoporous microspherical aerogel based on alginate. This study evaluated the effect of emulsion conditions, including surfactant concentration, stirring rate, and alginate content, on the aerogel particles. The results revealed that stirrer revolution rate was the main factor determining the particle size distribution of the produced aerogel spheres, of which BET surface area was 680 m\textsuperscript{2}/g.

Figure 2.2 A glass fixture to produce silica gel films. Reprinted with permission from ref. 61.
Spraying system provides an alternative method to produce the gel particles which could be dried to achieve aerogel spheres by supercritical drying or freeze-drying.\textsuperscript{73-75} Figure 2.3 presents schematic diagram of the spray-freeze-drying process for fabricating cellulose aerogel microparticles.\textsuperscript{73} The system developed by Cai et al.\textsuperscript{73} could produce the cellulose aerogel microparticles with diameters around 60 to 120 µm. The procedure, including spraying, freezing, and drying, is representative for preparing aerogel microparticles by spraying system. In the work reported by Cai et al.,\textsuperscript{73} an aqueous suspension containing cellulose nanofibrils was sprayed into a liquid nitrogen tank to freeze the spherical shape of the suspension droplets. The aerogel microparticles were obtained after freeze-drying the frozen droplets without collapsing the 3D network of cellulose fibrils preformed in the water media. In this procedure, the immediate freezing by liquid nitrogen is crucial to maintain the shape of the droplets. The resultant aerogel microparticles have good biocompatibility and was proved to be useful for three-dimensional cell culture. Similarly, Kim and co-workers\textsuperscript{75} synthesized and characterized the micrometer-sized silica aerogel beads using the same mechanism as spraying system. The silica sol prepared by dissolving trimethylchlorosilane (silylating agent) and sulfuric acid (acid catalyst) in water was mixed in a nozzle and added to a container with kerosene as the upper layer and aqueous ammonia solution as the bottom layer. The sol was separated to micrometer-sized droplets in kerosene. When the droplets were added to the ammonia solution, the sol droplets solidified (gelled) in less than 1 min due to the fast condensation reactions induced by increasing the pH. This process had the same function as the liquid nitrogen as discussed previously. The obtained silica hydrogel particles were washed by water and dried under ambient condition.
2.2 Applications

Aerogels have successfully found applications in a number of fields, for example, thermal insulation, electrode materials, and so on.

2.2.1 Aerogels for thermal insulation

Aerogels have a very low thermal conductivity, resulting from a low solid skeleton conductivity and a low gaseous conductivity. Dense silica has a relatively high intrinsic solid thermal conductivity, but silica aerogels have a very small solid silica content (less than 3%) which exists as the nanometer-sized skeleton. Furthermore, the skeleton has many defects leading to low efficiency of thermal transport. The low gaseous thermal conductivity of aerogels can be explained by the Knudsen effect, expressing the gaseous conduction in a porous media as function of the air pressure and the characteristic pore size.\(^\text{76}\) Accordingly, the gaseous conduction of a porous media is proportional to the characteristic pore size of pores considering that air pressure is a constant. Silica aerogels have an intrinsic low characteristic pore size and a very high porosity. As a result, the
gaseous thermal conductivity of silica aerogel is strongly reduced at ambient pressure due to the Knudsen effect.

Figure 2.4 Translucent aerogel insulation used in a curtain wall at the Sculpture building (left) and gallery of Yale University (right). Reprinted with permission from Ref. 77.

As thermal insulation materials, the practical applications of aerogels are mainly in the market of building materials. Figure 2.4 shows the examples of transparent aerogels as insulation for building. Although the costs remain high, resulting in a limitation for aerogels to be widely used in building industries, aerogels are becoming a competitive alternative to traditional insulation due to their superior thermal insulation performance.

In the current commercial market, two types of aerogel materials are used in building applications. One is the insulations materials which only use the high thermal insulation performance of silica aerogel. For example, Aspen Aerogels, Inc. (Northborough, MA, US) are selling a product called Spaceloft®, which is available as flexible blankets in thickness of 1 cm (Figure 2.5). The blankets have a thermal conductivity of 13.1 mW/(m·K) at 273 K, 2-2.5 times lower than traditional thermal insulation materials. In other words,
Spaceloft® needs half of the thickness to offer the same thermal insulation effect as the traditional insulation products. Despite its high price, Spaceloft® may find applications in cases where space is an important topic. It is interesting that silica aerogels are known as brittle and fragile solids. Spaceloft® is bendable which is realized due to the bendability of the fiber matrix on which the silica gel was formed.

Figure 2.5 A photograph of Spaceloft® (Aspen Aerogel, Inc.).

Another one is the transparent aerogel monolith used as the window with high thermal insulation performance. A monolithic aerogel-based window was developed by the HILIT+ project of the European Union, a project that was launched to develop a monolith aerogel-based window. Aerogel tiles of 55×55 cm² was prepared with the technology of vacuum glazing. For glazing prototypes with an aerogel thickness of ~ 15 mm, a center heat-loss coefficient of < 0.7 W/(m²·K) and a solar transmittance of 76% were obtained. The heat-loss coefficient could reach as low as 0.5 W/(m²·K) by increasing the aerogel thickness to 20.0 mm while the solar transmittance remained at > 75%.79
2.2.2 Aerogels as electrodes materials

Considering the superior electrical properties, carbon aerogels are wildly used in electrical energy storage. They are ultralight, highly porous materials, predominantly with mesopores, and have the possibility of using without the binding substances. The most common application of carbon aerogels in this field is the electric double-layer capacitor (EDLC). The development of EDLC focuses on (1) increasing of energy and power densities, (2) increasing the operating voltage, and (3) decreasing the cost per Wh stored in the device. Carbon aerogels are ideally suited for this purpose as they are chemically inert, highly conductive, environmentally friendly, can be made from cheap and abundant raw materials, and most importantly, provide high specific surface area combined with a fully tunable 3D structure. Specifically, the tunability of the CA structure provides a tool for improving the energy and power densities, as both depend on the pore structure of the electrode. Fang and Binder developed an activated carbon aerogel with surfaces modified by vinyltrimethoxysilane functional groups.\textsuperscript{80} Surface modification provided better EDLC performance (i.e., 41% of enhancement in capacitance and 274% of enhancement in energy density), which is probably attributable to better hydrophobisation of vinyltrimethoxysilane modified activated carbon aerogels. Bordjiba et al.\textsuperscript{81} synthesized a unique carbon aerogel by dispersing aerogel uniformly on the carbon nanotube (CNT) matrix. The CNT-aerogel composite offers a high specific surface area of 1059 m\textsuperscript{2}/g and high specific capacitance of 524 F/g. For comparison, the specific capacitance of pristine carbon aerogel was 134 F/g in the same study. Carbon/metal oxide aerogel composites were also prepared by impregnation of metal oxides, such as manganese oxide\textsuperscript{82}, tin oxide\textsuperscript{83},\textsuperscript{84}, ruthenium oxide\textsuperscript{85}, in the gelation process of the gel precursor for carbon aerogels.
Improvements were achieved on the specific capacitance and/or cyclic stability because of the synergetic effect of two inorganic components.

2.2.3 Aerogels in catalysis

Catalytic reactions can be of the redox or of the acid-base type. To date, most of the studies on catalytic behaviors of aerogels are redox type. The major advantage of aerogels is the high specific surface area which increases the number of active sites per gram of the samples. Mesoporous oxide aerogel catalysts synthesized via sol-gel reactions were studied, and many review papers were published on this topic.\textsuperscript{86-89}

Application of aerogels as the catalyst support is also important and actually have been found to be more popular in recent studies. Carbon aerogel (derived from RF aerogel)\textsuperscript{90-92}, graphene aerogel\textsuperscript{93-95}, and silica aerogel\textsuperscript{96-98} doped with metal oxide or intermetallic compound were investigated as catalysts for various reactions. For instance, Yin et al.\textsuperscript{93} reported the iron nitride and nitrogen-doped graphene aerogel as synergistic catalysts for oxygen reduction reactions. The Fe\textsubscript{x}N nanoparticles were well dispersed and strongly anchored on the nitrogen-doped graphene surface realized by a two-step hydrothermal process. The hybrid materials showed higher onset potential and current density than both neat nitrogen-doped graphene aerogel, Fe\textsubscript{x}N and their physical mixtures, which was attributed to the high specific surface area and porosity of graphene substrate. Pt catalysts supported on carbon aerogels were tested as catalysts for toluene combustion reaction\textsuperscript{26} and proton exchange membrane fuel cells\textsuperscript{99}. The carbon aerogels were obtained by pyrolysis of organic aerogels in inert atmosphere. Pt particles can disperse in the carbon matrix with low tendency to agglomerate. As a result, Pt particles can show optimal catalysis efficacy for either fuel cell performance or combustion reactions. Silica aerogels
are also ideal catalyst supports due to their high specific surface area and excellent thermal stability. Dynn et al.\textsuperscript{100} prepared silica aerogel supported cobalt catalyst for Fischer-Tropsch synthesis. The results reveal that the unique mesoporous network of silica aerogels could be maintained at the synthesis temperature (300 °C). The cobalt exists as small particles (50-70 nm) which are active towards Fischer-Tropsch synthesis with good selectivity for the C\textsubscript{10+} range of hydrocarbons, which resulted from the enhanced mass transport with the silica aerogel.

2.2.4 Other applications

Several studies focused on using aerogel as the filter media for airborne nanoparticles.\textsuperscript{39, 101-103} Jana and co-workers recently reported a set of high efficiency (> 99.95\%) aerogel-based filter media for airborne sodium chloride nanoparticles.\textsuperscript{39, 103} The studies evaluated the importance of macropores (diameter greater than 50 nm) and mesopores (diameter in the range of 2 to 50 nm) of aerogel monoliths on air permeability and nanoparticle filtration efficiency. The results established the applicability of syndiotactic polystyrene aerogels, silica aerogels, and their hybrid materials on nanometric particle filtration and presented several strategies for achieving high filtration efficiency without decreasing the air permeability.

In 2004, NASA used silica aerogel in its space exploration mission, Stardust, to capture the hypervelocity, which are small comet particles with diameter in the range of 0.1 to 100 \(\mu\)m.\textsuperscript{104} Silica aerogels offer many specific qualities such as a suitable mesoporosity, a low thermal conductivity coefficient, and a low bulk density to meet the requirements of this mission. Aerogels were also used in Pathfinder Mars mission to insulate the Sojourner
Mars Rover. The silica aerogels protected the sensitive electronics from freezing during the night on Mars where the temperature is as low as -67 °C.

2.3 Types of organic aerogels

Organic aerogels are generally synthesized by polymerization of small molecules. In this section, history and properties of several typical polymer aerogels are introduced.

2.3.1 RF aerogel

In 1989, first RF aerogel was created by Pekala in Lawrence Livermore National Laboratory. The RF gel was synthesized through the polycondensation reactions of resorcinol with formaldehyde under alkaline conditions. The sol-gel processing was characterized to be similar to that of silica aerogel. RF aerogel was obtained after supercritical drying and exhibited high surface areas (400-900 m²/g), low bulk density (~0.3 g/cm³), and relatively high porosity (> 80%). It was discovered that carbon aerogels can be produced by pyrolysis of RF aerogel. RF aerogel-based carbon aerogels are promising candidates for various applications because of their excellent characteristics such as high electrical conductivity, high surface areas, and controllable pore structure. These exciting properties attracted researchers to study the factors that can decide the pore structure of the aerogels to fit a wide range of applications. Several synthesis conditions were found to play remarkable roles in tailoring the structures of RF aerogels and the corresponding carbon aerogels.

The concentration of raw ingredients has a significant effect on the surface area, pore volume, and average pore size. Liu et al. reported that high concentration of the raw material increased the micropore surface area and pore volume of the carbon aerogel while
caused a reduction of mesopores surface area, pore volume, and pore diameter. Low concentration of resorcinol and formaldehyde produced inhomogeneous gels. The products could be obtained in the form of gel particles instead of monolithic gels.$^{115}$

pH of the initial solution also exerted effects on RF gels. For example, as shown in Figure 2.6, the gelation process takes the longest time at a pH in the range of 3-4. When pH< 0.8, the reactants precipitated;$^{116}$ at pH> 9, the polycondensation reaction was hindered.$^{117}$ At pH< 6.0, the color of the resulting RF gel was yellowish brown; while at pH is between 6.5-7.5, the color of RF gel was darkish red.$^{23,118}$ In addition, the pH of the initial solution also influenced the pore size of RF aerogels. Job et al.$^{23}$ indicated that when the initial solution pH increased from 5.45 to 7.35, the microporosity and surface area of the aerogel samples also increased. More evidences were reported by Hwang and Hyun$^{118}$. They observed that carbon aerogels synthesized with an initial solution pH of 5.5 showed larger differential pore volume compared to that of a carbon aerogel with an initial solution pH of 6.5. Therefore, the pore structure of RF aerogels and derived carbon aerogels can be tailored by changing the pH of the initial RF solution in a specific range.
The molar ratio between resorcinol and catalyst (R/C) was commonly studied by researchers because R/C ratio can determine the element size of the aerogel network and the porosity of the aerogels.\textsuperscript{24, 113, 116, 119-121} Figure 2.6 indicated that both basic and acidic catalysts can accelerate the polymerization reactions of resorcinol-formaldehyde.\textsuperscript{25, 27, 109, 110-116, 122, 123} When using acidic catalyst at pH $< 5$, R/C ratio has an apparent effect on the size of the particles. An increase of the concentration of acidic catalyst led to smaller particles constituting the RF aerogel.\textsuperscript{124} SEM images in Figure 2.7 clearly present such a tendency which was also confirmed by Rao and co-workers.\textsuperscript{125} In the case of basic catalysts, the higher R/C ratio causes longer gelation time. Long gelation time allows the clusters to grow larger before the gel formed, resulting in lower specific surface area but higher mesoporosity.\textsuperscript{28, 114, 126} On the other hand, high basic catalyst concentration (low R/C) results in the smaller clusters because of more nucleation sites in the initial solution.
In 2013, an interesting work was reported by Schwan and Ratke who tried to tailor the flexibility of RF aerogels by adjusting the synthesis conditions. The results indicated that only when R/C = 50, resorcinol to formaldehyde (R/F) ratio = 0.5, resorcinol to water (R/W) ratio = 0.006-0.010 and pH = 5.4-5.6, the RF aerogels were flexible. The flexibility was proposed to result from the chemical structure as well as pore structure. In the specific regime, methylene bridges showed higher inhomogeneity of the positions connecting different resorcinol molecules.

Figure 2.7 SEM images of RF aerogels synthesized with R/C ratio of A: 100/35, B and C: 1300/35, D: 1300/45, E and F: 3/35. Reprinted with permission from Ref. 124.
In addition to the precursor of carbon aerogels, RF gels were used as the template for preparing mesoporous zeolite A. The zeolite precursor diffused into the mesopores of RF wet gels. After aging for more than two weeks, the products were dried and pyrolyzed in oxygen flow to remove the RF aerogels. Mesoporosity and microporosity of the zeolites were confirmed by N\textsubscript{2}-sorption analysis as well as SEM observations. Moreover, Leventis et al. explored the possibility of using RF aerogel as the fuel with CuO as the catalyst. CuO/RF aerogel composite with interpenetrating network burned rapidly in the flame while the neat RF neither sustained the flame nor burned in the flame. The catalytic mechanism of the combustion reaction of RF is shown below.

\[
\text{RF} + \text{CuO} \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Cu}
\]

\[
2\text{Cu} + \text{O}_2(\text{air}) \rightarrow 2\text{CuO}
\]

Figure 2.8 Combustion reaction of RF aerogel catalyzed by CuO nanoparticles.

2.3.2 Polybenzoxazine (PBZ) aerogel

The synthesis of small molecular weight benzoxazine started 70 years ago. In 1944, Holly and Cope first reported the synthesis of benzoxazine. In the 1950s, Burke et al. made significant contributions to the fundamental understanding of the benzoxazine chemistry. In the 1980s, a crosslinked PBZ was developed by Higginbottom using a multifunctional benzoxazine. The properties of PBZ were not reported until 1994 when Ning and Ishida presented their results on the properties of PBZ.

Benzoxazine molecules can be synthesized through combining a phenolic derivative, formaldehyde and a primary amine as the scheme shown in Figure 2.9. The substituents, R
can be aliphatic groups, or substituted benzene rings and R’ includes CH₃, C₂H₅, and benzene.

\[
\text{OH} + R'\text{NH}_2 + 2 \text{CH}_2\text{O} \rightarrow \text{O} \quad \text{R'}
\]

Figure 2.9 Synthesis of benzoxazine resins.

PBZs are obtained by thermally accelerated, cationic ring-opening polymerization (ROP), which typically occurs by heating the purified benzoxazine at temperatures between 160 to 220 °C.¹³⁶ It leads to a polymer with a phenolic structure. However, if the ROP is catalyzed by a nonlabile proton initiator at a relatively low temperature, the polymer shows an arylether structure.¹³⁷ The arylether structure is thermally unstable and can transfer to the phenolic-type at an elevated temperature (Figure 2.10).

Figure 2.10 Cationic ROP of benzoxazine. Redrawn from Ref. 137.
The benzoxazine polymerization is an autocatalytic process. The phenolic structure generated by ROP works as the source of proton and initiates the polymerization.\textsuperscript{138} In addition, the curing kinetics of benzoxazine monomers have been actively studied by researchers.\textsuperscript{139-143} Normally, the mono-functional benzoxazine leads to a linear (or perhaps branched) polymer with the molecular weight on the order of a few hundreds to a few thousands Dalton. The monomers with more than one oxazine rings lead to crosslinked PBZs.\textsuperscript{136}

In the early days of PBZ development, this new class of polymers was thought to be a candidate for replacing the traditional phenolic resins synthesized by condensation chemistry. ROP of PBZ can eliminate almost all the shortcomings appeared in the condensation chemistry approach. Moreover, recent development of PBZ resins revealed that PBZ possesses a number of unique properties. These properties provide PBZ many opportunities to find applications in various fields in addition to be the replacement materials for the existing resins.

In 2009, Lorjai et al.\textsuperscript{7} firstly presented the preparation of PBZ-based organic aerogels and carbon aerogels. In their work, the benzoxazine monomer, which was synthesized from bisphenol-A, aniline, and paraformaldehyde following Ishida’s method\textsuperscript{135}, was dissolved in xylene and then the solution was heated at 130 °C for 96 h. The gels were then dried under ambient condition to obtain the aerogels. The PBZ aerogels were further cured and pyrolyzed to carbon aerogels. The microstructure of both PBZ organic and carbon aerogels are shown in Figure 2.11. The carbon aerogels were characterized to be microporous, exhibiting a specific surface area of about 390 m\textsuperscript{2}/g.
Recently, Mahadik-Khanolkar et al.\textsuperscript{8} described an acid catalyzed synthesis of PBZ aerogel, where the gelation took place at room temperature in 90 min to 5 h depending on the concentration of the solution. They proposed the mechanism of acid-catalyzed polymerization of the benzoxazine monomer as follows. An unconventional structure of PBZ formed because the benzoxazine ring-opening into an iminium ion substitutes at the activated para position of the aniline moiety rather than at the sterically hindered ortho position of bisphenol- A at room temperature.
Figure 2.12 Mechanism of acid-catalyzed polymerization of the benzoxazine. Reprinted with permission from Ref. 8.

Additionally, they proposed the mechanism for oxidative aromatization of PBZ contributing to the high-yield of carbon (Figure 2.13). PBZ organic aerogels and their carbon aerogels show the morphology of aggregation of particles. Similar with Lorjai’s conclusion, the carbon aerogels are microporous with relatively low SSA (348 m$^2$/g- 524 m$^2$/g) compared to the RF-based carbon aerogels (500 m$^2$/g- 800 m$^2$/g). It is worthy to mention that the carbon aerogels prepared in this work show much lower electrical conductivity than the ones prepared from RF aerogels. It may have a severely negative influence on the electrical applications of these aerogels.
Researchers have studied the performance of PBZ aerogel used for removing metal ions from waste water.\textsuperscript{144, 145} Benzoxazine synthesized from bisphenol-A, formaldehyde, and aniline was used in the studies because of its convenient synthesis method. The PBZ aerogel worked as a chelating polymer for various heavy metal ions. Chaisuwan et al. reported that the sorption capacity of PBZ aerogel for metal ions was in the following order: Sn\textsuperscript{2+} > Cu\textsuperscript{2+} > Fe\textsuperscript{2+} > Pb\textsuperscript{2+} > Ni\textsuperscript{2+} > Cd\textsuperscript{2+} > Cr\textsuperscript{2+}, which was related with the Irving-Williams rule and the van der Waals radius.\textsuperscript{144} PBZ aerogel also showed the specific sorption
behavior towards Hg$^{2+}$ in the study done by Taskin et al.\textsuperscript{145} The sorption capacity of PBZ aerogel can be easily regenerated by adding acids which breaks the coordination bonds between Hg$^{2+}$ and PBZ chains.

