

Preparation and properties of polyimide aerogels cross-linked with 2,2',7,7'-Tetraaminobiphenyl-9,9'-Spirobifluorene

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Abstract: Polyimide gels combine high porosity, low thermal conductivity, flexibility, and low density with excellent mechanical properties. We describe polyimide gels are produced by cross-linking dianhydride capped polyamic acid oligomers with 2,2',7,7'-Tetraaminobiphenyl-9,9'-Spirobifluorene (TABS) in solution and chemically imidizing. The gels are then supercritically dried to form nanoporous polyimide aerogels with densities as low as 0.11 g/cm³ and surface areas as high as 584.92m²/g. All of the aerogels are suitable candidates for high-temperature insulation with glass transition temperatures ranging from 230-310°C and onsets of decomposition above 520°C.

Introduction

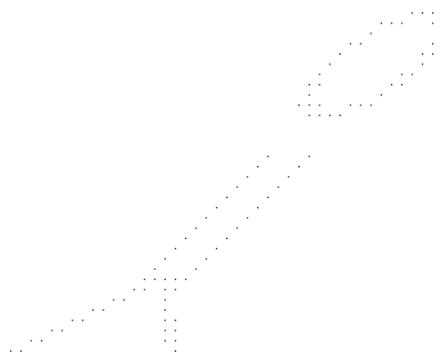
Aerogels are highly porous solids characterized by very small pore sizes and large internal surface areas, making them excellent as thermal insulator, catalyst, supports, filtration devices, etc.^[1] However, the most widely studied silica aerogels tend to be quite fragile because of the nature of their skeletal structure. Mechanical properties of silica aerogels are improved by applying a conformal coating of polymer to the silica backbone.^[2] Unfortunately, polymers used for reinforcement tend to be stable up to at most 100–150°C, such as epoxy,^[3] isocyanate,^[4] cyanoacrylates,^[5] and styrene,^[6] etc. On the other hand, much higher use temperatures are needed for many aerospace applications, such as insulation for launch vehicles or for planetary entry, descent, and landing (EDL) systems. Because of their thermal stability, good mechanical properties, and high glass transition temperatures, aromatic polyimides are the polymer of choice for applications such as insulation of aircraft engines needing high performance at elevated temperatures.^[7] Polyimide aerogels have been reported. Rhyne W et al.^[8-10] (USA Aspen Company) has reported polyimide aerogels which have been synthesized via pyromellitic dianhydride and ether diamine. The material had good thermal stability and mechanical properties, but the aerogels had a strong tendency to shrink during processing up to as much as 40%, and reduced the specific surface area and increased the density, which limited its application. Chidambareswarapattar C et al. presented a new synthesis for polyimide aerogels using 4, 4'-diphenyl methane diisocyanate and pyromellitic dianhydride at room temperature, this method requires only one step.^[11] This approach resulted in less shrinkage if the polymer gels were allowed to cure at room temperature, but weight loss at 200°C from thermal gravimetric analysis revealed that this results in much less than complete imidization. For linear polyimide aerogels shortcomings, the National Space Administration (NASA) and research institutions of other university have synthesized a series of cross-linked polyimide aerogels. Meador MAB.^[12] and coworkers used 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA), 2,2'-dimethyl-biphenyl-diamine (DMBZ) as monomer, 1,3,5-threaminophenoxy benzene (TAB) as the cross-linking agent, prepared the excellent mechanical properties of polyimide aerogels. The cross-linking polymer aerogels showed smaller shrinkage than linear polyimide aerogels materials, but the surface area was larger, its porosity was 90% or more. However, a flexible cross-linking agent was an aromatic triamine, reducing the ability of resisting contraction. Meanwhile, the cross-linking agent contains flexible ether oxygen bond, which

