Organic Sol–Gel Synthesis of Microporous Molecular Networks Containing Spirobifluorene and Tetraphenylmethane Nodes

Su-Young Moon, Hye-Rim Mo, Min-Kyoon Ahn, Jae-Sung Bae, Eunkyung Jeon, Ji-Woong Park

Department of Materials Science and Engineering, Gwangju Institute of Science and Technology, 261 Cheomdan-gwagiro, Buk-gu, Gwangju 500-712, Korea Correspondence to: J.-W. Park (E-mail: jiwoong@gist.ac.kr)

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ABSTRACT: The microporous molecular networks based on rigid tetrafunctional units are synthesized via organic sol–gel polymerization of 2,2',7,7'-tetraamino-9,9'-spirobifluorene (TASBF) and/or tetrakis(4-aminophenyl)methane (TAPM) with a diisocyanate, hexamethylene diisocyanate (HDI), or *p*-phenylene diisocyanate. This study is performed as an extension of our previous report on the first organic sol–gel method, which enabled the synthesis of microporous molecular networks via a two-stage mechanism involving the formation of colloidal dispersions of the nanoparticulate molecular networks and their subsequent growth to monolithic networks obtained by incorporating TASBF as a network former show improved porosity, processability, and thermal stability than the TAPM-based system. The improved porosity of TASBF-based networks is attributed to higher rigidity

INTRODUCTION Microporous materials with high surface area (200-8000 $\text{m}^2 \text{g}^{-1}$) and small pore size (<2 nm) have long been regarded important for various energy- and environment-related technology such as gas storage and separation, heterogeneous catalyst, and drug delivery.¹⁻⁸ Zeolites and activated carbons are examples of the conventional microporous systems.^{9–11} In recent years, crystalline microporous materials such as metal organic frameworks,^{3,12} covalent organic frameworks,13 and zeolitic imidazolate frameworks14 have been studied intensively. In addition, various amorphous organic or polymer networks such as polymers of intrinsic microporosity,¹⁵⁻¹⁷ porous polymer networks,¹⁸⁻²¹ conjugated microporous polymers,²²⁻²⁵ and hypercrosslinked poly- $\mathrm{mers}^{26\text{--}29}$ have been studied for their microporous characteristics. These polymer networks are attractive because of their simple synthesis and chemical functionalization methods^{30,31} and the availability of diverse monomer systems for them.

Many organic networks are synthesized by polymerization of rigid multifunctional organic compounds based on tetraphenylmethane (TPM), adamantane, and spirobifluorene (SBF) of the spirobifluorene compared with the tetraphenylmethane units. We also demonstrate the synthesis of mixed organic molecular networks by sol-gel copolymerization of the two network formers, TASBF and TAPM, and a diisocyanate monomer. The sol-gel transformation of TASBF/TAPM/HDI occurred at longer reaction times with increasing the amount of TASBF in the TASBF/TAPM/HDI mixture. The results indicate that the organic sol-gel method can be further optimized by adjusting various synthesis parameters to create new functional organic molecular network materials. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 1758–1766

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units.^{15,20,32–36} These materials consist of the molecular networks whose crosslink sizes are on the molecular length scale. However, most of the network materials synthesized to date, either crystalline or amorphous, are produced as intractable solids, limiting their chemical functionalization or postprocessing into useful forms. Emulsion-templated synthesis of the nanoparticles of the organic molecular network may be a potentially useful method for functionalization or hybridization of the networks.^{37,38} However, if the organic molecular networks can be made solution processable by using a simple method without using dispersing agents or template, there would be ample opportunity of creating new materials via their chemical functionalization, morphological control, and hybridization.

We reported recently the first organic sol-gel method based on the crosslinking condensation polymerization between multifunctional amine and isocyanate monomers in polar aprotic solvents.³⁹ The resultant network consisted of TPMbased units crosslinked via urea bonds. The growth of the organic network proceeded via a two-stage mechanism

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FIGURE 1 Organic sol-gel synthesis of molecular networks.

involving the formation of colloidal dispersions in solution and the subsequent growth to monolithic networks on evaporation of solvent, analogous to the sol-gel growth of inorganic oxide networks.^{40,41} The organic molecular networks could be produced in the form of thin films or nanoparticles using the organic sol-gel method. Below a critical gelation concentration (c_g), the polymerization solution maintained its fluid (sol) state without gelation. Above c_g , the polymer solution became gel after a certain elapsed time, which we defined as the gelation time (t_g). However, the molecular networks exist still in the sol state during the time before t_g , being available for further processing such as chemical functionalization or blending with other materials.