2.3.3 Polyimide aerogels

Polyimide aerogels were firstly described in a U.S. patent filed by Aspen Aerogel, Inc. in 2002.\textsuperscript{146} Polyimide is synthesized by reactions of aromatic dianhydrides and aromatic diamines or a combined aromatic and aliphatic diamines. The polyimide aerogels composed of aromatic dianhydrides and aromatic diamine were proved to be good carbon aerogel precursors.\textsuperscript{146} Polyimide aerogels synthesized from bifunctional monomers having low crosslinking density resulting in poor mechanical properties. 1,3,5 tris(4-aminophenyl)benzene (TAB), a trifunctional amine was first used by Kawagishi et al. as a chemical crosslinker to synthesize polyimide aerogel with a combination of diamines and dianhydrides.\textsuperscript{32} The flexibility of the aerogels showed strong dependence on the diamine and the dianhydride, for example, pyromellitic dianhydride (PMDA) and p-phenylenediamine (PDA) produced rigid polyimide aerogel while 4,4’-oxydiphthalic anhydride (ODPA) and 4,4’-oxydianiline (ODA) produced flexible polyimide aerogels. Shen et al. synthesized 2,4,6-tris(4-aminophenyl)pyridine (TAPP) as a crosslinker substituting TAB for preparing polyimide aerogels.\textsuperscript{147} The authors proposed that TAPP shows higher stiffness than TAB so that the resulting polyimide aerogels can achieve a good balance between the thermal and dimensional stability. A group of interesting studies were reported about using polyoligomeric silsesquioxane (POSS) molecules with multi-amine groups as the chemical crosslinkers for polyimide synthesis.\textsuperscript{30, 31, 148} Guo et al. used octa-aminophenyl decorated polysilsesquioxane (OAPS) as the crosslinker, 3,3’,4,4’-
biphenyltetracarboxylic dianhydride (BPDA), and various diamines to synthesized polyimide aerogels. The properties of the OAPS cross-linked aerogels exhibited lower shrinkage and lower density compared to the TAB cross-linked aerogels.\textsuperscript{30} The polyimide aerogels composed of BPDA, bisaniline-p-xylidene (BAX), and OAPS showed excellent thermal properties, only losing 1-2\% weight on aging for 24 h at 300 and 400 °C. The thermal conductivity was as low as 14.4 mW/(K·m) and the Young’s modulus was in the ranged of 1.7 MPa to 5.3 MPa.\textsuperscript{31} The hydrophobic polyimide aerogels from 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA), 2,2’-bis(trifluoromethyl)-4,4’-diaminobisphenyl (TFDB) and OAPS were reported by Shen et al.\textsuperscript{148} The incorporation of trifluoromethyl and cyclobutane units offered the polyimide aerogel low polarity and low surface energy. The water contact angle on the polyimide aerogel was around 135°.

However, the mentioned crosslinkers, TAB, TAPP, and OAPS, either are not commercially available or are prohibitively expensive. The price of crosslinkers became a limitation for manufacturing polyimide aerogels in large quantities. Meador and co-workers described an approach to crosslink amine capped oligomers by 1,3,5-benzenetricarbonyl trichloride (BTC).\textsuperscript{149} Although the crosslinking structure is linked by the amide bonds, the results indicated that no obvious decline was found on the thermal stability of the polyimide aerogels compared to the TAB crosslinked samples. On the other hand, modulus from compression was as high as or higher than OAPS crosslinked polyimide aerogels of similar density, while surface areas were significantly higher than the polyimide aerogels synthesized with TAB, OAPS, and TAPP.

Shinko et al. studied the properties of polyimide aerogels with low crosslink density (< 1\%).\textsuperscript{36} It was indicated that all the polyimide aerogels showed excellent thermal stability.
Aerogels prepared with PMDA and 2,2'-dimethylbenzidine (DMBZ) exhibited a surface area of 858 m$^2$/g, much higher than that of polyimide aerogels from BPDA and ODA. It was attributed to the increased surface roughness in the polyimide fibers that constitute the aerogel network. Polyimide aerogels synthesized from PMDA and DMBZ exhibited good optical translucency which may lead to unique applications such as tinted window insulation.

In terms of imidization, some researchers choose thermal imidization by heating the gel to a high temperature (usually over 150 °C) for hours.$^{32,150}$ The polyimide aerogel were found to show relatively lower surface areas than that of polyimide aerogels imidized chemically. Chemical imidization using acetic anhydride and pyridine at room temperature was involved in the synthesis of polyimide aerogels.$^{30,31,34,147,148,151}$ Leventis et al. synthesized the polyimide aerogel via ring-opening metathesis polymerization (ROMP) of a norbornene end-capped diimide.$^{33}$ No imidization took place in the polymerization of the polyimide network as shown in Figure 2.15. The polyimide aerogels were characterized to be mesoporous materials with density ranging from 0.134 to 0.625 g/cm$^3$. The aerogels showed high porosities (90.1%), high surface areas (632 m$^2$/g), high Young’s modulus (288 MPa), and low thermal conductivity (0.031 W/(m·K)).
Figure 2.14 Molecules of dianhydride, diamine, and crosslinker mentioned in this section.

Figure 2.15 Polymerization of bis-NAD via ROMP. Reprinted with permission from Ref. 33.
Polyimide aerogels made from 2,2′-dimethylbenzidine (DMBZ), biphenyl 3,3′,4,4′-tetracarboxylic dianhydride (BPDA), and TAB show a dielectric constant of 1.16. The aerogels were characterized by Meador et al. as the substrate for antennas. The results were compared with commercial materials, indicating that the aerogels exhibited broader bandwidth, higher gain, and lower mass. In addition, another type of polyimide aerogels which containing fluorinated blocks showed potential for lightweight antennas for aeronautic and space applications. The dielectric constant of the aerogels synthesized from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and ODA could reach as low as 1.08. It was revealed that increasing the amount of 6FDA resulted in a concomitant decrease in the dielectric properties. The polyimide aerogels with the lowest bulk density and lowest dielectric constant still have fair compression modulus (4–8 MPa).

2.3.4 Polyurea aerogels

Polyurea aerogels were first mentioned in a U.S. Patent 5484818. The inventors presented a series of the organic polyisocyanate based aerogels including polyurea aerogels, polyurethanes, polyallophanate aerogels, etc. Lee et al. synthesized polyurea aerogels by reacting Jeffamine with ethylene diphenyl diisocyanate (MDI) catalyzed by triethylamine (TEA). The authors studied the relationship between the bulk density and thermal conductivity of the polyurea aerogels. The samples with a bulk density of 0.16 g/cm³ showed the minimum thermal conductivity of 13 mW/(m·K) which is comparable with RF aerogels and silica aerogels. The PU aerogel with low density (0.06 g/cm³) exhibited a fibrillar morphology while the one with a density of 0.1 g/cm³ exhibited a denser and particulate morphology. Lee et al. mentioned that the large pores in the fibrillar morphology may increase the gaseous and radiation thermal conductivity contribution so
that the thermal conductivity of the aerogel goes up. But increasing the solid content also increases the solid conduction heat transfer. Overall, polyurea aerogels with the best thermal insulation property need to be developed with more optimization of processing methods.

Morphology change due to the changes in concentration was also observed in the polyurea aerogel work done by Leventis and co-workers.\textsuperscript{4} Trifunctional isocyanate molecules with water were used to synthesize the polyurea with high crosslinking density. The functional group NCO reacts with water to produce NH\textsubscript{2} which reacts further with yet-unreacted NCO, yielding urea bonds. Polyurea aerogels with a wide range of bulk density (0.016─0.055 g/cm\textsuperscript{3}) were prepared and characterized. It is clear that the network of polyurea aerogels was constituted of polymer fibrils when the bulk density is no more than 0.13 g/cm\textsuperscript{3}. However, it became the aggregation of globlues as the density reached to a value of 0.19 g/cm\textsuperscript{3} (Figure 2.16). Two morphologies were formed because of distinct aggregation mechanisms, where low concentration preferred a reaction limited aggregation to form the fibers, while high solution concentration led to cluster-cluster crowding. Young’s modulus of the polyurea aerogel with the highest bulk density was 300 MPa which is comparable to the polymer reinforced silica aerogels. The polyurea aerogels were proved to have high strength and high acoustic attenuation capabilities. Polyurea aerogels synthesized from Desmodur RE exhibited high carbon yield due to its high aromatic ratio.

Shinko et al. used MDI, ODA or DMBZ, and TAB to synthesize a group of polyurea aerogels varying the number of repeat unites (\(n\)) of polyurea oligomers.\textsuperscript{5} It was indicated that \(n\) determined the gelation time- lager \(n\) led to longer gelation time. When using ODA as the diamine, larger \(n\) caused more shrinkage due to the higher extent of hydrogen
bonding in the aerogels. Moreover, $n$ has direct impact on the compression modulus of the aerogels. It is easy to understand that smaller $n$ corresponds to higher portion of crosslinker (TAB) in the polyurea networks. Higher crosslinking density in turns results in a higher compression modulus of the aerogels.
Figure 2.16 SEM images and N$_2$-sorption isotherms of polyurea aerogels with different solid contents. Reprinted with permission from Ref. 4.
2.3.5 Syndiotactic polystyrene aerogel

Syndiotactic polystyrene (sPS) presents a very complex polymorphic behavior, and is able to form co-crystalline structures with a number of low-molecular-mass guest molecules. Highly porous aerogels are obtained after solvent extraction of the guest molecules under supercritical conditions.

sPS aerogels with microporous δ-crystalline structure was first reported by Daniel et al. in 2005.9 The gelation of δ-form sPS in solvents relies on the intermolecular physical bonding which forms simultaneously when the solution cools down. The gel collapses by heating over a critical temperature. Accordingly, sPS gel is a type of thermos-reversible gels. sPS aerogels can be obtained by exchanging the original solvents, such as chloroform, toluene, tetrahydrofuran, with ethanol and subsequently supercritical drying.9, 154-162 A typical SEM image of sPS aerogel is shown in Figure 2.17 (c). The sPS δ-aerogel shows fibrous network with void which are defined as macropores. The elements of the aerogel-nanofibrils- are characterized to contain micropores with diameters less than 2 nm.9 The micropores were formed by extracting the solvent molecules from the sPS-solvent co-crystal structure. Accordingly, sPS aerogel have absorption capacity for several small molecules, for example, dichloroethane (DCE), which are able to fill into the nanocavities in the δ-form crystalline domains.162 Therefore, sPS δ-aerogel is suitable for removing the volatile organic compounds (VOCs) from water or air. Its high sorption capacity and fast sorption kinetics compared to other forms of materials (film, powder) makes nanoporous aerogel a good candidate for cleaning of polluted-water and for purification of air.9, 162
sPS is relatively chemically inert due to its crystalline form and aromatic hydrocarbon structures. As of now, only two reports were published on chemically modified sPS aerogel. Wang et al. studied the influence of the degree of sulfonation on the properties of sulfonated sPS aerogels.\textsuperscript{158} The authors demonstrated that sulfonated sPS aerogel took longer time to gel due to the sulfonic acid groups disturbing the arrangement of sPS chains during crystallization. Differential scanning calorimetry (DSC) results suggested that $T_g$ increased from 98 °C of neat sPS to 106 °C of 5% sulfonated sPS and to 140 °C of 22% sulfonated sPS. However, the melting peak disappeared on the DSC curves of 22% sulfonated sPS resulting in a gelation time of 3 days, much longer than that of neat sPS solution of the same concentration (20 min). Sulfonation also reduced the BET surface area of the aerogels,
e.g. a reduction of 30% related to 10 mol% sulfonation level. In spite of the disadvantages associated with sulfonation, sulfonic acid groups can work as the active sites on the polymer chains to induce the in situ polymerization of polyaniline. A uniform coating layer of polyaniline formed on the nanofibrils of sPS network has the potential of expanding the applications of sPS aerogels to supercapacitors or macroporous–mesoporous membranes for fine charged particle separation.

Venditto et al.\textsuperscript{160} also functionalized sPS aerogels by solid state sulfonation. Amorphous phase of the aerogel is hydrophilic due to the sulfonic acid groups. On the other hand, crystalline phase of the aerogel is hydrophobic and is able to adsorb VOCs in the micropores. The water uptake rate and the capacity of sulfonated sPS aerogels were dramatically improved associated with the hydrophilic phase in the sulfonate sPS aerogels. In the 1,2-dichloroethane (DCE) sorption measurements, the DCE apparent diffusivity constant for a 10 ppm aqueous solution and a sulfonated aerogel is more than 3 orders of magnitude larger the DCE diffusivity constant for the unsulfonated aerogel with the same porosity. Thus, the semicrystalline sPS δ-aerogel with 5% to 10% sulfonation was found to be useful for water purification, particularly absorbing VOC molecules from water.

sPS aerogel composites are relatively easier to prepare by physically mixing sPS with other polymers during the thermo-reversible gelation process. Wang et al. presented a method for tailoring the hydrophilicity of sPS aerogels by adding polyethylene oxide (PEO) of different molecular weights. PEO was dissolved together with sPS in THF and formed a homogeneous solution when heated at 110 °C. Gelation of sPS is induced by cooling the solution at ambient condition. The gels were dried under supercritical condition to obtain aerogels. The results revealed that the concentration and the molecular weight of PEO as
well as the cooling rate during gelation determines the size and the morphology of PEO domains in sPS aerogel matrix, and eventually controls the pore structures and the surface energy. The effects of PEO on the morphology and surface energy of sPS aerogel are shown in Figure 2.18. In case I, PEO of low molecular weight or low concentration was invisible in the SEM image of sPS aerogel. The resulting aerogels showed superhydrophobic surfaces presenting the ‘lotus effect’, which is similar to neat sPS aerogels. In case II, PEO at higher concentration or with higher molecular weight forms the phase separated domains yielding new hydrophilic macropores (>10 μm) in the aerogel structures. These macropores contributed to superhydrophobic surfaces with the ‘petal effect’. In case III, higher molecular weight and higher concentration of PEO caused irregular surfaces with large PEO pieces (>100 μm).

Figure 2.18 Effects of PEO with various concentrations and molecular weights on the morphology and surface energy of sPS aerogels. Reprinted with permission from Ref. 157.
Poly(2,6-diphenyl-1,4-phenylene oxide) (PPO) was incorporated into sPS aerogel matrix by Longo et al. in order to obtain high efficiency pollutants sorbent.\textsuperscript{159} PPO is a porous material for trapping many tapes of volatiles.\textsuperscript{163-166} PPO has good solubility in \( \text{CH}_2\text{Cl}_2 \) and benzene which are solvents for preparing sPS \( \delta \)-from gels. PPO/sPS gels were obtained by thermo-reversible gelation of sPS blended with PPO. The aerogel monoliths were recovered after supercritical drying. The PPO/sPS aerogels exhibited many advantages as sorbent materials with respective to the commercially relevant PPO powders. First, the aerogel monoliths showed higher specific surface areas than PPO powders contributed by the sPS nanofibrils. Second, CCl\(_4\) uptake from the vapor phase was nearly double than for the PPO powders. Third, the aerogel composites can uptake much more CCl\(_4\) from diluted aqueous solutions than that of neat sPS aerogels (8 wt% vs. < 0.1 wt%).

Figure 2.19 Schematic illustration of sPS/silica hybrid aerogel preparation procedure. Reprinted with permission from Ref. 155.

Wang et al. reported a class of sPS/silica hybrid aerogels using an innovative method called growing a gel in a gel (Figure 2.19).\textsuperscript{155} sPS gel was first prepared followed by exchange of THF in the gel with ethanol. Afterwards, the silica sol was allowed to diffused into the sPS network and the silica network was formed by an \textit{in situ} gelation inside the sPS gels. The sPS/silica hybrid aerogels were recovered by supercritical drying. It is well known that silica aerogels prepared by acid-base catalyzed method show high
mesoporosity and BET surface areas. Therefore, the surface areas increased in the hybrid aerogels with respect to the neat sPS aerogels, by factors of roughly 1.5 to 2.0 depending on the concentration of sPS solutions. The SEM images and TGA tests indicated that silica formed continuous network inside the pores of sPS framework. The resulting hybrid aerogels exhibited the advantages of the parent materials, such as structural stability towards moisture, a combination of high compression strain and high compression modulus, and fast crude oil sorption kinetics.

2.4 Laser light scattering

Scattering techniques are widely known to characterize the solutions of particles having sizes ranging between 1 nm to 1 µm. In scatterings, as shown in Figure 2.20, an incident beam ($k_0$) with a radiation wavelength ($\lambda$) hits the sample. Subsequently, a scattered wave vector $k$ is generated and is detected by the collector placed at a scattering angle of $\theta$. The relevant scattering vector $q$ can be calculated as by subtracting $k_0$ from $k$ as $q = (4\pi/\lambda) \sin(\theta/2)$.

![Figure 2.20 A schematic representation showing basic principle of the scattering techniques.](image)

Figure 2.20 A schematic representation showing basic principle of the scattering techniques.
Different radiation sources, including laser light, X-ray, neutron, and γ-ray, covered different regions of the principal applications corresponding to their momentum-transfer and energy-transfer.\(^{167}\) Since most of the polymer colloids have the sizes in the range of hundreds of nanometer, laser light scattering (LLS) will be the ideal technique to measure the dimensions of particles in polymer-related solutions. LLS often involves determination of optical line-shapes and frequency shifts as well as their angular variations and depolarizations. Therefore, LLS can be used to monitor the evolution of dimensions and shapes of the nanoparticles in solutions.\(^{168-172}\) Operations of LLS can be done in dynamic light scattering (DLS) and static light scattering (SLS), of which the theories are introduced below.

2.4.1 Static Light Scattering (SLS)

For very dilute solutions of small scattering particles, for example, nanoparticles or polymer chains of size smaller than \(\lambda/20\), the scattering intensity is independent of the scattering angle. In this case, scattering from the density fluctuations of the solvent itself is ignored. The intensity of scattering only depends on the scattering power of the dissolved particles, their mass concentration, and the osmotic pressure. Rayleigh scattering is applicable when the scattering centers are much smaller than the wavelength of the radiation. Based on the Rayleigh equation, equation (1) was derived to describe the relation between the scattered intensity form the sample and the intensity of the incident light,

\[
\frac{i}{I} = \frac{4\pi^2 n^2 (\frac{dn}{dc})^2 c (1 + \cos^2 \theta)}{N_A \lambda^4 r^2 (\frac{1}{M} + 2A_2 c)}
\]  

(1)
In equation (1), \( i \) is the intensity of solution, \( I \) is the intensity of the incident light, \( n \) is the refractive index, \( c \) is the concentration, \( M \) is the weight average molecular weight, \( A_2 \) is the solvent interaction parameter, \( N_A \) is Avogadro’s number and \( r \) is the radius of the particle. By introducing the Raleigh ratio \( (R_\theta) \) in equation (2), and the constant \( K \), equation (1) can be rewritten as equation (4).

\[
R_\theta = \frac{ir^2}{I(1+\cos^2\theta)} \tag{2}
\]

\[
K = \frac{4\pi^2n^2(dn/dc)^2}{N_A\lambda^4} \tag{3}
\]

Therefore,

\[
\frac{Kc}{R_\theta} = \frac{1}{M} + 2A_2c \tag{4}
\]

As the particle sizes grow, the scattered intensity is no longer independent of the scattering angle. Interference of the scattered light occurs as a result of the multiple locations that the incident radiation can hit the sample. The interference causes the scattering intensity to be angular dependent, thus a new term, also called the particle form factor \( P(\theta) \), should be added to equation (4) to describe the angular dependence, as shown in equation (5)

\[
\frac{Kc}{R_\theta} = \frac{1}{P(\theta)} \left[ \frac{1}{M} + 2A_2c \right] \tag{5}
\]

where,

\[
\frac{1}{P(\theta)} = \left( 1 + \frac{q^2R_\theta^2}{3} \right) \tag{6}
\]
with $R_g$ being the radius of gyration of the particles in solution. Plotting $Kc/R_\theta$ vs. $\sin^2(\theta/2) + 2A_2c$ at different concentrations and different scattering angles gives a Zimm plot. We need to perform two extrapolations, to zero scattering angle ($\theta = 0$ or $q = 0$) and to zero concentration ($2A_2c = 0$), and the result gives a value of $1/M_w$. Furthermore, angle extrapolation to $c = 0$ gives the information about $R_g$, while concentration extrapolation to $\theta = 0$ gives information regarding the solvent interaction parameter $A_2$. An example of a Zimm plot is shown in Figure 2.21.