also declined the glass transition temperature of the material. When other reaction conditions remained unchanged, used eight amino benzene polysilsesquioxanes (OAPS) ^[13] instead of TAB as cross-linking agent, the density of aerogels is smaller, but the mechanical properties of the material decreased. Currently, there are a variety of polyimide monomers, but fewer types of cross-linker agent. Among them only a few are commonly used, such as TAB ^[14] and OAPS. Design and synthesis of novel cross-linking agent, and use it preparing high performance polyimide aerogels material, it has important scientific value and broad application prospects. Williams JC et al. prepared polyimide aerogels which had been used m-phenylenediamine (m-PPA) and terephthaloyl chloride (TPC) as polymerizable monomer, and N-methylpyrrolidone (NMP) as a solvent, then trimesoyl chloride (BTC) crosslinked reaction finally with supercritical CO₂ drying, preparing a polyamide aerogel material, it is a linear polyamide, it certain degree of polymerization. Despite it has relatively good mechanical properties, it has greater shrinkage with supercritical CO₂ drying, and a specific surface area and porosity is too small. Cross-linked agent has a rigid and planar structure, the polymer is less soluble in the solvent, the product did not form a better, more rigid three-dimensional network structure, it caused the ability of resist shrinkage is smaller.

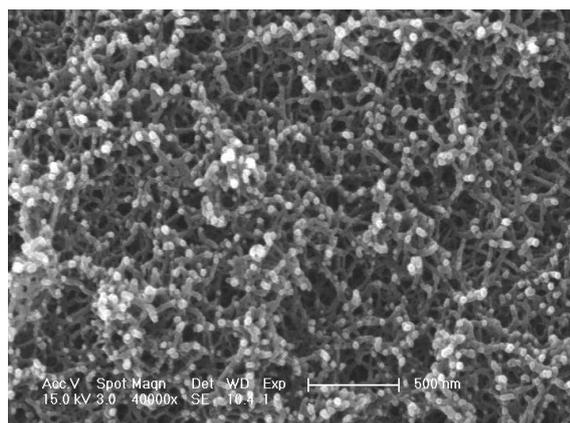
In order to overcome these shortcoming, we synthesize 2,2',7,7'-Tetraaminobiphenyl-9,9'-Spirobifluorene (TABS) as cross-linker agent to prepare a series of polyimide aerogels, because TABS has a non-planar and cross vertical spatial structure, the polymer aerogel can be formed before the phase separation happen. This more rigid network structure helps the aerogel to resist shrinkage. Meanwhile, polyamide aerogel has a lower density and larger surface area.

Experimental Section

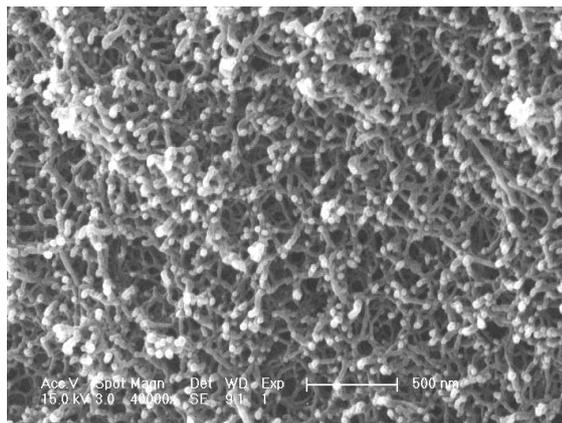
Materials 2-Bromobiphenyl, Magnesium powder, 9-Fluorenone, Fuming nitric acid, Hydrochloric acid, Palladium carbon, Pyridine, acetic anhydride, and anhydrous N-methylpyrrolidinone (NMP from TCI), 4,4'-oxydianiline (ODA from TCI), and biphenyl-3,3',4,4'-tetracarboxylic dianhydride (BPDA). Dianhydride was dried at 125 °C in vacuum for 24 h before use. All other reagents were used without further purification.