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Therefore, to exploit the organic sol-gel methods, it is desirable to identify the monomer systems that polymerize at the higher $c_{\rm g}$ or the longer $t_{\rm g}$ to ensure a sufficient time for processing of the molecular networks in the sol state. In the present work, we use the SBF-based monomers in the organic solgel method in addition to the previous TPM-based systems for the generation of microporous networks by the organic sol-gel method. The 90°-kinked structure of SBF unit prevents efficient packing of segments in the matrix, yielding the frameworks with greater morphological stability and higher surface area than the tetrahedral structure.^{32,42–44} The results show that the SBF-based organic networks allow longer processing time, higher thermal stability, and greater microporosity than the TPM-based networks. We also demonstrate the synthesis of mixed molecular networks via sol-gel copolymerization of SBF- and TPM-based monomers. The gelation time (t_{α}) of the mixed network sols increased with the amount of TASBF in the copolymerization mixture. The study indicates that the potential of organic sol-gel method for creation of new functional organic molecular network materials can be enhanced by further optimizing various synthesis parameters.

RESULTS AND DISCUSSION

Sol-Gel Synthesis of Organic Molecular Networks Based on SBF and TPM Monomers

We used two tetra-amines, TASBF or TAPM, as network former (Fig. 1) in our sol-gel polymerization. The two monomers were synthesized by the procedure reported previously.^{45,46} Four combinations of monomer pairs, TASBF/HDI, TASBF/PDI, TAPM/HDI, and TAPM/PDI were studied for their sol-gel polymerization in N,N'- dimethyl formamide (DMF).

The gelation time (t_g) of each monomer pair was determined with varying the concentration of the monomer solution. The reaction time elapsed until the gel was visually observed at room temperature was recorded as t_{g} . Figure 2 shows the gelation time (t_g) plotted against their polymerization concentration for all monomer pairs. The critical gelation concentration (c_g) is the monomer concentration at which the gelation time is infinite; it is the maximum monomer concentration in the sol state that do not transform to the gel state. From the data in Figure 2, the $c_{\rm g}$ values for TASBF/PDI and TAPM/PDI networks were estimated to be ~ 0.01 g mL⁻¹, and those of TASBF/HDI and TAPM/HDI to be ${\sim}0.03~g~mL^{-1}$ varying with the type of isocyanate monomers. At a concentration above $c_{\rm g}$, the $t_{\rm g}$ values increased in the order of TASBF/PDI, TAPM/PDI, TAPM/HDI, and TASBF/HDI. For instance, the t_g for each of the four monomer pairs at a concentration of 0.04 g mL⁻¹ were 1, 8, 85, and 170 h, respectively. It is shown that the monomer pairs with HDI tend to exhibit longer t_g 's and higher c_g 's than those with PDI. Because both TASBF and TAPM have the same aminophenyl nucleophiles, the different $t_{\rm g}$ and $c_{\rm g}$ values should arise from the reactivity (electrophilicity) difference of the diisocynates



FIGURE 2 Gelation time t_g for solution with different initial concentration for four different monomer pairs in DMF.



FIGURE 3 In situ ¹H NMR spectra of the 0.07 g mL⁻¹ TASBF/ HDI crosslinking polymerization solution in DMF- d_7 .

toward aromatic amine groups. It is known that aromatic diisocyanate is more reactive than aliphatic diisocyanate.⁴⁷ It is most likely that the functional groups in the growing network in the sol state have the reactivity similar to the monomers. Therefore, the networks from more reactive monomers grow outward more rapidly, resulting in the formation of macroscopically interconnected networks (gels) at lower concentrations and shorter reaction times. The network systems with longer gelation time (t_g) (TASBF/HDI or TAPM/HDI) may be advantageous for blending or chemical functionalization that can be performed in the sol state.