![Zimm plot](Image)
2.4.2 Dynamic Light Scattering

If the scattering particles are moving, fluctuations in the scattered intensity with time are directly reflecting the Brownian particle motion of the scattering particles, caused by thermal density fluctuations of the solvent. The detected scattered intensity measured at a given scattering angle is varied caused by the change in the interference pattern with changing interparticle position. To quantitatively analyze the particle mobility by light scattering, it is helpful to express the scattering intensity fluctuations in terms of correlation functions. A multichannel digital correlator is used in order to detect the small changes in the frequency resulting from Brownian motion and to generate a correlation function.\textsuperscript{174} The \textit{CONTIN} algorithm is then used to analyze the correlation function to yield information regarding the characteristic linewidth ($\Gamma$), which is related to the particle’s diffusion coefficient ($\Gamma = Dq^2$, where $D$ is the diffusion coefficient). The Stokes-Einstein equation can then be used to convert the diffusion coefficient to hydrodynamic radius ($R_h$) of the particles,

$$R_h = \frac{k_B T}{6 \pi \eta D_0} \quad (7)$$

where $k_B$ is the Boltzmann constant, $T$ is the temperature of the solution, and $\eta$ is the viscosity of the solvent.\textsuperscript{174} $D_0$ is the diffusion coefficient at zero scattering angle and zero concentration. $R_h$ is the radius of an equivalent sphere, experiencing a friction $f$ identical to that of the real scattering particle during its Brownian motion in solution. The real scattering particle itself is not necessarily a sphere.
2.4.3 The ρ-ratio

The ρ-ratio is an experimental quantity derived from a combination of the particle size characteristics, $R_h$ and $R_g$, determined from static and dynamic light scattering measurements. The ρ-ratio provides an important indication of the scattering particle topology especially for comparatively small particles (size 10–100 nm).

$$\rho - \text{ratio} = \frac{R_g}{R_h} \quad (8)$$

When all of the mass of the particle is distributed on the surface, the $R_h$ is equivalent to the $R_g$. When the $R_g/R_h = 0.77$, solid spheres are expected to exist in solution. When $R_g > R_h$, cylindrical, rod-like or anisotropic structures are expected in solution. Figure 3.3 shows a summary of the different shapes and their corresponding shape factors.\textsuperscript{175}

![Solid Sphere](image)

$R_g = 0.77 \ R_h$

![Hollow Sphere](image)

$R_g \sim R_h$

![Rod](image)

$R_g > R_h$

Figure 2.22 The shape factor of the corresponding particle shapes in solutions.
2.5 Polyurea/polyurethane foam

Traditional polyurea/polyurethane foams were commercialized and widely used in our daily life. We briefly present the foam preparation as well as their properties in this section.

2.5.1 Foam formation process

Generally, the polymer foaming process usually starts from dispersing or generating a gas throughout a fluid polymer phase. The source of the gas can originate from polymerization, thermal decomposition of the additives, auxiliary blowing agent vaporization, or blending/dissolution of a liquid. A uniform polymer fluid/gas mixture is crucial for obtaining high quality foam structure.\textsuperscript{176} This uniform foam formation can be controlled by system pressure and temperature.

Most foam system was designed with nucleating agents assisting controlled nucleation of the bubbles, and seeding for desired cellular structures.\textsuperscript{177} Therefore, bubble initiation occurred by heterogeneous nucleation when a second phase allows the bubbles to form at a liquid-liquid or solid-liquid interface.

Bubble growth is promoted from diffusion of gas into the nucleated bubbles. Additionally, the heat generated also play a large role in expanding the gas in the liquid to form the desired cellular morphology.\textsuperscript{178} The bubbles are spherical in shape in the beginning stage. As the bubbles grow to the point of spatially interfering with each other, the bubbles begin to restrict each other’s growth. The liquid phase is forced to accommodate the shape change, staying around and between the developing polyhedral, forming the lamellae and plateau borders as it is shown in Figure 2.23.
Close-cell foams formed when the lamellae are strong enough to withstand rupture at the maximum foam rise and to keep the dimension stable. The gas is permanently trapped within the foam. Open-cell foam can be formed when the lamellas thins out and opens up, while the strut is strong enough to hold the structure, leading to formation of interconnected pore structure.

2.5.2 Foaming mechanism of polyurea/polyurethane foams

One of the most appealing attributes of polyurea/polyurethane (PU) is its ability to be turned into a foam. Typically, the PU foaming process is accomplished with the polymerization of polyisocyanates and polyols in the presence of catalysts, surfactants, blowing agents, etc. The presence of water leads to the formation of urea and carbon dioxide. It proceeds through the formation of a thermally unstable carbamic acid, which is decomposed to give carbon dioxide and an amine functionality, as it is shown in Figure
2.24. The produced amine functionality can react with other isocyanate groups to form a disubstituted urea linkage (Figure 2.25).

\[
\text{R-N=C=O} + \text{H}_2\text{O} \xrightarrow{\Delta} \left(\text{R-N=C(OH)}\right) \rightarrow \text{R-N-O-C=O} \rightarrow \text{R-N-H} + \text{CO}_2
\]

Figure 2.24 Gas generation reaction for PU foaming.

\[
\text{R-N=C=O} + \text{R'}-\text{NH}_2 \xrightarrow{\Delta} \text{R-N-C(=O)-N-C(OH)R'}
\]

Figure 2.25 Formation of urea linkages during PU foaming.

The generated carbon dioxide from water-isocyanate reaction provides the primary blowing mechanism for PU foaming. However, some PU foam products require the use of auxiliary blowing agents to achieve desired foam density. These added blowing agents are materials that generate gases as a result of physical transformations. Chlorofluorocarbons (CFCs) have been utilized to create foam structures because of its noncombustibility, low diffusion coefficient, and lower thermal conductivity. However, environmental concerns regarding ozone depletion have made this a problem. As an alternative to CFCs, volatile organic compounds (VOCs) were also used as blowing agents. But they are flammable and still have negative impacts on the ozone layer. The studies on foaming behavior using inert gas such as carbon dioxide\textsuperscript{179} and nitrogen\textsuperscript{180} were also reported. Carbon dioxide is able to produce good foam structure because of its higher solubility in polymers compared to other
gases. But it will affect foam thermal insulation property due to its high thermal conductivity.

2.5.3 Structure and properties of PU foams

Due to the versatility of PU chemistry, the selection of different raw materials results in the final PU foam structure and property to vary significantly. The PU foam can be classified into closed-cell foams and open-cell foams depending on the connectivity of the cells. The typical morphology of open cell and close-cell foams is shown in Figure 2.26. Closed cell foams consist of the blowing agent permanently locked into place during the curing of the foam. The trapped gas increases the insulation capability of the cured foam. The cured foams are usually rigid foams with a medium density in order to lock in the gas bubbles. Open cell foams with a high percentage of open-cell windows feel soft and allow air to flow through so that they are comfortable when used in seat cushions or mattresses and as sound absorbing materials.

Figure 2.26 Morphology comparison of (a) open-cell and (b) closed-cell PU foams.$^{181}$ Reprinted with permission from Ref. 181.
A mechanisms regarding PU foam cell opening was demonstrated by Zhang et al.\textsuperscript{182} It is reported for a variety of PU formulations, the onset of cell opening always occurs several seconds after the urea phase separation, and the timing does not depend on the structure of the surfactant.\textsuperscript{183, 184} This implies that the cell opening is triggered by the urea phase separation. The foam matrix after urea phase separation exhibits extensional thinning behavior, which causes local stretching of the thinner part of the cell window and induces cell opening. The cell window affects film rupture times for individual cell windows and results in cell windows in different states. For example, some windows are totally missing, some leaves torn-off films, some with a pin hole, and some are still keep closed.\textsuperscript{181}
POLYBENZOXAZINE AEROGELS WITH CONTROLLABLE PORE STRUCTURES

3.1 Introduction

Aerogels are three-dimensional highly porous networks of solids with the pores filled with air. They are obtained from the corresponding precursor gels by replacing the liquid with air.\textsuperscript{9, 185-189} The precursor gels are synthesized via thermo-reversible gelation process\textsuperscript{9, 185, 188, 189} or by sol-gel chemistry.\textsuperscript{185-187} It is interesting to note that aerogels are open-celled materials with micro-, meso-, or macropores with pore sizes respectively less than 2 nm, 2-50 nm, and greater than 50 nm and offer extremely high specific surface area.\textsuperscript{187}

In last two decades, carbon aerogels received considerable attention triggered by its micro- and meso-porous carbon network structures, excellent electrical conductivity, and widespread application potential in sorption, catalysis, acoustic/thermal insulators, and electrode materials. In 1989, first carbon aerogel was prepared via pyrolysis of organic aerogel synthesized from condensation of resorcinol-formaldehyde (RF).\textsuperscript{2, 190} Recently, researchers reported nitrogen-doped (N-doped) carbon aerogels with superior performance as CO\textsubscript{2} absorbent\textsuperscript{46} and as electro-catalyst for oxygenreduction reactions.\textsuperscript{47, 48} Researchers demonstrated several methodologies to prepare carbon aerogels with nitrogen atom doping in the carbon network. For example, Wohlgemuth et al. mixed 2-pyrrol-carboxaldehyde as the nitrogen source into the organic carbon precursor before gelation. The wet gels were
then dried to obtain organic aerogels. The organic aerogels were then carbonized under inert gas atmosphere during which nitrogen atoms form C-N bonds to form N-dopant in the carbon matrix.\textsuperscript{191} A number of similar works that mixing various nitrogen sources, such as melamine,\textsuperscript{192} urea,\textsuperscript{193} into carbon precursors have been reported in current literature.\textsuperscript{194, 195} An alternative way is to derive carbon aerogel from nitrogen containing carbon precursor. Benzoxazine (BZ) was exploited by many researchers in synthesis of N-doped carbon materials using polybenzoxazine (PBZ) as the precursor.\textsuperscript{6-8, 196} 

Polybenzoxazines represent a class of phenolic resins with a number of unique characteristics, such as high mechanical strength, near-zero shrinkage upon polymerization of its monomer, and high char yield.\textsuperscript{137} Interestingly, ring-opening polymerization of BZ in solvents leads to gelation and formation of three-dimensional polymer networks. Lorjai et al. first reported the synthesis of PBZ gels by thermally-induced ring opening polymerization of BZ in xylene at 130 °C.\textsuperscript{7} Recently, Mahadik-Khanolkar et al.\textsuperscript{8} published a new method for preparation of PBZ gels at room temperature by using hydrochloric acid as the catalyst of cationic ring opening polymerization. The scanning electron microscopy images revealed that the corresponding aerogels consisted of spherical polymer particles as the building block and that the diameter of spherical particles reduced with an increase in the concentration of BZ in solution.

In this section, we present an alternative method of preparation of PBZ gels in various solvents using p-toluenesulfonic acid (TSA) as the catalyst and study the effects of polymerization temperature and the type of solvent on pore structure, porosity, and surface area of PBZ aerogels. Benzoxazine monomer used in this work was synthesized from bisphenol A, aniline, and paraformaldehyde.\textsuperscript{135} The mechanism of ring-opening
polymerization of BZ into PBZ in the presence of TSA was proposed by Chutayothin and Ishida\textsuperscript{197} as shown in Figure 3.1. The addition of TSA (2\% w/w of BZ) to a solution of BZ in dimethyl sulfoxide (DMSO) (0.275 g/mL BZ) reduced the time of gelation to approximately 10 min at 130 °C. In comparison, the time of gelation was 12 h at 130 °C without any catalyst.\textsuperscript{7,8} It is noted that the gel time is a function of specimen size and is dependent on the speed of heat transfer from the heating medium. In this work, the gel time is reported for a solution of 10 g at a fixed concentration of 0.275 g/mL of BZ. Details of sample preparation method are provided in the Experimental section.

Figure 3.1 Possible cationic polymerization of PBZ catalyzed by TSA.\textsuperscript{197} Redrawn from Ref. 199.
3.2 Experimental

Materials used are listed in this section. In addition, the details of sample preparation and characterization are shown as following.

3.2.1 Materials

4,4’-isopropylidenediphenol (bisphenol A), paraformaldehyde (96%), aniline, p-toluenesulfonic acid monohydrate (TSA•H₂O), dimethyl sulfoxide (DMSO) were obtained from Sigma-Aldrich. All reagents and solvents were used as received.

3.2.2 Synthesis of benzoxazine monomer

Bisphenol A, aniline, and paraformaldehyde (molar ratio of 1:2:4) were added to a beaker and placed in a preheated oil bath at 130 °C. The ingredients were mixed for 1 h and the mixture turned into yellow, viscous liquid. The products solidified upon cooling to room temperature and were ground into powder form for further use.

3.2.3 Preparation of polybenzoxazine aerogel

0.5 g benzoxazine (BZ) monomer powder and 0.01 g TSA were added in 1.82 mL solvent and stirred at room temperature for 15 min to obtain BZ sol (0.275 g/mL). The BZ sol was placed inside an oven at two temperatures – 90 °C and 130 °C – to obtain the gel. All organogels were aged at the gelation temperature for duration of four times the gel time. The aged organogels were washed in acetone four times over a period of 12 h. The washed gels were dried under supercritical condition in carbon dioxide. Photograph of the PBZ aerogels are shown in Figure 3.2.
3.2.4 Determination of gel time

The gel time of BZ sols was determined using Cole-Parmer basic viscometer. The viscosity of 10 g sol kept at the gel temperature in an oil bath was monitored over a period of time. The gel time was determined as the time when the viscosity ($\eta$) increased dramatically. This was achieved by plotting $1/\eta$ vs. time and noting down the time as the quantity $1/\eta$ became negligibly small.

![Figure 3.2 Photograph of PBZ aerogels.](image)

3.2.5 Characterization

The morphology of aerogels was probed using scanning electron microscopy (SEM; JEOL JSM5310) with operating voltage 8 kV. Brunauer–Emmett–Teller (BET) surface area and pore size distribution of aerogel specimens were obtained from N$_2$-sorption isotherms at 77 K, analyzed using a Micromeritics Tristar II 3020 analyzer. The aerogel
specimens were sectioned and placed in designated chamber followed by degassing at 60 °C for 12 h before collecting data.

The bulk density $\rho_b$ of aerogels was obtained from the weight and volume of cylindrical aerogel specimens. The skeletal density $\rho_s$ was measured using an Accupyc 1340 helium pycnometer (Micromeritics). The skeletal density can be used in conjunction with the bulk density to calculate porosity $p$. The diameter shrinkage $\delta_d$ was determined from the difference of diameter of the aerogel ($D$) and the diameter of the corresponding gel specimen before supercritical drying ($D_0$). The bulk density ($\rho_b$), porosity ($p$), and diameter shrinkage ($\delta_d$) of the aerogel specimens were calculated using the following relationships:

$$\rho_b = \frac{4m}{\pi D^2h} \quad (9)$$

$$p = \left(1 - \frac{\rho_b}{\rho_s}\right) \times 100\% \quad (10)$$

$$\delta_d = \left(1 - \frac{D}{D_0}\right) \times 100\% \quad (11)$$

Infrared (IR) spectra were recorded on a Brucker FT-IR Alpha spectrophotometer using a Platinum ATR accessory. Attenuated Total Reflection (ATR) was conducted with Bruker Platinum ATR. The aerogel samples were ground and pressed under the probe for testing.

$^{13}$C CP MAS experiments were performed on Bruker Avance III 300 NMR spectrometer equipped with a 4 mm double resonance VT CPMAS probe. The $^1$H and $^{13}$C frequencies were 300.1 and 75.5 MHz, respectively. The magic angle spinning (MAS) was set to 12000 ± 5 Hz to eliminate chemical shift anisotropy. The $^1$H 90° pulse length was set to 3.75 μs. High-power two pulse phase modulation (TPPM) $^{198}$ decoupling with a field strength of 65 kHz was applied to $^1$H channel during acquisition. The cross-polarization (CP) contact time
and recycle delay were 1.5 ms and 2 s. Each spectrum was obtained by 4k scans at ambient temperature. The chemical shift was referenced to CH signal of adamantine (29.46 ppm) as an external reference.

3.3 Results and discussions

Figure 3.3 presents the states of BZ solutions before and after heating at 130 °C. In Figure 3.3(a), the top row presents the images of the solutions and the bottom row shows that the materials turned into gels.

3.3.1 Study of gelation process

In Figure 3.3(b), the states of the solution at three different times are shown. It is noted that the color of the materials became much darker once the gels were formed. The gelation process took different times depending on the type of the solvents.

Figure 3.3 Column (a): PBZ gels formed in different solvents by heating at 130 °C in solvents (left to right) DMSO, DMA, and NMP. Column (b): State of the liquid by heating BZ/DMSO solution at 130 °C for 0 min, 3 min, and 5 min.
Figure 3.4 shows the viscosity vs. time plots of BZ sols allowed to gel at 90 °C and 130 °C. The gel time was recorded as the time when the viscosity diverged. The gel times were found approximately 580 s for material BZ/DMSO solution heated at 130 °C, 59 min for BZ/DMSO solution heated at 90 °C, 63 min for BZ/NMP solution heated at 130 °C, and 218 min for BZ/NMP solution heated at 90 °C. The results imply that BZ formed gels the quickest in DMSO, e.g., in approximately 10 min compared to 63 min in NMP at 130 °C. Intuitively, the gel time shortened at higher temperature, e.g., gels were formed in 59 min at 90 °C and in 10 min at 130 °C in DMSO. The gels were solvent exchanged with liquid carbon dioxide and dried under supercritical condition of carbon dioxide to obtain the aerogels. The specimens are designated as "PBZ-s-T", where "s" represents the solvent used and "T" represents the gelation temperature. For example, the specimen PBZ-DMSO-
130 refers to PBZ aerogel synthesized in DMSO solvent at 130 °C. The aerogels were not subjected to further curing.

3.3.2 Skeletal frameworks of PBZ aerogels

The aerogels reported in literature to date can be classified into three skeletal frameworks – (1) aggregates of spheres, e.g., those found in silica aerogels\textsuperscript{15,199} and some polymeric aerogels, (2) fibrillar networks, e.g., the crystalline strands found in syndiotactic polystyrene aerogel\textsuperscript{9,156} or the phase separated amorphous polymer strands in polyimides, polyurea and polydicyclopentadiene,\textsuperscript{3,4,31,200,201} or (3) aggregates of layered structures, e.g., the ones found in clay aerogels.\textsuperscript{10} Intuitively, these frameworks offer differences in specific surface area, pore size, and mechanical strength.\textsuperscript{4,34,156} In this study, the skeletal framework of PBZ aerogels was revealed using scanning electron microscope (SEM) images. As highlighted in Figure 3.5, PBZ-DMSO-130 and PBZ-DMA-130 aerogels are composed of aggregates of spheres of diameters 43.5± 3.0 nm and 49.2 ± 6.9 nm, respectively. However, the primary frameworks of PBZ-NMP-130 aerogel are polymer strands of diameter of 32.1± 3.3 nm, shown in Figure 3.5c. The diameter values quoted above represent the averages of 10 individual measurements taken at random locations of the corresponding SEM images. Recall that these frameworks originated during gelation via polymerization-induced phase separation of the polymer. We now present a plausible argument to explain the formation of different building blocks identified in Figure 3.5 by making two general statements. First, a strand-like morphology as in Figure 3.5c can result only if phase separation occurred via spinodal decomposition. Second, the morphology with spherically connected domains, as in Figure 3.5a and Figure 3.5b, can result from nucleation and growth, spinodal decomposition, or a combination of spinodal
decomposition followed by nucleation and growth. Yamanaka and Inoue\textsuperscript{202} studied reaction-induced phase separation of crosslinked epoxy domains in poly(ether sulphone) and identified that interconnected globular domains of epoxy resulted from spinodal decomposition. In light of rapid gelation observed in our experimental system, as reflected from the large values of slope of viscosity vs. time plots in Figure 3.4, we believe that phase separation proceeded via spinodal decomposition and yielded co-continuous solid network structures. The viscosity vs. time slopes around gel time varied from 5-400 cP/s in our system. The just phase-separated domains quite possibly continued to evolve with time, e.g., via phase coarsening or shape relaxation into spherical globules. A thorough investigation is needed to determine the set of factors that govern the morphological differences seen in Figure 3.5. Investigation of the phase separation mechanism during the gelation of PBZ in different solvents will be presented in Chapter IV.