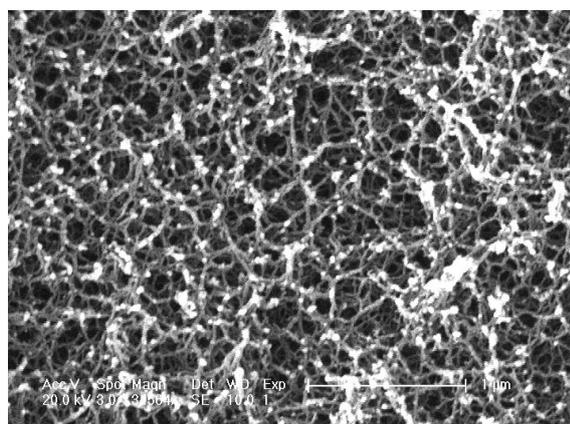
Scheme 1 Synthesis of 2,2',7,7'-Tetraaminobiphenyl-9,9'-Spirobifluorene (TABS)



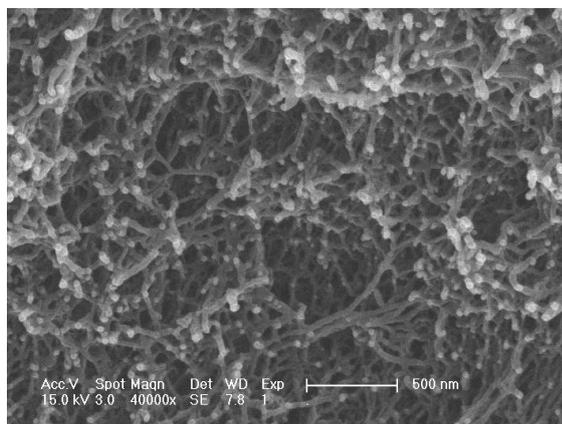
a) n=10



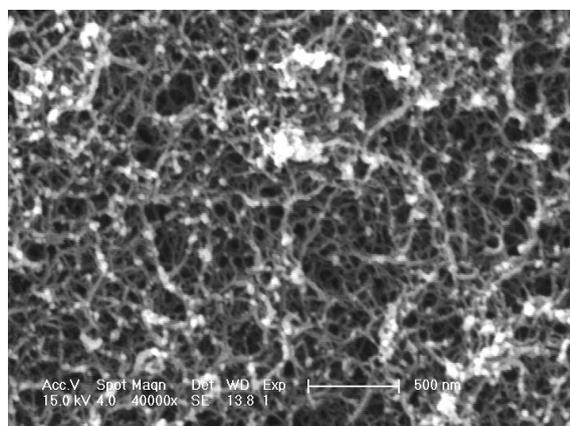
b) n=15



c) n=20



d) n=25



e) n=30

Figure 1 Comparison of SEMs of polyimide aerogels made with ODA and BPDA

Conclusion

Polyimide aerogels cross-linked with TABS were fabricated using dianhydride end-capped polyimide oligomers. The use of this effective cross-linker yields aerogels with better properties compared to those previously made with available cross-linkers, such as OAPS, TAPP, and TAB. When TABS is introduced into polyimide, the highly twisted structure of Spirobifluorene reduces the interaction between the polymer molecules, so the polymer has a greater solubility in the solvent, the polyimide aerogel can be formed before the phase separation. The formed more rigid network structure can resist

the shrinkage of the aerogels. Meanwhile, the non-planar spiral structure of the polymer promotes the accumulation of loose polymer backbone, leading to a large number of micro pores. Polyimide aerogel has a lower density and larger surface area.