The Growth of SBF Molecular Networks in the Organic Sols

In the previous study, we showed by monitoring in situ ¹H NMR spectra of the polymerization solution in DMF- d_7 that the amine and isocyanate groups continued to react and generate new urea bonds. We obtained similar ¹H NMR spectral data for TASBF/HDI system at two concentrations, 0.03 and 0.07 g mL⁻¹. In the spectra, the signal of the primary amine protons of TASBF moiety disappeared as they reacted with isocyanate groups to form the urea bonds (Fig. 3). Amine-to-urea conversion (α was estimated by comparing the integration of amine and urea protons, and plotted against the reaction time (t) as shown in Figure 4.

In both concentrations of 0.03 and 0.07 g mL⁻¹, the conversion increased roughly in two stages; an initial rapid increase to above 80% followed by a second stage in which the conversion increases slowly to a plateau near 95%. Because the c_g value of the TASBF/HDI system is slightly above 0.03 g mL⁻¹, the solution at 0.03 g mL⁻¹ maintained the fluid (sol) state even after the conversion exceeded 90%; whereas the solution at 0.07 g mL⁻¹ transformed to a gel after the t_g (50 h) where the conversion reached higher than 90%.

The sol state of the TASBF/HDI mixture at the concentration of 0.03 g mL⁻¹ was investigated by dynamic light scattering (DLS) (Fig. 5), which indicated that the polymerization proceeded via the formation of the sols consisting of the nanoparticle of networks and that the particle size continued to grow even after 150 h at which the NMR-estimated conversion reached over 90%.

The growth behaviors observed by the NMR and DLS study are attributed to the two stage sol-gel polymerization mechanism as reported previously for TAPM-based networks.³⁹ In the early stage, the monomers and oligomers react rapidly, giving a steep increase of NMR-estimated conversion. After consumption of most of the labile reactants, the reaction rate is slowed down because most of the remaining amino or isocyanate groups are bound to the crosslinked networks. The amine-isocyanate coupling reaction is then dominated by slow interparticle coupling. These account for continuous increase of the average particle size even after the reaction rate is significantly slowed down. Broadening of particle size distribution at longer reaction time is also an indication of interparticle coupling reaction in the later stage.

Sol-Gel Synthesis of Mixed Organic Networks by Copolymerization of TASBF and TAPM with Diisocyanate

We studied further the formation of mixed molecular networks via organic sol-gel copolymerization of the two network formers, TASBF and TAPM. The gelation time (t_g) of the polymerization solution consisting of a 50/50 mixture of TASBF/TAPM and an equimolar amount of HDI in DMF appeared nearly the average of the t_g valued for TAPM/HDI and TASBF/HDI [Fig. 6(a)]. For a fixed solution concentration of the TASBF/TAPM/HDI reaction mixture, the gelation time increased with the composition of TASBF [Fig. 6(b)].

The Structure and Properties of the Organic Molecular Networks

The urea bonds have been known as one of the strongest hydrogen-bond-capable organic moieties. The synthesized organic molecular networks were characterized by FTIR (Supporting Information Fig. S1). The network materials



FIGURE 4 Conversion α as a function of reaction time *t* for TASBF/HDI solution with different concentration; squares: 0.03, circles: 0.07 g mL⁻¹.



FIGURE 5 Growth of the nanoparticle comprised of 0.03 g mL⁻¹ TASBF/HDI molecular networks in the sol state. (a) Number distribution of particle diameter obtained from DLS measurements at the reaction time t = 150, 350, and 500 h, respectively. (b) Average DLS particle diameter as a function of reaction time (t).

reacted up to the conversion of 95% were purified by precipitation into a nonsolvent (acetone) followed by drying under vacuum at 200 $\,^\circ\text{C}.$ The resultant networks exhibited IR absorption at 1653 cm⁻¹ for carbonyl stretching and 3340 cm⁻¹ for N–H stretching, both of which are lower than those known for isolated urea bond,⁴⁸ indicating that the majority of the urea groups in the organic networks were hydrogen bonded. This means that the organic networks produced by the sol-gel polymerization of amine and isocyanate monomers possess crosslinking nodes consisting both of the covalent and hydrogen bonding. The degree of urea hydrogen bonding within the network should influence significantly the porous properties of the molecular networks. Relatively small specific surface areas of the sol-gelproduced networks may be attributed to the H-bonding of urea networks. Currently, we are seeking methods to modify the degree of H-bonding in the networks.