Figure 3.5 SEM images at 20,000× and 70,000× magnification of aerogel specimens (a) PBZ-DMSO-130, (b) PBZ-DMA-130, (c) PBZ-NMP-130.
3.3.3 Characterization of chemical structure

The data from infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy are now analyzed. The objective is to evaluate if the nature of polymer chains differed significantly from what is published literature or significant chain fusion occurred at higher reaction temperature. These are important considering that TSA was used as the catalyst and that polymerization was carried out 90 °C and 130 °C in different solvents. The curves in Figure 3.6 present the IR spectra of BZ and PBZ, which were analysed in reference to the existing IR data on ring-opening polymerization of BZ.\textsuperscript{8, 203, 204} All specimens show broad absorbance in the range 3090 cm\(^{-1}\)-3465 cm\(^{-1}\) which are attributed to stretching of the phenolic O-H groups. In addition, the peak at 940 cm\(^{-1}\) associated with the oxazine ring of BZ monomer is weak in all PBZ specimens. The peaks at 1230 cm\(^{-1}\) and 1029 cm\(^{-1}\) due to asymmetric stretching of Ph-O-C groups are absent and the peak due to phenolic Ph-O group at 1248 cm\(^{-1}\) \textsuperscript{204} is visible. Thus, the polymer chains obtained at different temperatures and using different solvents do not show distinctive features. However, the spectra in Figure 3.6 indicate that the gelation temperature had some influence on incorporation of the aniline moieties present in BZ monomer. In this context, the absorbance peaks at 693 cm\(^{-1}\) and 750 cm\(^{-1}\) in the spectra of BZ monomer are attributed to out-of-plane (OOP) C-H bending vibrations from dangling aniline.\textsuperscript{205} It is seen that the peak at 693 cm\(^{-1}\) became much weaker for PBZ-DMSO-90 and PBZ-NMP-90 aerogel specimens and nearly disappeared in aerogel specimens PBZ-DMSO-130 and PBZ-NMP-130. Thus, we infer that the aniline moiety participated in the gelation process of BZ at both 90 °C and 130 °C and that its incorporation into gel structure was complete at 130 °C.
Figure 3.6 Infrared (IR) spectra of BZ monomer and PBZ aerogels.

Solid-State NMR (SS-NMR) is a useful tool to reveal the molecular structures and the dynamics in polymer and supra-molecular systems. High resolution SS-NMR spectrum for BZ monomer is shown by the bottom black curve in Figure 3.7. The high resolution SS-NMR spectra show well separated chemical groups except in the benzene ring region. These chemical shifts correlate well with the solution NMR spectrum. With the use of high magic angle spinning (MAS) rate of 12000 Hz, the spinning sidebands were suppressed and out of the spectrum range. The peaks from benzene rings appear at 100 to 160 ppm, which can further be divided into two parts. The benzene ring directly connected to O, N and \(-\text{C(CH}_3)_2\) is shown above 137 ppm and can be well separated as in Figure 3.7. The peaks and the corresponding chemical structures are labelled in the structure of BZ.
presented in Figure 3.8. The rest of the carbons on the benzene rings appear below 137 ppm and the signals show much overlap. The peak at 80 ppm is well isolated and assigned to the carbon labelled \textit{d} in Figure 3.7. The three peaks in between 20-40 ppm can be assigned to the \textit{a} to \textit{c} aliphatic carbons. Although the peak intensity of each peak relies on cross polarization (CP) efficiency, the peak intensity correlates well with the chemical groups and the number of carbon atoms in BZ monomer.

The spectra for aerogel specimens are also shown in Figure 3.7. All the spectra of PBZ show the absence of resonance at 80 ppm (carbon \textit{d}) indicating the breakup of C-O bonds of oxazine rings during polymerization. The spectra for PBZ-DMSO-90 and PBZ-NMP-90 are identical which means that the same chemical structures were obtained in different solvents. The PBZ-DMSO-130 and PBZ-NMP-130 also show identical line shapes but slight differences are evident at 125 ppm. The shoulder peaks from PBZ-DMSO-130 and PBZ-NMP-130 are more apparent than those of PBZ-DMSO-90 and PBZ-NMP-90. Another important resonance to note is the peak at 50 ppm. After polymerization, the reacted carbon \textit{d} is supposed to move to 50 ppm (carbon \textit{p} in Figure 3.8). The intensity of this peak of PBZ aerogel synthesized at 130 °C is higher than that synthesized at 90 °C. It means higher conversion of BZ into PBZ in aerogel specimens PBZ-DMSO-130 and PBZ-NMP-130. In view of the IR data and NMR data we infer that the PBZ molecules obtained with TSA as the catalyst resemble the structure reported in Figure 3.8.
Figure 3.7 $^{13}$C-NMR spectra of samples for BZ monomer and the polymers at different conditions.

Figure 3.8 Chemical structure of (a) BZ monomer and (b) PBZ.
3.3.4 N$_2$-sorption analysis

We now examine if the small differences in characteristic dimension of the polymer frameworks (sphere and strands) seen in Figure 3.5 lead to any differences in surface area. The surface area and pore size distribution of the aerogel specimens were determined from nitrogen sorption porosimetry using Micromeritics Tristar II 3020 Analyzer. The nitrogen adsorption-desorption isotherms show hysteresis loops in Figure 3.9a, signifying the presence of mesopores. Specifically, the hysteresis loops of the isotherms of aerogel specimens PBZ-DMSO-130 and PBZ-DMA-130 can be categorized under IUPAC classification Type H2 signifying that the mesopores in these specimens were created by the aggregation of spheres.$^{210}$ In contrast, the desorption curve of PBZ-NMP-130 aerogel does not show a plateau at high value of P/P$_0$ (see inset of Figure 3.9a). In this case, the hysteresis loop is closer to Type H3. This observation corroborates the visual evidence of SEM image in Figure 2c that the pores created in this aerogel are due to fibrillar polymer frameworks.

The much wider hysteresis loop of PBZ-DMSO-130 aerogel in Figure 3.9a indicates that the pores in this aerogel specimen should be predominantly mesopores. This is supported by the data on pore size distribution in Figure 3.9b obtained using Barrett-Joyner-Halenda (BJH) method. The red and blue curves in Figure 3.9b confirm the existence of bimodal mesopores in PBZ-DMA-130 and PBZ-NMP-130 aerogels.
Figure 3.9 (a) Nitrogen adsorption-desorption isotherms and (b) pore size distribution of PBZ aerogels. The inset in (a) shows the hysteresis loops of three isotherms at high P/P₀.

3.3.5 Effect of gelation temperature

Another factor studied is the influence of gelation temperature on the pore structures of PBZ aerogels. For this purpose, the gels synthesized in DMSO as well as NMP at 90 °C and 130 °C were considered. It is apparent from SEM images presented in Figure 3.10a and 3.10b that both PBZ-DMSO-130 and PBZ-DMSO-90 aerogel specimens are constituted of similar size aggregates of polymer spheres. In contrast, PBZ-NMP-90 and
PBZ-NMP-130 show the fibrillar networks. The SEM images demonstrate that the skeletal network of PBZ aerogel is dependent on the solvent instead of the gelation temperature. Further evidence could be derived from the nitrogen adsorption-desorption isotherms in Figure 3.11. Figure 3.11a clearly shows two Type IV isotherms. PBZ-DMSO-90 has a perfect Type H1 hysteresis loop indicating that the network is composed of approximately uniform spheres in fairly regular array. However, the hysteresis loop of PBZ-DMSO-130 is closer to Type H2 as discussed in the previous section. As a result, the pore size distribution for PBZ-DMSO-90 aerogel specimen exhibits narrower peak and a significant fraction of smaller mesopores (mean diameter ~10.2 nm, Table 3.1) than PBZ-DMSO-130 aerogel specimen (mean diameter ~19.1 nm, Table 3.1). The nitrogen adsorption-desorption isotherms of PBZ-NMP-90 and PBZ-NMP-130 are both Type IV isotherms with Type H3 hysteresis loops. Similarly, PBZ-NMP-90 possesses higher surface area and smaller mean pore diameter than PBZ-NMP-130 (Table 3.2). PBZ aerogels prepared at 130 °C show lower BET surface area than the ones prepared at 90 °C independent of the solvents used.
Table 3.1 Properties of PBZ-DMSO-130 and PBZ-DMSO-90 aerogel specimens.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>BET surface area (m$^2$/g)</th>
<th>Pore volume $V_{1.7-300\text{ nm}}$ (cm$^3$/g)</th>
<th>Predominant pore diameter (nm)</th>
<th>Calculated specific surface area ($A_{\text{est}}$) (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBZ-DMSO-130</td>
<td>99.5</td>
<td>0.63</td>
<td>19.1</td>
<td>99.0</td>
</tr>
<tr>
<td>PBZ-DMSO-90</td>
<td>129.6</td>
<td>0.54</td>
<td>10.2</td>
<td>158.8</td>
</tr>
</tbody>
</table>

In view of the data presented in Table 3.1 and Table 3.2, the higher BET surface area of PBZ-DMSO-130 and PBZ-DMSO-90 specimens can be attributed to relatively higher pore volume $V_{1.7-300\text{ nm}}$. The pore volume $V_{1.7-300\text{ nm}}$ in Table 3.1 refers to the cumulative volume of pores of diameter between 1.7 and 300 nm. It is however, intriguing to find that PBZ-DMSO-130 aerogel specimen with higher value of $V_{1.7-300\text{ nm}}$ (0.63 cm$^3$/g) has lower surface area (99.5 m$^2$/g) than PBZ-DMSO-90 aerogel specimen with smaller pore volume (0.54 cm$^3$/g) but higher BET surface area (129.6 m$^2$/g). As discussed earlier, aerogel specimens PBZ-DMSO-130 and PBZ-DMSO-90 contained predominant mesopores with diameter in the range 2-50 nm, with the peak values of 19.1 nm for PBZ-DMSO-130 and 10.2 nm for
PBZ-DMSO-90. If one assumes that all pores have diameter the same as the peak diameter, the specific surface area ($A_{est}$) can be estimated using equation (12):

$$A_{est} = \frac{3V_{1.7-300\text{nm}}}{R_p}$$ (12)

In equation (12), $V_{1.7-300\text{nm}}$ is the pore volume and $R_p$ is the peak pore radius. It is evident from Table 3.1, the estimated area of PBZ-DMSO-90 is almost 160% as much as the value for PBZ-DMSO-130 aerogel. This calculation supports that the much smaller pore diameter of PBZ-DMSO-90 aerogel specimen more than compensates for the lower pore volume in producing higher BET surface area.

Figure 3.10 SEM images of (a) PBZ-DMSO-130, (b) PBZ-DMSO-90, (c) PBZ-NMP-130, (d) PBZ-NMP-90.
Figure 3.11 Nitrogen adsorption-desorption isotherms of (a) PBZ-DMSO-90/130, (b) PBZ-NMP-90/130 and pore size distribution of (c) PBZ-DMSO-90/130, (d) PBZ-NMP-90/130.

Table 3.2 Properties of PBZ aerogels.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Shrinkage</th>
<th>Bulk Density (g/cm$^3$)</th>
<th>Skeletal Density (g/cm$^3$)</th>
<th>Porosity</th>
<th>BET Surface Area (m$^2$/g)</th>
<th>Pore Volume $V_{1.7-300nm}$ (cm$^3$/g)</th>
<th>Total Pore Volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBZ-DMSO-90</td>
<td>26.1%</td>
<td>0.52</td>
<td>1.22 ± 0.003</td>
<td>57.4%</td>
<td>129.6</td>
<td>0.54</td>
<td>1.10</td>
</tr>
<tr>
<td>PBZ-DMSO-130</td>
<td>26.8%</td>
<td>0.45</td>
<td>1.26 ± 0.004</td>
<td>64.3%</td>
<td>92.2</td>
<td>0.63</td>
<td>1.43</td>
</tr>
<tr>
<td>PBZ-NMP-90</td>
<td>23.8%</td>
<td>0.46</td>
<td>1.19 ± 0.002</td>
<td>61.1%</td>
<td>90.9</td>
<td>0.50</td>
<td>1.32</td>
</tr>
<tr>
<td>PBZ-NMP-130</td>
<td>20.3%</td>
<td>0.37</td>
<td>1.26 ± 0.007</td>
<td>70.2%</td>
<td>81.8</td>
<td>0.26</td>
<td>1.88</td>
</tr>
</tbody>
</table>

* Total pore volume = $1/\rho_b - 1/\rho_s$. 
3.4 Conclusions

In summary, we demonstrated a time efficient preparation of PBZ aerogel using TSA as the catalyst. All of the aerogels synthesized in DMSO, DMA, and NMP were found to be mesoporous materials. Interestingly, the study revealed that the skeletal frameworks of PBZ aerogels can be tuned using appropriate solvents and suitable polymerization temperature. The use of DMSO and DMA as the solvents led to spherical particle networks while fibrillar networks were obtained using NMP. The temperature of polymerization played critical role in controlling the pore structures of PBZ aerogels. Of the aerogels studied, PBZ-DMSO-90 specimens exhibited the largest BET surface area owing to predominantly mesopores with peak diameter of ~10 nm. It is anticipated that such vast changes in pore structures and pore surface area due to use of different solvents and polymerization temperature can be efficiently captured in the design of other polymeric aerogels.
CHAPTER IV

A LASER LIGHT SCATTERING STUDY ON THE FORMATION MECHANISM OF POLYBENZOXAZINE GEL NETWORK

4.1 Introduction

Mesoporous materials received tremendous attention in the last two decades due to their widespread applications in gas storage, chemical separation, and catalysis. Aerogels are a class of mesoporous solid materials formed by nanometer-sized solid networks filled with high percentage of air. They offer a set of interesting properties such as, low thermal conductivity, high specific surface area, and low bulk density. Aerogels are generally obtained from precursor gels by replacing the liquid with air in a supercritical drying step. The supercritical drying process leaves interconnected voids without structural collapse which are viewed as the pores in aerogels. These pores show diversity in geometry depending upon the nature of the solid building blocks, the amount of solids in the precursor gels, and mechanism of polymerization induced phase separation. The diameter of the pores range from 1 nanometer to a few micrometer.

In Chapter III, we reported the dependence of the solid networks in polybenzoxazine (PBZ) aerogels on the nature of the solvents. The mesoporous PBZ aerogels prepared with the same solid content showed different building blocks, e.g., spheres in dimethylsulfoxide (DMSO) and cylindrical strands in N-methyl-2-pyrrolidone (NMP) which in turn produced
different BET surface area, pore size distribution, and pore volume. We proposed that *spinodal decomposition* were responsible for production of respectively the spherical and cylindrical building blocks. In the study of silica aerogels, Kanamori and co-workers also achieved silica aerogels with fibrous and globular networks.\textsuperscript{41} In their explanations, two types of networks were formed because that they formed in different stages of *spinodal decomposition*. The spheres formed in the early state while the strands formed in the later stage where structural coarsening proceeded to lower the surface energy. Leventis et al.\textsuperscript{4} discovered that the morphology of polyurea aerogels could change from collections of strands to aggregation of spheres by increasing the concentration of the monomer. In contrast, the authors attributed the formation of two types of polyurea networks to polymerization induced *nucleation and growth*. However, there was no direct evidence shown in current literature to prove how the gel network from during gelation. To fully understand the formation mechanism of these two building blocks, in this Chapter, we introduced Laser Light Scattering (LLS) technology to dynamically characterize the gelation process.

LLS, including static light scattering (SLS) and dynamic light scattering (DLS), is often used to study polymers and nanoparticles in dilute solutions.\textsuperscript{217-220} SLS measures the total scattered intensity from the solution which can lead to information on radius of gyration (Rg) and weight-average molecular weight of the particles. The scattered intensity can be regarded as an indicator of the gelation process based on Rayleigh-Gans-Debye equation,\textsuperscript{217, 221} where the scattered intensity increases as the number and size of the scattering site increase. The magnitude of intensity is, however, more sensitive to the size variation.\textsuperscript{217,221} On the other hand, DLS data provide hydrodynamic radius (R\textsubscript{h}) values with
the assistance of CONTIN analysis. The combination of $R_h$ and $R_g$ values can help in the understanding of the geometry of particles in the solutions. In this work, we determined the size and the shape of PBZ nanoparticles at different times during the gelation process in solvents NMP and DMSO.

In a typical experiment, 1.100 g of benzoxazine (BZ) and 0.011 g of p-toluenesulfonic acid (TSA) were dissolved in 4.0 mL pure solvent (DMSO or NMP). The filtered solution was kept in an oil bath at 120 °C in order to initiate and continue the cationic polymerization process (Figure 4.1) until the solution turned into a gel. Specimens were taken out of the reaction system at prescribed time intervals, diluted with fresh solvent, and were examined by LLS method to record the structural information of the polymer domains until the gel point was reached. Each time, a 5.0 µL hot solution taken out of the reaction system was added into 2.0 mL filtered solvent (DMSO or NMP) to reach a final concentration of 0.68 mg/mL. The solutions were then cooled down to room temperature and the data were taken by LLS method. It should be noted that dilute solutions were used in LLS study to ensure the accuracy of the results. The LLS tests were conducted at room temperature due to the requirement of the instrument. We assumed homogeneity of the reaction mass such that the extracted 5.0 µL solution truly represented the reaction mass, polymerization of PBZ was terminated due to dilution with the solvent and lowering of temperature to room temperature, and the polymer domains did not undergo swelling and their morphologies did not change much before data were taken by LLS method.
4.2 Experimental

Materials used are listed in this section. In addition, the details of sample preparation and characterization are shown as following.

4.2.1 Materials

4,4’-isopropylidenediphenol (bisphenol A), paraformaldehyde (96%), aniline, p-toluenesulfonic acid monohydrate (TSA•H₂O), dimethyl sulfoxide (DMSO), and N-methyl-2-pyrrolidone (NMP) were obtained from Sigma-Aldrich. Millipore MILLEX-LG 0.20-μm PTFE filters were purchased from Millipore Corporation.

4.2.2 Synthesis of benzoxazine monomer

Bisphenol A, aniline, and paraformaldehyde (molar ratio of 1:2:4) were added to a beaker and placed in a preheated oil bath at 130 °C.¹³⁵ The ingredients were mixed for 1 h and the mixture turned into yellow, viscous liquid. The products solidified upon cooling to room temperature and were ground into powder form for further use.

4.2.3 Preparation of polybenzoxazine aerogel

1.1 g of benzoxazine (BZ) monomer powder and 0.011 g of TSA were added in 4.0 mL solvent and stirred at room temperature for 15 min to obtain BZ sol (0.275 g/mL). The BZ sol was placed inside an oven at 120 °C to obtain the gel. All organogels were aged at 120 °C for duration of four times the gel time. The aged organogels were washed in acetone four times over a period of 12 h. The washed gels were dried under supercritical condition in carbon dioxide.
4.2.4 Characterization

**Laser Light Scattering (LLS) Measurements** A commercial Brookhaven Instrument light-scattering spectrometer equipped with a solid-state laser (model Compass 215M) operating at 532 nm and a BI-9000AT digital correlator, was used for both the SLS and DLS measurements. The instrument can detect over an angular range of 15-155°. The temperature of sample chamber was kept at 25.00 ± 0.01 °C during the measurements. The particle average hydrodynamic radius ($R_h$) could be obtained by DLS measurements, analyzed by CONTIN$^2$ method and the scattered intensity as well as radius of gyration ($R_g$) can be determined by SLS measurements. In SLS measurements, data was collected automatically by instrument every 2° between 30° and 120°, and analyzed based on Rayleigh-Gans-Debye equation, giving $R_g$ values of the nanoparticles in solutions. Before each measurement, dilution of concentrated PBZ/BZ solution was conducted by adding 5.0 µL of heated solution into 2.0 mL pure and filtered solvent (DMSO or NMP) to reach a final concentration of 0.68 mg/mL.
Scanning electron microscopy (SEM) One piece of sectioned aerogel sample was attached on the substrate by conductive tape. The samples have to be sputter coated with gold nanoparticles before SEM tests. The morphology of aerogels was probed using scanning electron microscopy (SEM; JEOL JSM5310) with operating voltage 8 kV.