References

- [1] Pierre, A. C.; Pajonk, G. M. *Chem. Rev.* **2002**, 102: 4243–4265.
- [2] For a recent review, see Randall, J. P.; Meador, M. A. B.; Jana, S. C. *ACS Appl. Mater. Interfaces*, **2011**, 3: 613–626.
- [3] Meador, M. A. B.; Scherzer, C. M.; Nguyen, B. N.; Quade, D.; Vivod, S. L. *ACS Appl. Mater. Interfaces*, **2010**, 2: 2162–2168.
- [4] Meador, M.A.B.; Capadona, L.A.; McCorkle, L.; Papadopoulos, D. S.; Leventis, N. *Chem. Mater*, **2007**, 19: 2247–2260.
- [5] Boday, D. J.; Stover, R. J.; Muriithi, B.; Keller, M. W.; Wertz, J. T.; Obrey, K. A. D.; Loy, D. A. *ACS Appl. Mater. Interfaces*, **2009**, 1: 1364–1369.
- [6] Nguyen, B. N.; Meador, M. A. B.; Tousley, M. E.; Shonkwiler, B.; McCorkle, L.; Scheiman, D. A.; Palczer, A. *ACS Appl. Mater. Interfaces*, **2009**, 1: 621–630.
- Sun HY, Xu Z, Gao C. *Adv. Mater*, **2013**, 25: 2554–2560.
- [5] Nguyen BN, Meador MAB, Tousley ME, Shonkwiler B, McCorkle L, Scheiman DA, Palczer A. *ACS Appl. Mater. Interfaces*, **2009**, 1: 621–630.
- [6] Boday DJ, Stover RJ, Muriithi B, Keller MW, Wertz JT, Obrey KAD, Loy DA. *Chem. Mater*, **2008**, 20: 2845–2847.
- [7] Sydlik SA, Chen ZH, Swager TM. *Macromolecules*, **2011**, 44: 976–980.
- [8] Rhyne, W.; Wang, J.; Begag, R. U.S. Patent WO/2004/009673, Jan. 29, **2004**.
- [9] Chidambareswarapattar, C.; Larimore, Z.; Sotiriou-Leventis, C.; Mang, J. T.; Leventis, N. *J. Mater. Chem*, **2010**, 20: 9666–9678.
- [10] Rhine W, Wang J, Begag R. US Patent 7074880, **2006**.
- [11] Chidambareswarapattar C, Larimore Z, Sotiriou-Leventis C, Mang JT, Leventis N. *J. Mater. Chem*, **2010**, 20: 9666–9678.
- [12] Meador MAB, Malow EJ, Silva R, Wright S, Quade D, Vivod SL, Guo H, Guo J, Cakmak M. *ACS Appl. Mater. Interfaces*, **2012**, 4: 536–544.
- [13] Guo, H.; Meador, M. A. B.; McCorkle, L.; Quade, D. J.; Guo, J.; Hamilton, B.; Cakmak, M.; Sprowl, G. *ACS Appl. Mater. Interfaces*, **2011**, 3: 546–552.
- [14] Mary Ann B. Meador, Ericka J. Malow, Rebecca Silva, Sarah Wright. *Appl. Mater. Interfaces*, **2012**, 4: 536–544.

(continued from p159)

- [27] Takeichi T, Kano T, Agag T. Synthesis and thermal cure of high molecular weight polybenzoxazine precursors and the properties of the thermosets[J]. *Polymer*, 2005, 46(26): 12172–12180.
- [28] Shieh J Y, Lin C Y, Huang C L, et al. Synthesis and characterization of novel dihydrobenzoxazine resins[J]. *Journal of applied polymer science*, 2006, 101(1): 342–347.
- [29] Takeichi T, Kano T, Agag T, et al. Preparation of high molecular weight polybenzoxazine prepolymers containing siloxane units and properties of their thermosets[J]. *Journal of Polymer Science Part A: Polymer Chemistry*, 2010, 48(24): 5945–5952.
- [30] Kiskan B, Demirel A L, Kamer O, et al. Synthesis and characterization of nanomagnetite thermosets based on benzoxazines[J]. *Journal of Polymer Science Part A: Polymer Chemistry*, 2008, 46(20): 6780–6788.