The organic networks containing SBF units showed higher thermal stability than the TPM-based networks. On the thermogravimetric analysis (Supporting Information Fig. S2), the temperatures at 5% weight loss appeared at 290, 310, and 312 °C for TAPM/HDI, TAPM/TASBF/HDI, and TASBF/HDI networks, respectively. The greater thermal stability of the

SBF-based networks than the TPM-based ones is attributed to the additional aromatic C--C bonds of the SBF-nodes when compared with the TPM nodes. The uniqueness of the sol-gel-synthesized organic networks when compared with other types of organic or polymer network materials is that the crosslinked networks can be produced as thin coatings or free-standing films by simple casting of the sols onto the substrate surface. Thin films of the TASBF/HDI networks were prepared on the glass plates from 0.03 g mL^{-1} sol showed a cross section with thickness of $\sim 20 \ \mu m$ and smooth surface (Fig. 7). We controlled the thickness of films by casting different amounts of sols in a flat substrate with side walls (such as petri dish). In addition, when the same volume of sols was used, higher monomer concentrations gave thicker films. The surface roughness of the films was below 0.6 nm as estimated by the AFM images. The smooth surface of the resulting films indicates that sol-gel transformation occurred without formation of the precipitates during solvent evaporation. Because the films become insoluble monolithic networks after evaporation of the solvent, the organic sol-gel material is potentially useful as a protective interfacial layer in the solvent-involved device fabrication processes.



FIGURE 6 (a) Comparison of gelation times (t_g) for homopolymer (TAPM/HDI and TASBF/HDI) and copolymer (TAPM/TASBF/HDI, molar ratio = 1:1:2) networks. (b) Gelation time (t_a) of the copolymers with different TAPM/TASBF compositions.



FIGURE 7 (a) SEM image of the cross section, and (b) tapping mode AFM image of the surface of a free standing film. The films were prepared on a glass plate by solvent evaporation of 0.03 g mL^{-1} TASBF/HDI solution.

Synthesis of Network Powders Prepared by Precipitation of the Sols into Nonsolvent

In addition to the films, the organic networks could be produced in particulate forms by precipitating the sols into nonsolvents such as acetone or water. The network nanoparticles constituting the sol have different sizes and crosslink densities, varying with the reaction time. Therefore, the morphology and property of the network materials vary according to the reaction time when the solution was poured into nonsolvent.

We used acetone as the nonsolvent for precipitating the sols. The collected solids were washed with acetone and dried under vacuum at 200 °C. The porosity of the resulting powdery molecular networks was obtained by measuring carbon dioxide adsorption isotherms at 273 K. The resulting powdery materials exhibited a typical type-I adsorption isotherm for carbon dioxide, indicative of the microporosity [Fig. 8(a)]. The specific surface area and micropore volume were estimated by applying Dubinin-Astakhov (DA) equation,^{49–51} which appeared in the range of 200–500 m² g⁻¹ and 0.1–0.3 cm³ g⁻¹, respectively (Table 1).

In Figure 8(b), the specific surface area of the TASBF/HDI network powder was plotted as a function of the conversion at the time of precipitation of the sols. When the samples were prepared from the sol with the concentration of 0.03 g mL⁻¹, which is near the c_g , the specific surface area and the adsorbed amounts of gas reached the maximum for the samples prepared at the conversion of 70% [Fig. 8(b)]. In contrast, the samples prepared from the sols with the concentration of 0.07 g mL⁻¹, which is higher than c_g , the specific surface area values did not show much variation with the conversion. This trend is different from that observed in the TAPM/HDI system in which the surface area maxima were observed for the networks prepared at the higher concentrations.³⁹ Currently, it is unclear how the difference between SBF and TPM-based networks arose. We think that the