4.3 Results and discussions

Figures 4.2a and 4.2b show the plots of scattered intensities (I) versus time obtained from SLS measurements. In both solvents, at the very beginning of polymerization, the values of I are close to zero as only the small BZ monomer molecules were present in the solution. With the progress of polymerization, the intensity increased slowly (Stage I) followed by a rapid growth (Stage II). Specifically, in Stage I, the monomers participated in initiation reactions with H+, formed the propagation centers, and produced oligomers.\(^{223}\) Although the number of oligomers increased in this stage, no obvious increase of scattered intensity was observed indicating that the increase of size of the oligomers was limited. In contrast, the scattered intensity increased dramatically in Stage II, indicating a significant increase in size of the polymer domains due to intramolecular crosslinking.\(^{224}\) This trend was later confirmed by the data from DLS measurements. The scattered intensities were monitored until the extracted solutions were found too viscous and could not be diluted any further. Such time was recorded as the gelation time. It was found that PBZ gels were formed in 51 min in DMSO and 350 min in NMP at 120 °C. The nature of the solvents plays an important role in determining the gelation time. It was reported that pKa of acids in NMP is 1.2 unit more than that in DMSO calculated from the free energies of dissociation of acids in NMP and DMSO, respectively.\(^{225}\) In view of this, TSA/DMSO solution produced a factor of 3 to 4 higher concentration of H+ than TSA/NMP solution at
the same initial concentration of TSA. Accordingly, more BZ monomers underwent initiation and subsequent polymerization in DMSO leading to faster gelation. This is also evident from significantly higher intensity counts in Figure 4.2a than in Figure 4.2b for a given time.

Figure 4.2 Change of total scattered intensities of (a) DMSO solution and (b) NMP solution at 90° angle. CONTIN analysis of DLS studies of (c) DMSO solution and (d) NMP solution at different times.

To further establish a mechanism of PBZ gelation, DLS measurements were used to obtain average values of $R_h$ as well as the size distribution of the nanoparticles. The CONTIN analysis of DLS data revealed two peaks as the PBZ particles grew larger in both
solvents, where $\Gamma G(\Gamma)$ denotes the relative contribution to the total scattered intensity due to the particles with a given $R_h$. The main peaks are attributed to highly crosslinked polymer particles while the minor ones correspond to oligomers or polymers with relatively low molecular weights. In this regard, in order to simplify the analysis the following discussion focused on the main peaks with moderate correction of the minor peaks. $^{226}$ focused on the main peaks in order to simplify the analysis. Figures 4.2c and 4.2d present the size distribution of PBZ in DMSO and NMP at different reaction times. Similar to the trend of scattered intensity from SLS measurements presented in Figure 4.2a and 4.2b, the $R_h$ of the predominant particles increased slowly initially, followed by a rapid increase. We attribute particle growth in both solvents to *nucleation and growth* mechanism. Small particles were observed at the very beginning and their size gradually and slowly increased reminiscent of the nucleation stage. The DLS results indeed nullified the possibility that the networks of strands observed in the case of NMP grew out of *spinodal decomposition*.

However, we have not found an answer to the question on how the spheres that formed by nucleation and growth mechanism in NMP led to the strands. To gain a further understanding of the shape of PBZ particles in the solvents, a series of $R_h$ measurements by DLS at different scattering angels and $R_g$ measurements by SLS were performed (Figure 4.4 and 4.5). It should be noted that, for solid spheres, $R_h$ at different scattering angles should be almost invariant to angle of view and $R_g$ should be smaller than $R_h$ at $0^\circ$ ($R_{h,0}$). In the case of cylindrical particles, however, both angle dependent $R_h$ values and usually, larger $R_g$ values should be observed.$^{218}$
Figure 4.3 At 120 °C, $R_h$ distribution of particles in DMSO after heating for (a) 45 min and (b) 50 min at different scattering angles. (c) SEM image of network of PBZ aerogel synthesized in DMSO. $R_h$ distribution of particles in NMP after heating for (d) 320 min and (e) 340 min at different scattering angles. (f) SEM image of network of PBZ aerogel synthesized in NMP.
Figure 4.4 Partial Zimm plot for PBZ nanoparticles formed in DMSO at 120 °C, 50 min, \( R_g = 69.4 \pm 1.2 \) nm.

Figure 4.5 The \( R_h \) distribution and partial Zimm Plots of PBZ nanoparticles formed in NMP at 120 °C. a) \( R_h \) distribution at 300 min; b) \( R_h \) distribution at 310 min; c) partial Zimm Plots, 310 min, \( R_g = 29.0 \pm 0.4 \) nm, 320 min, \( R_g = 48.3 \pm 0.5 \) nm, 340 min, \( R_g = 113.1 \pm 1.3 \) nm.
Table 4.1 $R_h$ and $R_g$ values of PBZ nanoparticles formed in DMSO at 120 °C.

<table>
<thead>
<tr>
<th></th>
<th>$R_{h, 90°}$</th>
<th>$R_{h, 75°}$</th>
<th>$R_{h, 60°}$</th>
<th>$R_{h, 45°}$</th>
<th>$R_{h, 0°}$</th>
<th>$R_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>45 min</td>
<td>21.6</td>
<td>22.5</td>
<td>23.0</td>
<td>19.0</td>
<td>19.5</td>
<td>*</td>
</tr>
<tr>
<td>50 min</td>
<td>62.0</td>
<td>65.4</td>
<td>77.3</td>
<td>92.4</td>
<td>111.8</td>
<td>69.4</td>
</tr>
</tbody>
</table>

Radius unit: nm; *$R_g$ at 45 min is not available due to the size is not detectable.

Table 4.2 $R_h$ and $R_g$ values of PBZ nanoparticles formed in NMP at 120 °C.

<table>
<thead>
<tr>
<th></th>
<th>$R_{h, 90°}$</th>
<th>$R_{h, 75°}$</th>
<th>$R_{h, 60°}$</th>
<th>$R_{h, 45°}$</th>
<th>$R_{h, 0°}$</th>
<th>$R_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>250 min</td>
<td>10.3</td>
<td>9.9</td>
<td>10.2</td>
<td>10.4</td>
<td>10.3</td>
<td>*a</td>
</tr>
<tr>
<td>310 min</td>
<td>30.7</td>
<td>34.8</td>
<td>34.7</td>
<td>32.8</td>
<td>35.3</td>
<td>29.0</td>
</tr>
<tr>
<td>320 min</td>
<td>42.6</td>
<td>46.5</td>
<td>40.3</td>
<td>44.9</td>
<td>43.5</td>
<td>48.3</td>
</tr>
<tr>
<td>340 min</td>
<td>47.1</td>
<td>65.6</td>
<td>72.5</td>
<td>116.9*</td>
<td>241.7</td>
<td>113.1</td>
</tr>
</tbody>
</table>

Radius unit: nm; *a: $R_g$ at 250 min is not available due to the size is not detectable; *b: some large PBZ aggregations might lead to the large value.
Figure 4.6 PBZ nanoparticles growing process in DMSO at 108 °C determined by LLS measurements. (a) The scattered intensity change from SLS measurements as time; (b) the $R_h$ distribution at 90° at different time.

Figure 4.7 The LLS study results on PBZ nanoparticles formed in DMSO at 108 °C. (a) and (b) At 120 min, the $R_h$ distribution and Partial Zimm plot, $R_g = 30.4 \pm 0.4$ nm; (c) and (d) at 130 min, the $R_h$ distribution and Partial Zimm plot, $R_g = 68.8 \pm 0.4$ nm.
Figure 4.8 PBZ nanoparticles growing process in NMP at 108 °C determined by LLS measurements. (a) The scattered intensity change from SLS measurements as time; (b) the $R_h$ distribution at 90° at different time.

Figure 4.9 LLS studies on PBZ gel formed in NMP at 108 °C. (a) $R_h$ distribution at 12.0 h; (b) $R_h$ distribution at 13.0 h; (c) $R_h$ distribution at 14.0 h; (d) $R_h$ distribution at 14.5 h; (e) $R_h$ distribution at 15.0 h; (f) partial Zimm Plots at different times.
Table 4.3 $R_h$ and $R_g$ values of PBZ nanoparticles formed in DMSO at 108 °C.

<table>
<thead>
<tr>
<th></th>
<th>$R_{h,90^\circ}$</th>
<th>$R_{h,75^\circ}$</th>
<th>$R_{h,60^\circ}$</th>
<th>$R_{h,45^\circ}$</th>
<th>$R_{h,0^\circ}$</th>
<th>$R_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>120 min</td>
<td>43.5</td>
<td>43.3</td>
<td>43.2</td>
<td>43.1</td>
<td>42.9</td>
<td>30.4</td>
</tr>
<tr>
<td>130 min</td>
<td>80.3</td>
<td>79.1</td>
<td>83.3</td>
<td>80.7</td>
<td>82.3</td>
<td>68.8</td>
</tr>
</tbody>
</table>

Radius unit: nm

Table 4.4 $R_h$ and $R_g$ values of PBZ nanoparticles formed in NMP at 108 °C.

<table>
<thead>
<tr>
<th></th>
<th>$R_{h,90^\circ}$</th>
<th>$R_{h,75^\circ}$</th>
<th>$R_{h,60^\circ}$</th>
<th>$R_{h,45^\circ}$</th>
<th>$R_{h,0^\circ}$</th>
<th>$R_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.0 h</td>
<td>17.4</td>
<td>19.0</td>
<td>18.3</td>
<td>19.0</td>
<td>19.6</td>
<td>29.1</td>
</tr>
<tr>
<td>13.0 h</td>
<td>34.7</td>
<td>35.2</td>
<td>32.1</td>
<td>35.9</td>
<td>34.3</td>
<td>48.7</td>
</tr>
<tr>
<td>14.0 h</td>
<td>52.6</td>
<td>55.5</td>
<td>55.5</td>
<td>57.9</td>
<td>60.0</td>
<td>91.6</td>
</tr>
<tr>
<td>14.5 h</td>
<td>55.7</td>
<td>58.6</td>
<td>71.0</td>
<td>80.6</td>
<td>98.6</td>
<td>146.2</td>
</tr>
<tr>
<td>15.0 h</td>
<td>66.0</td>
<td>83.4</td>
<td>84.2</td>
<td>127.7</td>
<td>171.1</td>
<td>175.2</td>
</tr>
</tbody>
</table>

Radius unit: nm
It is apparent from the data in Figure 4.3a, 4.3b, and Table 4.1 that in the case of DMSO solution, no obvious difference was observed in values of $R_h$ at different angles, even when the system was close to the gel point. This indicates that PBZ particles were present as single spheres during the polymerization process in DMSO very close to the point of gelation. At or beyond the gel point, the spheres might have formed random aggregates leading to the PBZ gel network (Figure 4.3c). The same spherical shape was also observed in the case of NMP solution before the 320 min mark (Figures 4.3d, 4.5). However, the particles transformed their geometries during the time period between 320 to 340 min (Figure 4.3e). The $R_h$ values at different scattering angles showed huge differences (Figure 4.3d, Table 4.2), and the calculated $R_g$ values are larger or close to the $R_{h,0}$ values, suggesting the formation of cylindrical structures.

In addition, we also conducted similar PBZ gelation experiments at a lower temperature 108 °C, followed by LLS measurements at room temperature (Figures 4.6-4.9). The gelation took relatively longer time, 130 min in DMSO and 15 h in NMP. As shown in Figure 4.6 and 4.8, SLS results indicated that the change of the particles during the gelation at 108 °C was consistent with that at 120 °C. In terms of DLS tests, the polymer particles also showed the same growth process in both DMSO and NMP solutions. (Figure 4.7 and 4.9).

Based on the evidences gleaned from SLS techniques and SEM images, the mechanism of spherical and cylindrical building block formation of PBZ gels can now be proposed for polymerization in solvents DMSO and NMP. As illustrated in Figure 4.10, in the first step, tiny polymer nuclei are formed due to polymerization-induced phase separation. The size of the nuclei increases with the molecular weight and the crosslinking density. Such an
increase in the particle dimension is referred to as the primary growth regardless of the solvents. In DMSO, nucleation occurs earlier and the particles grow faster due to high proton concentration. Also, diffusion-limited cluster aggregation\textsuperscript{4, 227} leads to random packing of the spheres to form the particulate gel network. However, in NMP, the concentration of the initial nuclei is lower at the beginning of gelation due to lower proton concentration. The particles eventually grow larger due to primary growth. Meanwhile, the secondary growth takes place as the reactive molecules on the surfaces of different particles connect during inter-particle collision. In this case, the steric hindrance may account for the end-to-end assembly of the spheres during the secondary growth. In addition, the size of secondary particles increased with time and the voids between two spheres are partially filled due to concurrent primary growth. Eventually, the secondary particles turned into interconnected cylindrical rods as shown in Figure 4.3f.

![Growth models of PBZ gel networks in DMSO and NMP.](image)

Figure 4.10 Growth models of PBZ gel networks in DMSO and NMP.
4.4 Conclusions

The study showed that LLS technology could be used to probe the evolution of nanoparticles during gelation of PBZ gels. The analysis of SLS and DLS data confirmed that nucleation and growth was responsible for formation of both spherical and cylindrical building blocks in PBZ gels. The primary growth of spherical particles continued in DMSO until the gel point, while in NMP, the secondary growth occurred via fusion of spheres into cylinders. The method and the observations presented in this letter can be used as basis for design of microstructures of promising aerogel products.
CHAPTER V

OPEN CELL AEROGEL FOAMS WITH HIERARCHICAL PORE STRUCTURE

5.1 Introduction

Aerogels offer high specific surface area, low thermal conductivity, and high porosity. Silica aerogels were first to receive the attention of researchers due to their excellent thermal stability and structural tunability. In 1989, Pekala reported the first organic aerogel synthesized by the polycondensation of resorcinol and formaldehyde (RF). Following that, various organic aerogels were produced based on different polymers, for instance polyimide, syndiotactic polystyrene, and polybenzoxazine.

Polyurea aerogels were first mentioned in a U.S. patent. The inventors presented a series of organic polyisocyanate-based aerogels including those of polyurea, polyurethanes, and polyalloonate. Lee et al. synthesized polyurea aerogels by reacting Jeffamine with ethylene diphenyl diisocyanate (MDI) catalyzed by triethylamine (TEA). These authors studied the relationship between the bulk density and the thermal conductivity of polyurea aerogels. The specimens with a bulk density of 0.16 g/cm³ showed the minimum thermal conductivity of 13 mW/(m·K) which is comparable with the values for RF aerogels and silica aerogels. The PU aerogels with low density (0.06 g/cm³) exhibited a fibrillar morphology while the one with a density of 0.1 g/cm³ exhibited a denser and particulate morphology. Lee et al. mentioned that the large pores in the fibrillar morphology may
increase the gaseous natural convection and radiation thermal transport contributions so that the thermal conductivity of the aerogel goes up. The contributions of solid conduction heat transfer also increases with an increase of the solid content. These results indicate that design of polyurea aerogels with the best thermal insulation properties is not a simple task and that studies on optimization of processing methods is required to attain such objectives.

Morphology variation in polyurea aerogels as function of solids concentration was earlier observed by Leventis and co-workers.\(^4\) Trifunctional isocyanate molecules with water were used in synthesis of polyurea networks with high crosslinking density. Polyurea aerogels with a wide range of bulk density (0.016—0.055 g/cm\(^3\)) were prepared and characterized. The network of polyurea aerogels was constituted of polymer fibrils when the bulk density was no more than 0.13 g/cm\(^3\). However, the networks of aggregation of globules were observed as the density reached 0.19 g/cm\(^3\).\(^4\) These two morphological were the results of distinct aggregation mechanisms. For example, at low concentration, a reaction limited aggregation led to fibers, while at high concentration, cluster-cluster crowding occurred to yield globular morphologies. The Young’s modulus of polyurea aerogels with the highest bulk density (0.55 g/cm\(^3\)) was 300 MPa which is comparable to the values for polymer reinforced silica aerogels. The resultant polyurea aerogels offered high strength and high acoustic attenuation capabilities.

Shinko et al. used diphenyl diisocyanate (MDI), 4,4’-oxydianiline (ODA) or 2,2’-dimethylbenzidine (DMBZ), and 1,3,5 tris(4- aminophenyl)benzene (TAB) to synthesize a group of polyurea aerogels with varying the number of repeat unites (\(n\)) of polyurea oligomers.\(^5\) It was indicated that \(n\) determined the gelation time, e.g., longer gelation time for lager \(n\). In the case of materials synthesized using ODA as the diamine, a larger \(n\) caused
higher shrinkage due to higher extent of hydrogen bonding in the aerogels. Moreover, $n$ has direct impact on the compression modulus of the aerogels, e.g., higher crosslinking density would result in a higher compression modulus. It is easy to understand that smaller $n$ corresponds to higher portions of the crosslinker (TAB) in the polyurea networks.

In the present work, we report a new class of materials, the open cell aerogel foams (OCAFs) that combine the attributes of polymer foams and mesoporous aerogels in one material. The proposed structure of OCAFs can be divided into two parts, the interconnected, and, therefore, open macropores with diameter around 5 µm and the mesoporous aerogel skin walls of the open cells. Leventis$^4$ indicated an interesting material that combines large foam-like macroporosity with nanoporous wall. It was created by trapping CO$_2$ bubbles in gel during an ultrafast gelation process. In this case, CO$_2$ works as the porogen as is generally used in manufacturing polyurethane foams.$^4$ However, the parameters, such as the total volume of CO$_2$ and the dispersity of the bubbles in the gel system are difficult to control to produce stable and systematic products. In this paper, thermoset polyurea (PUA) aerogels were considered for synthesis of OCAFs. Sol-gel synthesis of PUA gel occurred in a macroporous polyethylene oxide (PEO) template which was prepared through selective dissolution of atactic polystyrene (PS) from a co-continuous PS/PEO blend. The PEO template was then removed and the resulting macroporous PUA gel was washed using acetone followed by supercritical drying to obtain the OCAF. Several questions were answered in this paper. First, what is the mechanism of formation of PUA gel network inside the macroporous PEO template? Specifically, does PEO exert any influence on the morphology of PUA gel networks? Second, does the hierarchical pore structure of OCAFs improve the liquid uptake and the gas permeability?
In addition, the properties of PUA aerogel and OCAF were evaluated as a function of the concentration of the solids in the sol.

5.2 Experimental

Materials used are listed in this section. In addition, the details of sample preparation and characterization are shown as following.

5.2.1 Materials

Monomer Desmodur N3300A triisocyanate was required from Covestro LLC. (Pittsburgh, PA). Triethylamine (TEA), tetrahydrofuran (THF), acetone, atactic polystyrene (M_w ~ 192,000 g/mol) and polyethylene oxide (M_w ~ 300,000 g/mol) were purchased from Sigma Aldrich. Vacuum pump oil 19 was obtained from VWR.

5.2.2 Preparation of macroporous PEO template

30 g of PEO and 30 g of PS were mixed in a Brabender Plasticorder mixer at 170 °C for 10 min at a rotor speed of 50 rpm and cooled to room temperature for further use. The blend was ground to powder state and compression molded at 170 °C and 3000 psi pressure into 2.8 cm disks (Figure 5.1). The disks were soaked in THF for 24 h at room temperature to remove the PS phase and subsequently dried at room temperature to obtain the PEO template.

5.2.3 Synthesis of PUA gel, aerogel, and OCAF

The sols of PUA were prepared by dissolving Desmodur N3300A, water, and TEA in acetone using the formulation shown in Table 5.1. The sample names in Table 5.1 contain information on the molar concentration of the isocyanate. For example “PUA-0.1M”, refers
to the sol containing 0.1 mol/L of Desmodur N3300A. The PUA gels were obtained from sol-gel reactions at room temperature. The gelation times were 6 h for PUA-0.1 M, 3 h for PUA-0.15 M, and 45 mins for PUA-0.2 M. All gels were aged for 12 h before taking out of the mold. The gel specimens of volume about 5 cm$^3$ were then washed with fresh acetone (50 mL) for six times with 6 h intervals in order to remove any unreacted moieties. The PUA gel specimens were dried under supercritical conditions to obtain PUA aerogels. Note that “PUA Aerogel” in this paper refers to the aerogel monoliths to distinguish them from “PUA OCAF”. The PUA OCAF specimens were obtained by supercritical drying in carbon dioxide of PUA gels grown inside the PEO templates. For this purpose, the PEO templates were immersed in the sol of PUA for 1 min to fill the macropores of PEO templates, immediately placed in a container, and kept under sealed condition for gelation and aging over a period of 12 h. The resultant materials were washed with deionized water 4 times in 6 h intervals and with acetone 6 times in 6 h intervals. The PUA OCAF materials were dried under supercritical condition of carbon dioxide.