FIGURE 8 Microporous characteristics of organic molecular networks. (a) Carbon dioxide adsorption isotherms measured for the networks precipitated at various conversions from 0.03 g mL⁻¹ TASBF/HDI sol states: triangles 70%, circles 50%, inverted triangles 80%, crosses 25%, respectively. (b) Specific surface area for the TASBF/HDI networks prepared at different solution concentrations as a function of the conversion (α) at the time of deactivation: squares 0.03 g mL⁻¹ and circles 0.07 g mL⁻¹, respectively.

TABLE 1 Porosity of TAPM/HDI, TASBF/HDI, and TAPM/TASBF/HDI Precipitated at the Conversion of 70% with the Solution of the Concentration 0.03 g $\rm mL^{-1}$

	TAPM/ HDI	TASBF/ HDI	TAPM/TASBF, HDl ^a
Surface area (m ² g ⁻¹) ^b	229	431	205
Micropore volume (cm ³ g ⁻¹) ^b	0.11	0.21	0.10

^a Molar ratio of TAPM/TASBF/HDI = 1:1:2.

^b Calculated by Dubinin-Astakhov equation.⁴⁷

different porosities of the powdery samples are related to their different morphological structures that formed upon precipitation of the sols into nonsolvent.

The pore size distribution was calculated by density functional theory model.⁵²⁻⁵⁴ The pore size of the networks was typically in the range of 5–9 Å (Fig. 9).

The specific surface area and micropore volume of TAPM/ HDI, TASBF/HDI, and TAPM/TASBF/HDI precipitated at the same conversion of 70% were measured (Table 1), where TASBF/HDI networks exhibited higher specific surface area than TAPM/HDI networks. The improved porosity may be attributed to the structural stability of kinked and rigid SBF crosslinks. However, the porosity of the mixed network obtained by copolymerization of TAPM/TASBF/HDI with 1/ 1/2 ratio rather decreased and the effect of TASBF was not revealed. This is in part consistent with the result shown in Figure 8 in that the monomer concentrations and conversions giving the best microporosity are different for each of the two network formers. Further optimization of synthesis parameters may be needed to obtain maximum porosity for the mixed networks.

To understand the porosity dependence on the conversion and polymerization concentration, we compared the SEM images of the samples precipitated at the conversion of 30 and 70% for each of the 0.03 and 0.07 g mL⁻¹ sols (Fig. 10). All of the samples showed particulate morphology varying with the sample preparation conditions. The sizes of the particles appeared much greater than those observed by DLS (Fig. 5), indicative of aggregation during the precipitation process. The samples from 0.03 g mL^{-1} sol consist of the particles a few tens of nanometer for 30% conversion and about a hundred nanometers for 70% conversion. The samples from 0.07 g mL⁻¹ sols showed mixture of the particles with a wide range of diameters from several tens to several hundred nanometers. Because we used similar amounts of nonsolvent and stirring speed in the precipitation of each sample, the morphological difference may be attributed to the degree of phase segregation of the sol phase in the nonsolvent at the time pouring into the nonsolvent.

The specific surface areas of the four samples cannot be correlated to the SEM-observed particle sizes because the microporosity is not related to the apparent mesoscopic size of the particles but to the micropores inside the particles that cannot be imaged by the SEM. Maximum porosity was observed for the powder [Fig. 10(b)], which was prepared at the intermediate conversions of the low concentration sols. We postulate that the micropores within the bigger nanoparticles from high concentration sols may be more difficult to be accessed by the adsorbing gas molecules and that the networks formed from low conversion sols may be collapsed, exhibiting low microporosity.

We could not obtain nitrogen or argon adsorption isotherm curves for most samples synthesized by the sol-gel method. We attribute these to the difficulty of gas diffusion into the ultra-micropores at 77 K and tightened urea H-bonded networks.¹⁵ Interestingly, however, the network samples precipitated at low conversions (~25, 35, 40%), exhibited N₂ adsorption behavior (Fig. 11). The samples appeared to have mesopores of 2–3 nm and low specific surface area (20–60 m² g⁻¹) as calculated by the BET equation. This indicates that the powdery samples prepared from low conversion network possess both mesopores and micropores. We think that the mesopores formed with interconnection of immature oligomeric networks by quenching of the reaction in the nonsolvent.