Figure 5.1 Photograph of (a) PEO/PS blends disks, and (b) PUA Aerogels and OCAFs.
Table 5.1 Mass ratio of ingredients for synthesizing PUA gels.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Desmodur N3300 (g)</th>
<th>Water (g)</th>
<th>TEA (g)</th>
<th>Acetone (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUA-0.1 M</td>
<td>5.046 (0.01 mol)</td>
<td>0.54 (0.03 mol)</td>
<td>0.505 (0.005 mol)</td>
<td>100</td>
</tr>
<tr>
<td>PUA-0.15 M</td>
<td>7.569 (0.015 mol)</td>
<td>0.81 (0.045 mol)</td>
<td>0.7575 (0.0075 mol)</td>
<td>100</td>
</tr>
<tr>
<td>PUA-0.2 M</td>
<td>10.092 (0.02 mol)</td>
<td>1.08 (0.06 mol)</td>
<td>1.01 (0.01 mol)</td>
<td>100</td>
</tr>
</tbody>
</table>

5.2.4 Characterization

The aerogel monoliths were of cylindrical shape while OACFs were of circular disk shape. The bulk density ($\rho_b$) was calculated by measuring the mass and volume of the specimens. The skeletal density ($\rho_s$) was determined from Accupyc 1340 helium pycnometer (Micromeritics). The porosity ($p$) was obtained from the values of skeletal density and bulk density according to equation (13).

$$ p = \frac{\rho_s - \rho_b}{\rho_s} \times 100\% $$

Brunauer–Emmett–Teller (BET) surface area and pore size distribution of the specimens were obtained from N$_2$-sorption isotherms at 77 K, analyzed using a Micromeritics Tristar II 3020 analyzer. The morphology of the specimens was probed using scanning electron microscopy (SEM; JEOL JSM5310) at an operating voltage of 8 kV. Infrared (IR) spectra were recorded on a Bruker FT-IR Alpha spectrophotometer using
a Platinum ATR accessory. The values of liquid contact angle were measured by VCA-Optima™ (AST Products, Inc). The specimens were compressed at a pressure of 2000 psi into a dense film to eliminate the influence of the porous surfaces on the contact angle values. In the static sessile drop method, 2.5 µL of water droplet was placed on the sample film and the image of the drop was captured and analyzed using ImageJ software.

5.2.5 Oil absorption test

The initial mass of the PUA Aerogel or OCAF (volume ~ 1 cm³) was measured and recorded as $M_0$. The specimen was soaked in the pump oil for 5s, 1 min, 5 min, 30 min, 1 h, and 4 h and its weight, $M_t$ (t= 5s, 1 min, 5 min …) was recorded. The mass ratio ($\Gamma$) of absorbed oil and the initial specimen was calculated using equation (14).

$$\Gamma = \frac{M_t - M_0}{M_0} \times 100\%$$

(14)

5.2.6 Air permeability test

Air permeability was measured by Frazier Tester according to the modified Darcy’s Law as shown in equation (15),

$$Q = \frac{kG}{\mu} \frac{A}{L}$$

(15)

where $Q$, $k$, $G$, $A$, $\Delta P$, $\mu$ and $L$ correspond respectively to the volumetric air flow rate, permeability constant, shape factor, cross-sectional area of the face normal to air flow direction, pressure drop, viscosity of air, and the thickness of the aerogel specimen. The method to measure air permeability and the efficiency of nanoparticle capture using polymer aerogels were reported elsewhere.39, 103
5.3 Results and discussions

PUA gels were obtained from the reactions of Desmodur N3300 with water following the reactions presented in Figure 5.2. The catalytic influence of TEA was introduced by Leventis et al.\textsuperscript{4} As presented in Table 5.1, the molar ratio of triisocyanate, water, and TEA was fixed at 1:3:0.5 so that all NCO groups could react completely.

\[
\begin{align*}
\text{R-NCO} + \text{H}_2\text{O} & \xrightarrow{\text{TEA}} \text{R-NH}_2 + \text{CO}_2 \\
\text{R-NH}_2 + \text{R-NCO} & \rightarrow \text{R-NH(CO)NH-R}
\end{align*}
\] (1) (2)

Figure 5.2 Synthesis of polyurea from isocyanate and water catalyzed by TEA.

5.3.1 Chemical characterization

The chemical structures of PUA molecules in PUA Aerogels and OCAFs were analyzed using IR. The IR spectra of Desmodur N3300 and PUA specimens are presented in Figure 5.3. The absence of an absorbance peak at 2258 cm\(^{-1}\) suggests that NCO groups were completely consumed in PUA Aerogels and OCAFs. A strong absorbance peak at 1680 cm\(^{-1}\) is due to carbonyl stretching as marked in the molecular structure of Desmodur N3300 A in Figure 5.3.\textsuperscript{4} Another peak at 1630 cm\(^{-1}\) with relatively low intensity signifies the \(\text{C=O}\) group in the urea bonds.\textsuperscript{4, 5} In addition, the absorbance at 1563 cm\(^{-1}\) and 3337 cm\(^{-1}\) respectively are attributed to the bending and the stretching vibrations of N-H in urea bonds. A wide absorbance band at around 1100 cm\(^{-1}\) and sharp peak at 697 cm\(^{-1}\) appear only in the case of OCAFs. These correspond to the benzene ring of PS (697 cm\(^{-1}\)) and C-O-C of...
PEO (1100 cm\(^{-1}\)),\(^ {230,231}\) which are due to the residues of the template materials remaining in PUA OCAFs.

Figure 5.3 IR spectra of Desmodur N3300A, PUA Aerogels and OCAFs.

5.3.2 Properties of PUA Aerogels and OCAFs

Table 5.2 summarizes some general properties of PUA Aerogels and OCAFs. The bulk density ratio of three PUA Aerogels is 1:1.53:2.14 which is close to the weight ratio of all reactants in the initial solutions. The bulk density of PUA OCAFs also increased with an increase of the concentration of Desmodur N3300A in the formulation.
The pore volume fraction of PUA OCAF should be around 50% in view of 50 wt% PEO and 50 wt% PS used in the fabrication of the template materials. Therefore, $\rho_b$ of PUA OCAF should be half of that of PUA Aerogel monolith synthesized from the sol of the same solid concentration. The data presented in Table 5.2 show that the values of $\rho_b$ of OCAFs are actually higher than what was expected. This may be due to greater shrinkage and the remnants of PEO and PS as confirmed by the IR spectroscopic data. The approximate weight percentage of PEO/PS in OCAFs can be calculated using the method described in Figure 5.4. The results revealed that albeit more than 97.5% of the template was successively washed by THF and water, the mass of residual PE and PS is significant (>19 wt%) considering the low solid content in the aerogels (shown in Table 5.3). The presence of remnant PEO and PS not only increases the $\rho_b$ of PUA OCAFs but also reduces the values of $S_{BET}$, $V_{1.7-100\,nm}$ and porosity.

$S_{BET}$ of PUA Aerogels are all around 220 m$^2$/g as they show similar fibrillar networks (Figure 5.5). The values of $S_{BET}$ and $V_{1.7-100\,nm}$ of PUA OCAFs were reduced by 40% and 30% respectively due to the presence of residual PEO and PS in the materials, which closed down some of the pores. No significant difference was observed on $\rho_s$ of PUA Aerogels as similar chemical structures were formed. Meanwhile, $\rho_b$ is ~1.21 g/cm$^3$ of PEO and ~1.06 g/cm$^3$ of PS which actually has slight influence on $\rho_b$ of PUA OCAFs.
Figure 5.4 Calculation of the weigh percent of PEO/PS residues in PUA OCAF and the weight percent of PEO/PS washed by THF and water compared to the original PEO/PS blends. PUA-0.1 M OCAF was used as an example in this calculation.

Table 5.2 Selected properties of PUA Aerogels and OCAFs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\rho_b$ (g/cm$^3$)</th>
<th>$\rho_s$ (g/cm$^3$)</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_{1.7-100}$nm (cm$^3$/g)</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUA-0.1 M Aerogel</td>
<td>0.055±0.0040</td>
<td>1.276±0.0040</td>
<td>196</td>
<td>0.66</td>
<td>95.7%</td>
</tr>
<tr>
<td>PUA-0.15 M Aerogel</td>
<td>0.084±0.0045</td>
<td>1.268±0.0111</td>
<td>221</td>
<td>0.68</td>
<td>93.4%</td>
</tr>
<tr>
<td>PUA-0.2 M Aerogel</td>
<td>0.118±0.0123</td>
<td>1.299±0.0091</td>
<td>218</td>
<td>0.61</td>
<td>90.9%</td>
</tr>
<tr>
<td>PUA-0.1 M OCAF</td>
<td>0.054±0.0008</td>
<td>1.2909±0.0197</td>
<td>128</td>
<td>0.45</td>
<td>95.8%</td>
</tr>
<tr>
<td>PUA-0.15 M OCAF</td>
<td>0.060±0.0016</td>
<td>1.2218±0.0077</td>
<td>131</td>
<td>0.48</td>
<td>95.1%</td>
</tr>
<tr>
<td>PUA-0.2 M OCAF</td>
<td>0.073±0.0030</td>
<td>1.2365±0.0063</td>
<td>124</td>
<td>0.43</td>
<td>94.1%</td>
</tr>
</tbody>
</table>
Note: $S_{\text{BET}}$ is the specific surface area determined by N$_2$- sorption analysis based on BET theory; $V_{1.77-100 \text{ nm}}$ is the volume of pores with diameters between 1.7 nm to 100 nm which is calculated by BJH desorption method.

Table 5.3 Summary of the results calculated by the method in Figure 5.4.

<table>
<thead>
<tr>
<th></th>
<th>Weight percent of residual PEO/PS in OCAF</th>
<th>Weight percent of washed PEO/PS from the original blends</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUA-0.1 M OCAF</td>
<td>51.4%</td>
<td>97.5%</td>
</tr>
<tr>
<td>PUA-0.15 M OCAF</td>
<td>29.0%</td>
<td>98.5%</td>
</tr>
<tr>
<td>PUA-0.2 M OCAF</td>
<td>14.3%</td>
<td>99.1%</td>
</tr>
</tbody>
</table>

5.3.3 Microstructures of PUA Aerogels and OCAFs

The microstructures of PUA Aerogels were studied by SEM and N$_2$-sorption analysis. Figure 5.5 presents three columns, each including SEM images of PUA Aerogel networks probed at different magnifications, N$_2$-sorption isotherm, and pore diameter distribution obtained from the BJH model. SEM images reveal that the networks of all PUA Aerogels consisted of 3D cross-linked polymer strands.

It is seen that the length of the strands between two neighboring joints of the network reduced with an increase of the solid content in PUA Aerogel. The network built by the shorter strands is denser with relatively lower void spaces in between. According to the SEM images at higher magnification ($\times$ 30000), the dimensions of most pores are larger than 50 nm, which are classified as the macropores. The same conclusions can be drawn
from the N₂-sorption isotherms. For all PUA Aerogel specimens, the quantity of adsorbed N₂ soared at relative pressure (P/P₀) greater than 0.9. However, no saturation plateau is observed at P/P₀=1, indicating the presence of significant macropore volumes in the PUA Aerogels. Mesopores also exist in the PUA Aerogels due to the narrow hysteresis loops observed in all N₂-sorption isotherm data. The distributions of the pores with diameter less than 100 nm shown as the insets were derived from BJH analysis of the N₂-desorption curves.

Figure 5.5 Each column includes SEM images of PUA Aerogel conducted with 2 magnifications (× 3000 and × 30000) and N₂-sorption isotherm with insert showing pore diameter distribution obtained by BJH analysis of N₂-desorption process.
Figure 5.7a reveals the microstructure of PUA-0.1 M OCAF. We anticipated that OCAF s would exhibit a bi-continuous structure of aerogel domains and large pores, similar to that of PEO template (Figure 5.6). Interestingly, PUA-0.1 M OCAF shows a unique network of interconnected thin films consisting of agglomerated particles. The thickness of the film is estimated from the SEM image in Figure 5.7a to be around 170 nm, much less than the width of the macropores (typically 10 μm) shown in Figure 5.6. Such film formation can be attributed to formation of 3D particulate networks on the surfaces of PEO template materials which were not previously observed in the studies of polymer aerogels. In Figure 5.6a, some micrometer-size particles marked by circles are recognized and are identified as the PEO/PS residues. Additional SEM images in Figure 5.8 also show the domains of PEO/PS residues in PUA OCAF s.

![Figure 5.6 SEM images of internal morphology of PEO template.](image-url)
Figure 5.7 SEM images of microstructure of (a) PUA-0.1 M OCAF, inset: demonstration of the thin porous film; (b) PUA-0.15 M OCAF, inset: fracture surface of aerogel domain; and (c) PUA-0.2 M OCAF, inset 1: fracture surface of aerogel domain, inset 2: skin layer of aerogel domain.
Figure 5.8 SEM images showing the residual PEO/PS in OCAF specimens.

The morphology of PUA-0.15 M OCAF and PUA-0.2 M OCAF is consistent with our anticipation. Discussions are focused on the morphology of PUA-0.2 M OCAF as these two materials have similar microstructures as shown in Figure 5.7b and 5.7c. In contrast to
the SEM images in Figure 5.5, the morphology of PUA-0.2 M OCAF includes independent aerogel domains and the voids of dimensions in the range of 5 to 20 \( \mu \text{m} \). These microstructures resemble the normal open cell foams except that the cell walls are now made of polymer strands as in aerogel monoliths. Two representative spots in Figure 5.7c are labelled, one showing the internal structures of aerogel domains and the second showing the surface morphology of the aerogel domains. Higher magnification SEM images of these two spots are presented as insets 1 and 2 in Figure 5.7c. The image in the inset 1 reveals that the internal structure was made of fibrillar networks as was observed in the case of PUA Aerogels. The surface morphology in inset 2 indicates a dense layer formed by agglomeration of the particles. In view of the above discussion, we infer that the aerogel domains in PUA-0.15 M OCAF and PUA-0.2 M OCAF are a combination of the fibrillar networks of PUA Aerogels that formed the bulk and the particulate network sheets similar to what was observed in the case of PUA-0.1 M OCAF that formed the surface. One question comes to mind as regards to the source of such differences in microstructures of the same materials.

In order to answer this question, we need to review the growth mechanism of the PUA networks. Recently, we used laser light scattering (LLS) method to study the growth of polybenzoxazine (PBZ) gel networks and observed different morphologies depending upon the solvents used. Following the same strategy, LLS technology was used to monitor the gelation process of PUA gel. The static light scattering (SLS) results presented in Figure 5.9a suggest that the scattered intensity \( I \) increased with time, indicating that the size and the concentration of particles in the solution increased during gelation step as per Rayleigh-Gans-Debye equation\(^{221}\) where the scattered intensity increases as the number and the size
of the scattering site increase. Figure 5.9b shows the hydrodynamic radius ($R_h$) distribution obtained by CONTIN analysis of dynamic light scattering (DLS) data. The values of $R_h$ of the predominant particles in the solution changed from 25 nm to 200 nm in the last 40 min before PUA turned into a gel. Furthermore, the shape of the particles was probed through DLS tests conducted at various scattering angles. The particles observed at the 155 min mark were spherical since the $R_h$ distributions of particles obtained from various angles (Figure 5.9c) overlapped with each other. In the next 10 min, the particles evolved into cylinders as is evident from the angle dependent $R_h$ values observed at 165 min and 175 min (Figure 5.9d and 5.9e). The data discussed so far indicate that the fibrils of PUA gel network formed due to polymerization-induced nucleation and growth mechanism. The spherical nuclei first formed in solutions and then self-assembled into cylindrical strands. The strands formed interconnected networks to build the 3D gel network.
Figure 5.9 (a) Change of total scattered intensities of the sol for PUA gel at 90° angle. (b) CONTIN analysis of DLS studies of the sol for PUA gel during gelation. $R_h$ distribution of particles in the sol for PUA gel after gelling for (a) 155 min, (b) 165 min and (c) 175 min at different scattering angles.
However, the formation of particulate networks of PUA OCAF specimens is still not resolved. We found that the surface layers of the aerogel domains in materials PUA-0.15 M and PUA-0.2 M OCAF s were obtained from the agglomerated spheres. As these surface layers were formed at the interfaces between the sol and the solid PEO template, we infer that the particulate networks were formed due to heterogeneous nucleation and growth on PEO surfaces. Generally, heterogeneous nucleation applies to phase transformation between two phases, such as gas, liquid, or solid, for example, condensation of vapor,
bubble formation from the liquid. In this case, heterogeneous nucleation can be considered as a surface catalyzed process in which the PUA nuclei are preferably formed on the surfaces of PEO template.\textsuperscript{232} The relationship between Gibbs free energy needed for heterogeneous nucleation ($\Delta G_{\text{hetero}}$) and homogeneous nucleation ($\Delta G_{\text{homo}}$) is expressed in equation (16):

$$\Delta G_{\text{hete}} = \Delta G_{\text{homo}} \times \frac{2-3\cos\theta + \cos^3\theta}{4}$$  \hspace{1cm} \text{(16)}$$

where $\theta$ is the contact angle of the sol for PUA gel on the surface of PEO template. It is evident that $0^\circ < \theta < 180^\circ$, so $\Delta G_{\text{hetero}} < \Delta G_{\text{homo}}$. Therefore, the barrier energy needed for heterogeneous nucleation is reduced so that nuclei first appear on the PEO surfaces. Figure 5.10 shows the schematic diagram of different stages in the formation of PUA OCAF network. (1) At the beginning, nuclei are formed only on PEO surface without any nucleation in the bulk.

(2) The diameter and the number of spherical nuclei near PEO surfaces increased with the progress of polymerization. Meanwhile, homogeneous nucleation takes place in the sol-filled cavity to generate the nuclei.

(3) The spherical nuclei agglomerate to form the particulate networks when the diameter and the number of nuclei reached the critical values. In this stage, a part of the nuclei in the sol may interact with the ones on PEO surfaces by the reaction of the active sites on the surface of PUA nuclei. Small quantities of spheres in the sol grow to form strings due to self-assembly induced by the reactions of NCO and NH\textsubscript{2} groups on different spheres. The two growth modes of the nuclei, agglomerate to particulate network formation, and self-assembly into strings are actually determined by the concentration of the nuclei. Leventis
and co-workers reported that morphology PUA Aerogel would switch from fibrillar networks to particulate network when the concentration of Desmodur N3300A was higher than a critical value. SEM images in Figure 5.5 presented evidence that the concentrations studied in this paper produced fibrillar gel networks. However, due to the heterogeneous nucleation, the local concentration of the nuclei near the PEO surfaces was higher than that in a normal homogeneous condition. The free energy needed for the nuclei to closely pack is lower than the free energy needed in forming the strings. At a relatively lower concentration, the PUA nuclei prefer to self-assemble driven by the reaction-limited aggregation at locations away from the PEO surface.

(4) In this stage, most polymer nanoparticles exist as strings or strands in the sol. The polymerization still continues. Thus, the diameter of the strands increases and the void in the particulate network on PEO surface are partially filled.

(5) Eventually, the strands interconnect to build the integral networks. It is observed in Figure 5.5 that the length of the strands between the joints decreased with an increase of the concentration of the isocyanate. Critically, the number of the nuclei to constitute the strands can be one as long as the concentration of the isocyanate is high enough.

We prepared the PUA Aerogel with homogeneous particulate networks. The five stages described above helped explain the growth process of the aerogel domains in PUA-0.15 M and PUA-0.2 M OCAFs. However, the microstructure of PUA-0.1 M OCAF is a specific case. Recall that significant amount of Desmodur N3300A molecules were reacted in stage (3) to produce the networks near PEO surfaces. It is possible that unreacted Desmodur N3300A was not sufficient to build the fibrillar networks in the sol-filled cavity. Only the nuclei near the surfaces constituted the overall gel networks. After removal of PEO, the gel
network retained the topology of the cavity wall and exhibited the morphology as seen in Figure 5.7a.

Figure 5.11 N$_2$-sorption isotherms and pore diameter distribution of PUA OCAFs.

The N$_2$ adsorption-desorption isotherms and pore diameter distribution curves of PUA OCAFs are shown in Figure 5.11. The isotherms indicate that OCAF specimens were macroporous materials with a small quantity of mesopores. There are a few differences in the distribution of pores with diameter ranging from 1.7 nm to 100 nm (BJH model).

5.3.4 Evaluation of air permeability and liquid absorption capacity

Owing to the ultra-high specific surface area and low bulk density, aerogels are often used as sorbent materials, generally for oil spill$^{233-235}$ and CO$_2$ capture$^{236-238}$. Researchers have made a variety of attempts to increase the oil absorption rate by enhancing the hydrophobicity of aerogels. For example, Wang et al. employed the silsesquioxane precursors with various alkoxy groups to prepare superhydrophobic silica aerogels.$^{235}$ The superhydrophobicity not only prevents cracking due to the condensation of moisture, but also enables the silica aerogel (91 mg) to absorb 1073 mg of toluene within 2.1 s. Korhonen
et al. prepared hydrophobic nanocellulose aerogels by coating the native cellulose nanofibrils with titanium dioxide.\textsuperscript{239} The hydrophobic nanocellulose aerogels can be repeatedly used to take oil and nonpolar solvents from water. Instead of following the routes of modification of aerogels to render them hydrophobic, we aimed to improve the oil absorption rates of the aerogel materials by exploiting the unique structural features of OCAFs.

As shown in Figure 5.12, the values of water contact angle of all compressed PUA specimens are around 70°. As per the contact angle values, PUA-based aerogels are hydrophilic and essentially not the best candidates for oil absorption. Nevertheless, we hypothesized that PUA OCAFs can offer higher absorption capacity and absorption rate attributed to the hierarchical pore structures. Figure 5.12 shows the weight gain vs. time curves of PUA Aerogels and OCAFs after soaking the samples into pump oil. Each test lasted for 4 h and two trends can be observed from the data presented in Figure 5.12. First, for PUA Aerogels, the amount of pump oil absorbed in 4 h reduces with an increase of the concentration of Desmodur N3300A. Second, for PUA OCAFs materials, the values of final weight gain are always higher than that for PUA Aerogels and that the concentration of Desmodur N3300A has small impact on the amount absorbed.
Figure 5.12 Plots of absorbed oil versus time of PUA Aerogels and OCAFs. Corresponding images of water droplets and contact angles on the compressed PUA Aerogels and OCAFs sheets are shown.
Table 5.4 Instantaneous absorption rate, total pump oil uptake in 4 h, and specific pore volume of large pores of PUA Aerogels and OCAF.

<table>
<thead>
<tr>
<th></th>
<th>$R_{5s}$ (g·g$^{-1}$·s$^{-1}$) *a</th>
<th>$M_{\text{total}}$</th>
<th>$V_{\text{large-pore}}$ (cm$^3$·g$^{-1}$) *b</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUA-0.1 M Aerogel</td>
<td>1.12</td>
<td>1449%</td>
<td>16.63</td>
</tr>
<tr>
<td>PUA-0.15 M Aerogel</td>
<td>0.49</td>
<td>985%</td>
<td>10.44</td>
</tr>
<tr>
<td>PUA-0.2 M Aerogel</td>
<td>0.31</td>
<td>528%</td>
<td>7.09</td>
</tr>
<tr>
<td>PUA-0.1 M OCAF</td>
<td>1.52</td>
<td>1570%</td>
<td>17.29</td>
</tr>
<tr>
<td>PUA-0.15 M OCAF</td>
<td>1.89</td>
<td>1308%</td>
<td>15.37</td>
</tr>
<tr>
<td>PUA-0.2 M OCAF</td>
<td>2.33</td>
<td>1324%</td>
<td>12.46</td>
</tr>
</tbody>
</table>

*Note: *a $R_{5s}$ was calculated using the equation $R_{5s} = (M_{5s} - M_0)/5M_0$; *b $V_{\text{large-pore}}$ was calculated by $V_{\text{large-pore}} = 1/\rho_b - V_{1.7-100 \text{ nm}}$.

In order to quantitatively analyze the oil absorption behavior of the samples, three important parameters, specific oil absorption rate in the first 5 s (instantaneous absorption rate), $R_{5s}$, weight percent of absorbed oil in 4 h compared to the initial weight of the sample, $M_{\text{total}}$, and the total volume of pores with diameter larger than 100 nm, $V_{\text{large-pore}}$ were calculated and shown in Table 5.4. For PUA Aerogels, it is evident that the instantaneous absorption rate is proportional to $V_{\text{large-pore}}$. $R_{5s}$ decreases significantly with increasing the concentration of the solids and an increase of bulk density. PUA-0.2 M Aerogel gives the highest resistance to the mass diffusion of pump oil in the aerogel network.

It is recognized that $M_{\text{total}}$ should be decided by the porosity if the aerogel was completely filled. In 4 h, PUA-0.2 M Aerogel with a porosity of 90.9% only uptakes 528% of its own weight, much less than that of PUA-0.1 M with 95.7% pores. Although PUA-0.2 M Aerogel has a high solid content and is more robust than the other two samples, its
low absorption efficacy would be a barrier for practical applications. In the cases of PUA OCAFs, the values of $R_{Ss}$ are higher than that of PUA Aerogels, especially the PUA-0.2 M group. $V_{\text{large-pore}}$ still plays a role here, but it is not the major factor. For instance, $V_{\text{large-pore}}$ of PUA-0.1 M Aerogel and PUA-0.2 M OCAF are 16.63 cm$^3$/g and 12.46 cm$^3$/g, respectively, but $R_{Ss}$ of PUA-0.1 M Aerogel is approximately half of $R_{Ss}$ of PUA-0.2 M OCAF. As presented in Figure 5.7, large pores or cavities with dimensions > 1 µm are present independently although are connected to the mesopores in the aerogel domains.

Mass transport in such large pores is convective flow dominated, while the mass transport in the pores with diameter < 500 nm are diffusion dominated. After being soaked in the pump oil, the outer cavities in PUA OCAFs allowed the oil to flow into the samples and to fill the large pores at the beginning. The oil then diffused into the aerogel domains in the final stage of the absorption process. The featured structure of OCAFs not merely increased the mass transportation rate but also shortened the diffusion path.

Macroscopically, $R_{Ss}$ increased by 750% when PUA-0.2 M OCAF is compared with PUA-0.2 M Aerogel. Moreover, considering the poor hydrophobicity of PUA, we expect that OCAF prepared with superhydrophobic materials, such as syndiotactic polystyrene, could show more excellent oil absorption performance.

Aerogels also have the potential to be used as the filter media for nanoparticles. Jana and co-workers developed various aerogel-based filters for airborne nanoparticles and investigated the importance of mesoporosity on the filtration efficacy. Herein, we hypothesized that hierarchical pore structure of OCAFs can also enhance the air permeability of aerogel-based filters. Air permeability of PUA Aerogels and OCAFs were measured by Frazier Tester and summarized in Table 5.5. The OCAFs indeed possess air...
permeability a factor of 2-3 greater than that for the aerogels prepared with the same concentration of Desmodur N3300A. However, the enhancement is not dramatic and the permeability values are still of the order of $10^{-10}$ m$^2$.

Table 5.5 Values of air permeability of PUA Aerogels and OCAFs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Air Permeability ($\times 10^{-10}$ m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PUA-0.1 M Aerogel</td>
<td>4.88 ± 0.034</td>
</tr>
<tr>
<td>PUA-0.15 M Aerogel</td>
<td>2.18 ± 0.019</td>
</tr>
<tr>
<td>PUA-0.2 M Aerogel</td>
<td>1.60 ± 0.023</td>
</tr>
<tr>
<td>PUA-0.1 M OCAF</td>
<td>8.02 ± 0.041</td>
</tr>
<tr>
<td>PUA-0.15 M OCAF</td>
<td>4.01 ± 0.050</td>
</tr>
<tr>
<td>PUA-0.2 M OCAF</td>
<td>4.87 ± 0.052</td>
</tr>
</tbody>
</table>

5.4 Conclusions and perspective

The templating method was successfully used to prepare PUA OCAFs which exhibited bicontinuous structures of micrometer-sized cavity and mesoporous aerogel domains. In comparison with PUA Aerogels, PUA OCAF showed relatively low BET surface area and specific mesopore volume because of the incomplete removal of the template materials. However, incorporating a macroporous template in a sol-gel reaction system contributed to the formation of the characteristic morphology of PUA OCAFs. The very method also led us to discover the significance of heterogeneous nucleation and growth mechanism for gel network growth on the template materials surfaces. The hierarchical pore structures enabled PUA OCAFs to exhibit higher oil absorption rate and air permeability than PUA
Aerogels. The results presented in this paper suggest that several OCAFs can be designed to serve niche applications, such as making carbon OCAF for electrodes, amine-modified silica OCAF for CO$_2$ capture, transition metal oxide OCAFs for catalysis, and so on.
6.1 Introduction

It is now widely accepted that materials exhibit many remarkable properties when their dimensions are reduced from a few millimeters to a few micrometers to a few tens of nanometers. Substantial advancement in technologies occurred in the fields of energy, healthcare, and electronics aided by the ability to fabricate nanoscale functional elements. Aerogels are a class of highly porous materials and find applications in thermal insulation, energy storage, waste treatment, and drug delivery. Several best practices are now available in the literature for fabrication of bulk aerogel monoliths with dimensions greater than a few centimeters. Kistler reported the use of supercritical drying of organic liquids in synthesis of shrinkage-free aerogels. Supercritical drying was successfully used in synthesis of organic aerogels from chemically reacting systems such as resorcinol and formaldehyde, polyurea, and polybenzoxazine (PBZ). Aerogels were also synthesized from syndiotactic polystryrene via thermoreversible gelation process and from layered silicate clay via freeze-drying process. A host of chemical means were used in reinforcement of pearl-necklace structures of silica aerogels, e.g., via flexible silanes, diisocyanates, free-radical polymerization, organic-inorganic hybrid nanoparticles, epoxies, polyurethaneurea, and fluorosilanes. Researchers reported
fabrication of spherical aerogel microparticles which are suitable in energy and health research. Obtaining spherical aerogel microparticles using mechanical means such as by milling or crushing of previously formed monolithic aerogel structures is rather difficult as their intrinsic mechanical properties are weak.

Prior work on synthesis of aerogel microparticles focused primarily on hydrogels as the starting materials and generally included three main steps, such as solution drop splitting, formation of gel microparticles, and drying to obtain aerogel microparticles. Two methods were proposed in literature for manufacturing of aerogel microparticles. In method I, the aqueous polymer solution with a cross-linker was first transformed by a method known as splitting into micrometer-sized droplets by spray nozzle. The micrometer-sized droplets were quickly frozen in liquid nitrogen and subsequently freeze-dried (drying) and further cured to enhance the cross-linking density. In method II, the aqueous sol was dispersed into micrometer size droplets in an oil phase to form a water-in-oil emulsion (splitting). The micrometer size droplets turned into gel microparticles via sol-gel process (gelling). Finally, the gel microparticles were converted into aerogel microparticles via supercritical drying process (drying). Cellulose aerogel microparticles were synthesized by method I, while silica and alginate aerogel microparticles were prepared by method II. We note that the freeze-drying process or water-in-oil emulsion systems require aqueous solutions containing the gel precursor. Accordingly, existing research on aerogel microparticles is restricted only to water-soluble systems.

The methods presented above are not suitable for producing aerogel microparticles of a family of polymeric precursor materials that do not dissolve in water, such as polyimides.
(PI), sPS, and PBZ, or are sensitive to moisture, such as isocyanates for polyurethanes and anhydrides for PIs. The aerogel monoliths based on PI, sPS, and PBZ exhibit unique properties but fabrication of microparticles of these polymers was never attempted.\textsuperscript{4, 34, 250}

A number of applications may benefit from aerogel microparticles of thermally stable polymers, such as sPS, PI, or PBZ. The large size (~10 cm) monoliths are not conducive to high mass diffusion rates and, therefore, cannot be used in the design of catalysts, energy storage devices (such as capacitors), drug delivery systems, scaffolds, or absorbers of small organic molecules. The mass diffusion rates can be significantly enhanced - by 3 orders of magnitude or more- if the same internal structures, porosity, and specific surface area are packaged in aerogel particles of 100 nm – 200 µm in diameter. Some of the advantages of aerogel microparticles are much shorter characteristic times of diffusion of mass in and out of the particles compared to bulk aerogel monoliths, the coexistence of macropores (pore diameter \( d_p > 50 \text{ nm} \)), mesopores (2≤\( d_p \leq 50 \text{ nm} \)), and micropores (\( d_p < 2 \text{ nm} \)) for facilitated transport of the solvated ions, e.g., in capacitors and drug molecules, and for expedited absorption of organic liquids from air, and high surface area for adsorption of small molecules and ions.

In this work, we demonstrated preparation of aerogel microparticles of PI and PBZ systems using oil-in-oil emulsion method as both PI and PBZ have considerable chemical stability and thermal stability at high temperatures. Two polar/nonpolar aprotic organic solvents were considered to form the immiscible oil phases for the emulsion. Dimethylformamide (DMF), a good solvent of organic monomers, was selected to form the dispersed phase while cyclohexane was used to form the continuous phase. A number of other organic liquid pairs can be considered, but oil-in-oil emulsion stabilization remains
a challenge. Klapper et al.\textsuperscript{251} used DMF-in-cyclohexane emulsion system for fabrication of polymer nanoparticles by stabilizing them with polyisoprene-\textit{b}-poly(methyl methacrylate) (PIP-\textit{b}-PMMA). PIP block is soluble only in cyclohexane while PMMA is soluble in DMF because of the closer Hansen solubility parameter values. The blocks acted as anchors to fix the interfaces between DMF droplets and cyclohexane. In this work, low-cost, commercially available nonionic surfactants, SPAN 85 and Hypermer 1599, were used as emulsion stabilizers.

PBZ gels can be prepared through either heating or acid-triggered ring-opening polymerization of benzoxazine.\textsuperscript{7, 8} Heating-triggered gelation usually requires 120 °C or higher temperature. We avoided heating-triggered gelation method in this work, as the boiling point of cyclohexane (80.7 °C) is lower than the minimum gelation temperature, which in turn could affect the stability of the emulsion system. In view of this, we resorted to room temperature gelation catalyzed by hydrochloric acid (HCl). DMF was found to be an optimal solvent for this polymerization method.\textsuperscript{8} PI aerogels are one of the most studied organic aerogels due to their high thermal stability and good mechanical properties.\textsuperscript{33, 229, 252, 253} PI gels in our work were synthesized via cross-linking of pyromellitic dianhydride (PMDA), 2,2-dimethylbenzidine (DMBZ), and 1,3,5-tris(4-aminophenoxy)benzene (TAB).\textsuperscript{34} Special care was exercised to avoid ingress of moisture into the system as PMDA is moisture sensitive. Our results suggested that oil-in-oil emulsion worked efficiently in preparing PBZ and PI aerogel microparticles. In addition, we answered several key questions. First, we answered if the aerogel microparticles differed significantly from their monolithic counterpart in terms of pore volume, pore structure, and surface area. Second,
we evaluated if carbonization caused any changes in pore structures compared to parent aerogel microparticles.

6.2 Experimental

Materials used are listed in this section. In addition, the details of sample preparation and characterization are shown as following.

6.2.1 Materials

4,4’-Isopropylidenediphenol (bisphenol-A), paraformaldehyde (96%), aniline, SPAN 85, and anhydrous dimethylformamide were obtained from Sigma-Aldrich. Hypermer™ 1599 was provided by Croda Inc. (Edison, NJ). Pyromellitic dianhydride was purchased from Alfa-Aesar and 2,2’-dimethylbenzidine was purchased from Shanghai Worldyang Chemical Co., Ltd. (Shanghai, China). 1,3,5-Tris(4-aminophenoxy)benzene was provided by Triton Systems (Chelmsford, MA) as a dull brown powder. Pyridine, acetic anhydride, and acetone were purchased from Fisher Scientific. All reagents and solvents were used as received.

6.2.2 Synthesis of the benzoxazine monomer

Bisphenol-A, aniline, and paraformaldehyde were mixed in a beaker with a molar ratio 1:2:4 and placed in a preheated oil bath (110 °C). The mixture was magnetically stirred for 1 h. The yellow product, benzoxazine-a, was cooled down to room temperature and ground into powder form for further use.
6.2.3 Synthesis of cross-linked poly(amic acid)

0.0830 g of PMDA and 0.0795 g of DMBZ were respectively added in 2.55 mL of DMF and 1.55 mL of DMF and magnetically stirred at 300 rpm until clear solutions were obtained. The solutions were mixed to obtain a translucent and homogeneous mixture which produced poly(amic acid) oligomers (A in Figure 6.1) upon stirring for 10 min. 0.0012 g of TAB dissolved in 1 mL of DMF was added to solution of A to form three-dimensional polymer network B (in Figure 6.1).

6.2.4 Preparation of benzoxazine sol

1 g of benzoxazine-a was dissolved in 4 mL of DMF to form a light yellow solution and the solution was added to 0.208 g of aqueous HCl solution (12.1 N) with stirring. The ingredients were mixed for 5 min. The color of the solution changed from yellow to dark red during this period.

6.2.5 Preparation of PI sol

As shown in Figure 6.1, 0.1660 g of PMDA and 0.1590 g of DMBZ were individually dissolved in 4.1 mL of DMF and 5.1 mL of DMF, respectively, to form homogeneous solutions. PMDA and DMBZ solutions were mixed to produce light yellow, translucent mixture which is poly(amic acid) oligomers with 60 repeat units. A solution of 0.0025 g of TAB in 1 mL of DMF was then added into the mixture. After 5 min of stirring, 0.5757 g of acetic anhydride and 0.4925 g of pyridine were added drop by drop into this solution. The mixture remained translucent, but the color turned to dark yellow.
6.2.6 Preparation of Monolithic Aerogels.

The sols were poured into 6 mL of polypropylene syringes and kept at room temperature for gelation and aging for 12 h. The cylindrical gels were soaked in acetone to exchange DMF. Acetone was replaced for 4 times with an interval of 6 h each time. The acetone filled gels were exchanged with liquid CO$_2$. Finally, the gels were dried under supercritical condition of CO$_2$ to obtain the aerogels.

![Figure 6.1](image_url) Reactions involved in synthesis of PI chains.
6.2.7 Preparation of Aerogel Microparticles

The preparation process includes four steps, as illustrated in Figure 6.2: (1) The sols in DMF were prepared according to the procedure described above. (2) 4 mL of sol was dispersed in 32 mL of cyclohexane with SPAN 85 (0.748 g) and Hypermer\textsuperscript{TM} 1599 (0.249 g) dissolved in it to form oil-in-oil emulsion. The emulsion was stirred for about 3 h using magnetic stirrer set at 400 rpm to obtain gel microparticles. (3) The emulsion was poured into acetone and the supernatant was removed to recover the gel microparticles. The gel microparticles were then washed 6 times with acetone in a Thinky\textsuperscript{®} Mixer at 1000 rpm, and each wash cycle spanning 5 min to remove the surfactants. (4) The gel microparticles were then dipped in liquid CO\textsubscript{2} to exchange acetone and supercritically dried to obtain aerogel microparticles. The gel microparticles were retained in the container during exchange of acetone with liquid CO\textsubscript{2} and subsequent supercritical drying step by using Kimwipes paper membrane. This allowed passage of the exchange liquid but prevented the loss of microparticles from the container (Figure 6.3).
Figure 6.2 Schematic representation of the aerogel microparticles preparation.

Figure 6.3 Container with gel microparticles when filled with liquid CO2 in the vessel of supercritical dryer.

Note: In the supercritical drying process, acetone in the gel needs to be exchanged with liquid CO2 in the supercritical dryer. Neck of the container was covered by KimwipesTM paper. Liquid CO2 can flow into the container when the vessel is fulfilled by liquid CO2. In this process, the particles can be retained in the container because that pores of KimwipesTM paper are smaller than the diameter of the gel particles. After this step, the supercritical dryer was heated to 50 °C and waited for 60 min before pressure release.
6.2.8 Pyrolysis of PBZ Aerogel Microparticles

The PBZ aerogel microparticles were cured at 160 °C for 1 h, 180 °C for 1 h, and 200 °C for 12 h, successively. The cured aerogel microparticles were carbonized at 850 °C. Typical heating schedule included temperature increase at 2 °C/min from 25 to 850 °C after which the temperature was held at 850 °C for 3 h, all under a N₂ atmosphere.

PI aerogel microparticles due to low solid content lost their integrity and shape after heating to 850 °C. Thus, carbon aerogel particles were not produced in pyrolysis of PI aerogel microparticles.

6.2.9 Instrumentation

The morphology of aerogels was probed using scanning electron microscopy (SEM; JEOL JSM5310) with operating voltage 8 kV. Brunauer−Emmett−Teller (BET) surface area and pore size distribution of aerogel specimens were obtained from N₂-sorption isotherms at 77 K, analyzed using a Micromeritics Tristar II 3020 analyzer. The aerogel specimens were sectioned and placed in designated chamber followed by degassing at 25 °C for 12 h before collecting data. Infrared (IR) spectra were recorded on a Bruker FT-IR Alpha spectrophotometer using a Platinum ATR accessory. The gel microparticles were probed by optical microscope (OM; OLYMPUS BX51).

6.2.10 Measurement of Diameter of Microparticles

The open source software ImageJ was used for measuring diameter of the microparticles using optical microscope images of the gels and SEM images of the aerogels. At least 100
microparticles were considered in each case. The resulting diameter distribution chart are presented in Figure 6.4.