The Bulk Organic Networks Prepared by Solution-State Gelation above $c_{\rm g}$

Above the critical gelation concentration of the monomer solutions, the sols transform to gels on prolonged stirring. The gelled samples were isolated and purified by precipitation and washing with nonsolvent. We compared the porosity of the networks prepared from different initial concentrations. The networks gelled at higher concentrations showed smaller microporosity (Fig. 12). In particular, the bulk network synthesized at the concentration of 0.10 g mL⁻¹ exhibited nearly no microporosity. This result may be accounted for by the formation of the macroscopic networks with low crosslink density as the mixture gelled rapidly at a short reaction time. The formation of molecular scale networks are



FIGURE 9 The pore size distribution (PSD) of the network powders from different monomer combinations precipitated at the conversion of 70% from the sols with the concentration of 0.03 g mL⁻¹, which was calculated by density functional theory (DFT) model.



FIGURE 10 SEM images of the TASBF/HDI network powders prepared from different initial solution concentrations and reaction conversion (a) 0.03 g mL⁻¹, α : 30%, (b) 0.03 g mL⁻¹, α : 70%, (c) 0.07 g mL⁻¹, α : 30%, and (d) 0.07 g mL⁻¹, α : 70%; scale bar: 200 nm.

enhanced at the concentration near to the critical gelation concentration.

CONCLUSIONS

The microporous molecular networks based on rigid tetrafunctional units were synthesized via organic sol-gel polymerization of 2,2',7,7'-tetraamino-9,9'-spirobifluorene (TASBF) and/or tetrakis(4-aminophenyl)methane (TAPM) with two diisocyanate monomers, hexamethylene diisocyanate (HDI), or p-phenylene diisocyanate (PDI). The sol-gel-synthesized molecular networks obtained by incorporating TASBF as a network former showed improved porosity, processability, and thermal stability than the TAPM-based system. The improved porosity of TASBF-based networks was attributed to higher rigidity of the SBF compared with the TPM units. We also demonstrated the synthesis of mixed organic molecular networks by sol-gel copolymerization of the two network-formers, TASBF and TAPM, and a diisocyanate monomer. The sol-gel transformation of TASBF/TAPM/ HDI occurred at longer reaction times with increasing the amount of TASBF in the TASBF/TAPM/HDI mixture. The results indicate that the potential of the organic sol-gel method for creation of new functional organic molecular network materials

can be enhanced by adjusting detailed synthesis parameters. Studies on various aspects of the organic sol-gel synthesized networks such as the functionalization of particles surface and blending of the networks with other polymers are underway.



FIGURE 11 Nitrogen isotherms at 77 K of 0.03 g mL⁻¹ TASBF/ HDI networks precipitated for low conversion: diamonds 25%, circles 35%, and triangles 40%, respectively.



FIGURE 12 Carbon dioxide adsorption isotherms of gelled TASBF/HDI networks with different initial concentration after t_g at 273 K: diamonds 0.05, circles 0.07, triangles 0.10 g mL⁻¹, respectively.

EXPERIMENTAL

Materials

Anhydrous *N*,*N*-dimethylformamide (DMF) and anhydrous tetrahydrofuran (THF) were purchased from Aldrich and DC chemical company, respectively, and used without further purification. HDI (>97%, Aldrich) was freshly distilled under reduced pressure. PDI (Aldrich) were purified by sublimation. The other materials were purchased from Aldrich and used without further purification.

Synthesis of 2,2',7,7'-Tetraamino-9,9'-spirobifluorene

To 2,2',7,7'-tetranitro-9,9'-spirobifluorene (8.30 g, 16.7 mmol) in 250 mL of THF, 16.00 g (excess) of hydrazine monohydrate and \sim 80 g of Raney nickel were added and refluxed for about 3 h. The mixture was hot filtered and washed with ethanol. Solvent was evaporated and the residue was washed with ethanol and dried.