6.2.11 Shrinkage Calculation

The values of shrinkage of monolithic aerogel was calculated from equation (17), where \( \delta_d \) is the shrinkage, \( D \) is the diameter of the cylindrical sample, and \( D_0 \) is the diameter of the mold in which the monolith was formed. In the case of aerogel microspheres, \( D \) and \( D_0 \) refer respectively to the diameter of aerogel microparticles and gel microparticles. As the diameter of single gel microparticle and the corresponding aerogel microparticles could not be obtained, equation (17) uses the weighted average values \( D' \) and \( D_0' \), respectively the weighted average diameter of aerogel and gel microparticles. The values of \( D' \) and \( D_0' \) were obtained from diameter distribution data in Figure 6.4 using equation (18).

\[
\delta_d = \left(1 - \frac{D}{D_0}\right) \times 100\% \quad (17)
\]

\[
d = \sum_{i}^{n} 5(2i + 1) \lambda_i 
\quad (18)
\]

In equation (18), \( d \) (\( =D', D_0' \)) is the weighted average diameter, \( i \) refers to the percentage value assigned in Figure S2, and \( i \) and \( n \) are parameters listed in Table 6.1. The calculated values of average diameter and the shrinkage are listed in Table 6.2.
Figure 6.4 Diameter distribution of (a) PBZ gel microparticles, (b) PBZ aerogel microparticles, (c) PI gel microparticles, and (d) PI aerogel microparticles.
Table 6.1 Values of \( i \) and \( n \) for different microparticles.

<table>
<thead>
<tr>
<th></th>
<th>( i )</th>
<th>( n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybenzoxazine gel microparticles</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>Polybenzoxazine aerogel microparticles</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>Polyimide gel microparticles</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Polyimide aerogel microparticles</td>
<td>1</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 6.2 Diameter and shrinkage of gel and aerogel specimens.

<table>
<thead>
<tr>
<th></th>
<th>( D_0 ) (mm)</th>
<th>( D ) (mm)</th>
<th>( \delta_d )</th>
<th>( D_0' ) (µm)</th>
<th>( D' ) (µm)</th>
<th>( \delta_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polybenzoxazine</td>
<td>12</td>
<td>9.41</td>
<td>21.6%</td>
<td>34.6</td>
<td>32.7</td>
<td>5.5%</td>
</tr>
<tr>
<td>Polyimide</td>
<td>16</td>
<td>14.93</td>
<td>6.7%</td>
<td>41.8</td>
<td>40.0</td>
<td>4.3%</td>
</tr>
</tbody>
</table>
6.3 Results and discussions

In this section, we separately presented and discussed the results of PBZ aerogel microparticels and PI aerogel microparticels. Properties of both materials were compared with their monolithic samples.

6.3.1 PBZ aerogel microparticles

As evident from Figure 6.5a, the aerogel particles obtained in this work were indeed microspheres with mean diameter ~32.7 µm. The inset in Figure 2a shows pieces of tiny particles of size less than 50 nm on the surfaces of aerogel microparticles. We believe that these are the remnants of the surfactant moieties that were not completely removed in the washing step. These microspheres also show solid surfaces at a resolution of 2 µm attributed to compaction of the polymer chains near DMF/cyclohexane interfaces during growth of the gel network. However, an enlarged view of the microsphere in Figure 6.5b reveals nanoscale roughness on the particle surfaces, a globular internal structure, and a dense skin layer. The thickness of the dense skin layer is estimated from the image in Figure 6.5b to be about 100 nm. The dense skin layers are typical for aerogel monoliths as well and are attributed to 2-D network formation at the surfaces. Figure 6.5c focuses on the internal structure. It is evident that the internal framework consists of spheres of different diameter, in corroboration with what is observed for PBZ aerogels monoliths prepared in the presence of HCl (Figure 6.5d).
Figure 6.5 SEM image of (a) PBZ aerogel microparticles. The inset shows the image of the surface of the sphere. Scale bar: 2 µm. (b) Fractured surface of PBZ aerogel microparticles. (c and d) Ensemble of spherical PBZ domains that formed the internal structure of aerogel microparticles and monolith, respectively.

Figure 6.6 (a) N₂-sorption isotherms. (b) Pore size distribution of PBZ aerogels.
The porous structure of the aerogel microparticles was further investigated by nitrogen (N$_2$) adsorption-desorption isotherms. The data for PBZ aerogel monolith and microspheres are presented in Figure 6.6a. Both these isotherms show negligible quantities of N$_2$ adsorbed at P/P$_0$ close to 0, indicating that the microparticles and the monoliths of PBZ aerogel had no micropores. The narrow hysteresis loops observed in the range 0.9<P/P$_0$<1 suggest that a majority of the pores are macropores. The pore diameter distribution in the range 1.7 to 100 nm obtained from Barrett-Joyner-Halenda (BJH) model is presented in Figure 6.6b. The volume of N$_2$ adsorbed in the pores increased with pore diameter starting at 3 nm and reached a maximum at around 50 nm. The volume of N$_2$ adsorbed in the diameter range 1.7-300 nm in PBZ aerogel microparticles reached a plateau, while it reduced significantly in the case of monolith. The BJH cumulative pore volume, V$_{1.7-300\text{nm}}$, is found to be 0.20 cm$^3$/g for PBZ aerogel microparticles, which is twice as much that of the monolithic sample (0.10 cm$^3$/g). We attribute the larger value of V$_{1.7-300\text{nm}}$ to lower shrinkage of the aerogel microparticles compared to the monoliths. Generally, considerable diameter shrinkage (10-20%) is observed for aerogel monoliths during supercritical drying process. The results revealed that PBZ aerogel cylindrical monoliths underwent about 21.6% shrinkage in diameter while the diameter of aerogel microspheres shrank only 5.5%. It is quite possible that the solvent in the gel, for instance, acetone in this work, was not completely exchanged with liquid CO$_2$ in the case of monolith before turning to supercritical drying step. Note that the cylindrical monolithic gel with length ~4 cm and diameter ~1.5 cm posed greater diffusion length for acetone. Acetone evaporated when the temperature was raised subsequently to 50 °C during supercritical drying step, resulting in the shrinkage. The gel microparticles of 30 µm diameter on the
other hand did not pose much diffusional limitation for acetone and hence suffered much less diameter shrinkage.

The values of BET surface area, $S_{\text{BET}}$, were found to be 55.4 m$^2$/g for the aerogel microparticles and 57.8 m$^2$/g for PBZ aerogel monolith. These values are comparable in view of standard deviation of ±7 m$^2$/g in BET surface area measurement using standard mesoporous materials supplied by Micromeritics. The close values of surface area are not surprising; recall from Figure 6.5c and 6.5d that the aerogel microparticles and the monolith had similar internal microstructures, i.e., aggregates of spheres with close values of diameter and surface roughness.

PBZ aerogels were found to be good precursor materials to obtain carbon aerogel.$^7,^8$ In this work, the microparticles were cured and subsequently pyrolyzed into carbon aerogel. After pyrolysis, the surfactant moieties decomposed completely. The carbon aerogel microparticles in Figure 6.7a show smooth surfaces at a resolution of 2 µm. The BET surface area of carbon aerogel microparticles was found to be 256.6 m$^2$/g, about 360% higher than BET surface area of PBZ aerogel microparticles. We attribute such an increase of surface area to newly generated micropores and an increase of the content of mesopores during pyrolysis. Figure 6.7b shows N$_2$-sorption isotherms and pore size distribution of carbon aerogel microparticles. The isotherm suggests that the microparticles adsorbed about 60 cm$^3$/g of N$_2$ when the relative pressure, $P/P_0$, is close to 0. Such adsorption indicates the presence of micropores (diameter < 2 nm) in the carbon aerogel framework. In contrast to the isotherms of PBZ aerogel microparticles seen in Figure 6.6a, the isotherm in Figure 6.7b shows larger quantity of adsorbed N$_2$ as well as a wider hysteresis loop at
P/P₀ > 0.8. This implies that mesopores became more dominant in carbon aerogels. This conclusion is supported by the pore size distribution data in the inset of Figure 6.7b.

![Figure 6.7 (a) SEM image of carbon aerogel microparticles. (b) N2-sorption isotherm of carbon aerogel microparticles. The inset is the pore size distribution.](image)

One specific application that can benefit from the micrometer size carbon aerogel particles reported in Figure 6.7 is the electrical double-layer capacitor (EDLC). Chemically inert and electrically conductive carbon aerogel particles with high specific surface area and tunable internal structures are ideally suited for fabrication of the electrodes of EDLC. The charges in EDLC are stored in the form of ions accumulated on the surfaces of the electrode materials. In this context, high specific surface area and the internal, primarily mesoporous structures of the carbon aerogel microparticles will contribute positively to the performance of EDLC. Specifically, the tunability of the carbon aerogel internal structures to have significant mesopores is expected to enhance the energy and the power density.²⁵⁴-²⁵⁷
6.3.2 PI aerogel microparticles

PI aerogel microparticles were first reported by Kwon and co-workers.\textsuperscript{150} They created PI gel microparticles by thermally imidizing the poly(amic acid) in 1-methyl-2-pyrrolidinone (NMP) solution in an autoclave such that PI gel microparticles precipitated out of the solution.\textsuperscript{150} The porosity of the resulting PI aerogel microparticles was determined to be 80\%, and $S_{BET}$ was 103 m$^2$/g. We used an entirely different method of production of gel microparticles in the present work. Instead of imidization-induced precipitation, the micrometer size droplets of poly(amic acid) in DMF were preformed and chemically imidized by pyridine and acetic anhydride while in emulsion in cyclohexane. Figure 6.8 shows the IR spectra of cross-linked poly(amic acid), PI aerogel microparticles, and monolith. The strong absorbance at 1650 cm$^{-1}$ indicates amide bonds in the poly(amic acid) (B in Figure 6.1). In addition, the absorbance bands at around 2926 cm$^{-1}$ and 3273 cm$^{-1}$ correspond to the COOH and CONH groups in the structure of B. After chemical imidization, the characteristic absorbance peaks of poly(amic acid) disappeared in the spectra of PI aerogel microparticles and monolith (C in Figure 6.1). The bands at around 1724 and 1780 cm$^{-1}$ are attributed to the symmetrical stretching and asymmetrical stretching of the imide C=O group respectively. The absorbance peak at 1372 cm$^{-1}$ is associated with C-N stretching in the imide rings and the absorbance at 724 cm$^{-1}$ is due to C=O bending. Besides, a visible but weak absorbance peak at around 2926 cm$^{-1}$ for the microparticles indicates small quantities of unreacted COOH groups. Recall that PI gel microparticles were aged for shorter times than that of the corresponding monolith.
Figure 6.8 FT-IR spectra of poly(amic acid), PI aerogel microparticles, and monolith.

As shown in Figure 6.9a, the obtained PI aerogel microparticles did not have regular spherical shape as was observed in the case of PBZ microparticles in Figure 6.5. Note that the solid content of the PI gel was 3 wt%. As a consequence, the PI gel microparticles were soft and easily deformed in the shear field applied during preparation process, especially in the washing step using the Thinky Mixer. Although sol with higher concentration can form harder gels, a concentration higher than 3 wt% was avoided in this work to circumvent the difficulty associated with higher viscosity of the sol that in turn posed issues during emulsion preparation.
Figure 6.9 SEM images of (a) PI aerogel microparticles, (b) their skeletal networks, and (c) surfaces of PI aerogel microparticles. (d) Schematic diagram of the effect of interfacial tension on the gel network. In (b), network structures of monolith are shown.

Figure 6.9b indicates that the internal microstructures of the aerogel microparticles and the monolith had no significant difference. The polymer network in PI aerogels synthesized from DMBZ, PMDA, and TAB appears as collection of polymer strands. Interestingly, the surfaces of the aerogel microparticles seen in Figure 6.9c contained open pores in contrast to the dense surfaces observed for PBZ aerogel microparticles in Figure 6.5b. In addition, the fibrillar network on the surfaces in Figure 6.9c appear somewhat stretched and compact in comparison to the internal network structure of the same microparticle. We can invoke two possibilities. First, in the sol-gel reaction step, the gel network may have
nucleated as a 2-D layer formed by the interconnected polymer strands at the interface between DMF-rich droplets and cyclohexane. A 3-D gel networks possibly began growing afterward inside the droplets. Second, the interfacial tension operating at the interface between DMF-rich droplets and cyclohexane may have stretched the gel network. This possibility is demonstrated schematically in Figure 6.9d. Similar arguments also apply to explain the compact surfaces of PBZ aerogel microparticles seen in Figure 6.5b.

$N_2$-sorption isotherms and pore size distribution curves are presented in Figure 6.10. In the case of monolith, the $N_2$-adsorption isotherm shows a sharp rise of adsorbed quantity at $P/P_0 > 0.9$, but a well-defined saturation plateau is not observed. This is an indication of the presence of both meso- and macropores with relatively lower mesopore content. In the case of aerogel microparticles, however, the $N_2$-desorption isotherm shows a short saturation plateau and a wider hysteresis loop, suggesting that the microspheres contained more mesopores than the monolithic sample. This conclusion is consistent with the pore size distribution curve in Figure 6.10b. The area under the curve in Figure 6.10b approximately equals the cumulative pore volume. It is apparent that the aerogel microspheres had higher mesopore volume than the monolith. The data on pore volume and BET surface area of PBZ and PI aerogels are summarized in Table 6.3. As in the case of PBZ aerogels, the PI microspheres also contained higher pore volume than the monolith, e.g., 3.38 cm$^3$/g vs 2.36 cm$^3$/g, respectively, and lower $S_{BET}$, e.g., 512 m$^2$/g vs 716.7 m$^2$/g.
The shrinkage of microparticles and monolith was respectively 4.3% and 6.7%. As discussed above in the case of PBZ aerogel microparticles, a part of the shrinkage is attributed to evaporation of residual acetone in the gel. Capillary stress generated during the evaporation is proportional to $R^{-1}$, where $R$ is pore radius, and thus the capillary stress...
has stronger impact on the small pores (1.7 nm<2R<300 nm) than the pores with diameter larger than 300 nm. In view of this and although the shrinkage was comparable, the value of $V_{1.7-300\text{nm}}$ varied significantly from aerogel microparticles to monolith.

Table 6.3 Properties of PBZ and PI aerogel specimens.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{BET}$ (m² g⁻¹)</th>
<th>$V_{1.7-300\text{nm}}$ (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBA-Mi</td>
<td>55.4</td>
<td>0.20</td>
</tr>
<tr>
<td>PBA-Mo</td>
<td>57.8</td>
<td>0.10</td>
</tr>
<tr>
<td>PIA-Mi</td>
<td>512.0</td>
<td>3.38</td>
</tr>
<tr>
<td>PIA-Mo</td>
<td>716.7</td>
<td>2.36</td>
</tr>
</tbody>
</table>

* PBA: polybenzoxazine aerogel; PIA: polyimide aerogel; Mi: microparticle; Mo: monolith.

We observed in Figure 6.9 that the surface layers of PI microparticles were compact with significant surface pores, unlike the denser surface layers observed for PBZ aerogel microparticles. Considering typical particle diameter of ~ 25 µm, the microparticles had several orders of magnitude higher particle surface area to particle volume ratio than the monoliths. Consequently, the fraction of compact surface layers was much higher in aerogel microparticles and may explain lower BET surface area. However, this alone cannot explain 30% less BET surface area for PI microparticles, specifically in view of negligible BET surface area reduction in the case of PBZ aerogel microparticles, although the surface layers of PBZ microparticles were denser. Another possible factor may be the roughness of the polymer strands constituting the aerogel network which contributes importantly to $S_{BET}$.³⁶ Yet another factor may be shorter time (3 h) of aging in the case of
PI microparticles compared to 12 h of aging for PI monoliths. The PI gel particles were poured into acetone after only 3 h of aging to prevent the breakage of the gel particles during stirring over a longer period of time. Shinko et al. reported that the strands of PI in gel networks exhibit rougher surfaces if the dianhydride of lower flexibility are used.\(^\text{36}\) We infer that the PI chains in PI gel particles were less rigid due to shorter aging, thus leading to smoother strands and lower \(S_{\text{BET}}\) value compared to monolithic aerogel.

6.4 Conclusions

In summary, oil-in-oil emulsion was used to produce aerogel microparticles of PBZ and PI. The method described in this work is the first nonaqueous emulsion system used in successful preparation of micrometer-sized aerogel particles. The synthesis process adopted in this work reduced the diffusion length scale for solvent exchange to a few tens of micrometers, thus effectively reducing the degree of shrinkage in comparison to monolithic specimens. The BET surface area of aerogel microparticles and monolithic aerogels were close to each other for PBZ aerogels but were significantly different for PI aerogels and were attributed to shorter aging of PI gel microparticles. The study showed that the mesoporous nature of the parent PBZ aerogel microparticle can be easily realized in derivative carbon aerogel microparticles.
CHAPTER VII

OVERALL SUMMARY

This work focused on the study of building blocks of aerogel networks, covering the growth mechanism of solid networks investigated by laser light scattering (LLS), the effects of different building blocks on the porosity of polybenzoxazine (PBZ) aerogel monoliths, and the building blocks of aerogel microparticles and aerogel foams.

The first part of the work started with the observations of the globular-aggregates and fibrillar networks of PBZ aerogels synthesized in dimethyl sulfoxide (DMSO) and N-methyl-2-pyrrolidone (NMP), respectively. It was revealed that PBZ aerogels with globular networks showed higher BET surface area and mesoporosity, but lower porosity than PBZ aerogels with fibrillar network. In order to give a valid explanation, we successfully employed LLS technology to figure out the dynamic processes of the formation of spherical and fibrillar building blocks. The LLS results suggested that both building blocks resulted from polymerization induced nucleation and growth process. In DMSO, the diameter of the nuclei grew with polymerization and directly aggregated to form an integral 3D network. In contrast, we observed that the nuclei in NMP assembled into cylinders followed by fibrillar networks formation.

The second part of the work studied the microstructures of aerogels synthesized in a homogeneous system. Construction of gel networks in heterogeneous confinements and
the properties of the derived aerogel-like materials were studied in the second part. In Chapter V, templating method was used to prepare polyurea open cell aerogel foams (PUA OCAFs) which exhibited bicontinuous structure of micrometer-sized cavity and nanoporous aerogel domain. In comparison with PUA Aerogels, PUA OCAF show relatively low BET surface area and specific mesopore volume because of the incomplete removal of the template materials. However, incorporating a macroporous template in a sol-gel reaction system contributed to the formation of the characteristic morphology of PUA OCAFs. The very method also led us to discover the significance of heterogeneous nucleation and growth for gel network growth formation. The hierarchical pore structure enables PUA OCAFs to exhibit higher oil absorption rate and air permeability than PUA Aerogels.

In chapter VI, oil-in-oil emulsion was used to produce aerogel microparticles of PBZ and polyimide (PI). The synthesis process adopted in this work reduced the diffusion length scale for solvent exchange to a few tens of micrometers, thus effectively reducing the degree of shrinkage in comparison to monolithic specimens. Interfaces between continuous phase and dispersed phase catalyzed the nucleation process near the surface of each sol droplets in the emulsion systems. As a result, the aerogel microparticles showed denser surface networks than the internal ones. The BET surface area of aerogel microparticles and monolithic aerogels were found to be close to each other for PBZ aerogels but were significantly different for PI aerogels and were attributed to shorter aging of PI gel microparticles. The study showed that the mesoporous nature of the parent PBZ aerogel microparticles can be easily realized in derivative carbon aerogel microparticles.
The research in this study made several contributions to archival literature. First, we validated the applicability of LLS on investigating the growth of gel networks. The globular-aggregate and fibrillar networks were not novel observations which have been reported in the studies of silica aerogels, PI aerogels, resorcinol-formaldehyde (RF) aerogels and PUA aerogels. However, the relevant discussions were basically focused on attributing two morphologies to distinct stages of nucleation and growth or spinodal and decomposition. Using LLS was the first methodology to directly monitor the growth of the network formation, from nanoparticles with diameter of several nanometers to infinite 3D networks. With the assistance LLS analysis, researchers can find out the factors determining the microstructure of aerogels and eventually prepare the aerogels with desired properties.

Second, we developed the templating method to prepare the aerogel foams. The most important advantage of our method is the tunability of the macropores in the aerogel foams, which can be easily realized by engineering the size and volume ratio of the macropores in the polymer templates. Materials of the aerogel foams could expand from PUA to PI, RF, and the derivative carbon. Therefore, more applications, such as electrode materials for supercapacitor, can be pursued in the future.

Third, oil-in-oil emulsion could be a new alternative for creating aerogel microparticles. A number of gels are derived from isocyanates or anhydrides which are moisture sensitive. It limited the utilization of water-in-oil or oil-in-water emulsion for preparing such gel microparticles. As demonstrated in this work, oil-in-oil emulsion could overcome this problem and PBZ and PI aerogel microparticles were prepared which show comparable properties with their monolithic aerogels.
REFERENCES