¹H NMR (400 MHz, DMSO- d_6): 7.38 (d, 4H, J = 8.0 Hz), 6.59 (dd, 4H, J = 8.0 Hz, J = 2.0 Hz), 5.93 (d, 4H, J = 2.0 Hz), 4.35 (bs, 8H).^{45,46,55}

Synthesis of Tetrakis(4-aminophenyl)methane

To the solution of tetrakis(4-nitrophenyl)methane (3 g, 5.99 mmol) in THF (200 mL), 4.00 g (excess) of hydrazine monohydrate and 20 g of Raney nickel were added and refluxed for about 3 h. The mixture was hot filtered and washed with ethanol. The combined filtrates were evaporated, the residue was washed with chloroform, and then the crude product was recrystallized with ethyl alcohol to get white crystals of TAPM.

¹H NMR (400 MHz, DMSO- d_6): 6.65 (d, 8H, J = 8.7 Hz), 6.35 (d, 8H, J = 8.7 Hz), 4.80 (s, 8H).^{45,46,55}

Synthesis of Polyurea Network Solution by Crosslinking Polymerization of TASBF/HDI System

In a typical preparation of TASBF/HDI solution of 3 w/v %, TASBF (MW: 376.45, 0.112 g, 0.298 mmol) was dissolved in 7.1 mL of dry DMF. HDI (MW: 168.19, 0.100 g, 0.595 mmol)

was added to the solution, and the mixture was stirred at room temperature under nitrogen.

Synthesis of Polyurea Network Solution by Crosslinking Polymerization of TASBF/PDI System

In a typical preparation of TASBF/PDI 1 w/v % solution in DMF, TASBF (MW: 376.45, 0.118 g, 0.312 mmol) was dissolved in 21.8 mL of dry DMF. PDI (MW: 160.13, 0.100 g, 0.624 mmol) was added, and the mixture was stirred at room temperature under nitrogen.

Synthesis of Polyurea Network Solution by Crosslinking Copolymerization of TAPM/TASBF/HDI System

In a typical preparation of TAPM/TASBF/HDI, 3 w/v % solution in DMF, TAPM (MW: 380.48, 0.1056 g, 0.278 mmol), and TASBF (MW: 376.45, 0.1044 g, 0.278 mmol) was dissolved in 13.2 mL of dry DMF. HDI (MW: 168.19, 0.187 g, 1.11 mmol) was added, and the mixture was stirred at room temperature under nitrogen.

Preparation of free-Standing Films from Sols

In a typical preparation of thin film of TASBF/HDI, TASBF/ HDI free-standing films were prepared by casting TASBF/ HDI sol (5 mL) of 3 w/v % in DMF on the glass plate ($15 \times 15 \text{ cm}^2$) and the subsequent solvent evaporation at 80 °C. After 1 h, the film on the glass plate was separated by cutting with a razor blade and then the free-standing film was washed with water and acetone under sonication for 1 h, respectively. The resulting free-standing film was then dried under high vacuum at 50 °C for 1 h, 100 °C for 1 h, and 200 °C for 48 h.

Purification

The reaction mixtures remained in the fluid state (sol) before gelation time (t_g) . The nanoparticle aggregates were obtained by precipitation of the sol at a designated reaction time into a copious amount of acetone. The precipitates were stirred in pure acetone and filtered (repeated three times). The resulting powders were then dried under high vacuum at 50 °C for 1 h, 100 °C for 1 h, and 200 °C for 48 h. To obtain bulk dry gel samples, the wet gel (formed after t_g) was poured into acetone followed by the same purification procedure as the sample from the sol state.

Porosity Measurement

Gas adsorption isotherms were recorded on ASAP 2020 volumetric adsorption apparatus (Micromeritics) at 77 and 273 K for nitrogen and carbon dioxide within relative pressures from 0 to 1.0 and from 0 to 0.03, respectively. Before analysis, the samples were degassed in the degas port of the adsorption analyzer at 473 K for at least 12 h. The surface area, pore volume and pore size distribution were analyzed using ASAP 2020 v3.00 software (Micromeritics).

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