

Preparation and Gel Properties of Poly(ether ether ketone) with Pendent Sulfonimide Groups

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ABSTRACT: Poly(ether ether ketone) with pendent sulfonimide groups (B-SPEEK) was prepared from poly(ether ether ketone), sulfuric acid, thionyl chloride, *para*-toluene sulfonate, and pyridine. The prepared B-SPEEK was characterized by Fourier transform infrared spectroscopy, ¹H-NMR, and thermogravimetric analysis. The swelling of the gels was examined in *N,N*-dimethylacetamide (DMAC), *N,N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), and a DMSO/water mixture. The gel showed extremely high swelling in DMSO, DMF, DMAC, and NMP. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Gels are crosslinked polymer networks that undergo dramatic volume changes in aqueous systems, at times swelling up to several hundred times their original volume.¹ They can be variously classified, as synthetic gels or natural gels, organogels or hydrogels, and physical or chemical gels, according to their crosslinkage, liquid medium in the polymer network, and the source.² They have important analytical and industrial applications as separation agents and absorbent materials in various industries.^{3–8} For example, Sato et al.⁹ reported on the swelling behavior of poly(sodium acrylate) gels crosslinked by aluminum ions. When the surrounding water was changed at a constant interval, this gel exhibited two relaxation processes; the gel swelled in the first stage, then shrunk very slowly in the second stage, and recovered to its initial size just after the gelation (ultimately, the gel became smaller than that). These behaviors were attributed to the diffusion of aluminum ions and the formation of hydrogen bonds because of the replacement of sodium ions by protons.

Absorbent materials are attractive for organic solvent removal. There are several reports in the literature describing the synthesis and swelling properties of polymers for organic solvent cleanup.^{10–13} For example, Xie et al.¹⁴ prepared gels from a copolymer (2-acrylamido-2-methylpropane sulfonic acid and acrylamide), which could absorb ethanol and methanol well. Ono et al.¹² prepared copolymeric gels based on octadecylacrylate and an anionic comonomer for the absorption of nonpolar solvents. This gel could absorb nonpolar solvents, such as

carbon tetrachloride and toluene. To be a good absorbing material, a sorbent should have oleophilicity and hydrophobicity, a high and fast uptake capacity, and reusability.

In this article, we report on a synthesized organogel based on modified poly(ether ether ketone) (PEEK), which could be used as absorbents for organic solvents. These synthesized polymers were thermally stable and had good organic-solvent-uptake abilities. They had rapid and good sorption abilities for organic solvents, such as *N,N*-dimethylacetamide (DMAC), *N,N*-dimethylformamide (DMF), 1-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), and a DMSO/water mixture.

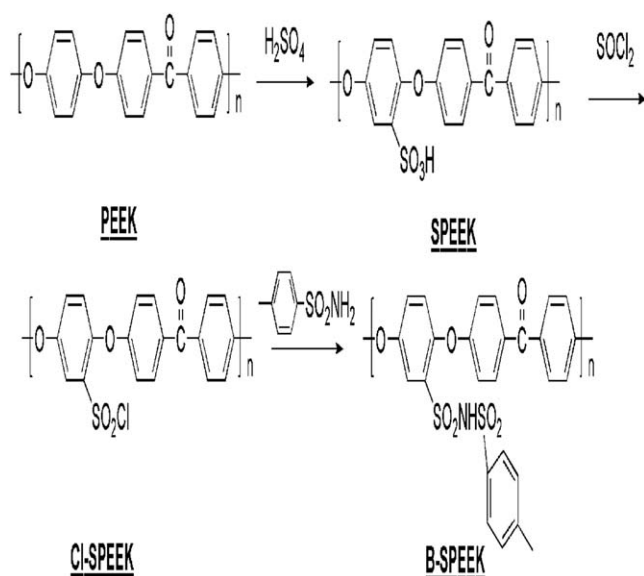
EXPERIMENTAL

Materials

PEEK (Victrex 450G, number-average molecular weight = 100,000) was dried at 100°C in a vacuum oven for 12 h for a pretreatment. DMF, DMSO, sulfuric acid (95 wt %), chloroform, NMP, DMAC, and pyridine were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). Thionyl chloride (SOCl₂), pyridine, triethylamine, paratoluene sulfonate, triethylamine, and chloroform were purchased from Aladdin Reagent Co., Ltd. (China).

Synthesis of Poly(ether ether ketone) with Pendent Sulfonimide Groups (B-SPEEK)

PEEK (40.0 g) was dissolved in sulfuric acid (800 mL) with stirring in a three-necked flask. The mixture was stirred further for 3 h at 60°C and was then diluted with water (8.0 L). The white precipitate that formed was washed with deionized water to PH7 and was then dried at 60°C for 24 h to give sulfonated



Scheme 1. Reaction scheme of B-SPEEK.

poly(ether ether ketone) (SPEEK; 45.8 g) as a little yellow powder.

SPEEK (40 g) was then treated with a large amount of thionyl chloride (200 mL) and a small amount of pyridine (5 mL) for 24 h at reflux temperature, immediately poured into ice-water and cooled to room temperature, washed with deionized water until the filtrate was neutral, and then dried *in vacuo* at 60°C for 24 h to give poly(styrylsulfonyl chloride) polymer (Cl-SPEEK; 41.5 g).

The ethylamine (7.0 mL) was carefully added dropwise to the mixture of Cl-SPEEK (4.0 g) and 4-methylbenzenesulfinamide (3.4 g) in 50 mL of CHCl_3 ; heated at 60°C for 48 h with stirring; filtered; washed successively with CHCl_3 , HCl, and H_2O ; and dried at 80°C for 24 h. B-SPEEK (6.1 g) was obtained as little yellow solids.

Characterization

Fourier transform infrared (FTIR) spectra of the neat SPEEK and B-SPEEK were measured with a Thermo-Nicolet 6700 FTIR spectrometer over a range of 4000 to 400 cm^{-1} .

$^1\text{H-NMR}$ measurement was performed on a Bruker Advance III spectrometer with deuterated DMSO as the solvent.

The thermal stability of the neat SPEEK and B-SPEEK were measured in a Mettler Toledo thermogravimetric analysis (TGA)/DSC I instrument. The samples were heated from 25 to 800°C under a nitrogen atmosphere at a rate of 10°C/min.

Solvent uptake was determined from the difference between the weight of the wet resin and the dried resin. The dried resin was weighed and then soaked in the corresponding solvent for a certain period to ensure absorption. After the stipulated time, the resin was taken out, excess solvent on the surface was quickly removed with the help of tissue paper, and the sample was weighed. The solvent-uptake percentage was calculated with the following formula:¹⁵

$$\text{Solvent uptake (\%)} = \frac{W_s - W_d}{W_d} \times 100\% \quad (1)$$

where W_d and W_s represent the weights of the dried and swollen crosslinked polymer samples, respectively.

The swelling kinetics measurements were conducted with the procedure described previously with DMSO as a solvent. The samples, after their dried weights were measured, were put into a wide-mouthed bottle and placed in DMSO. The sample was taken out at designed intervals; the solvent adhering to the surface was rubbed off, and the samples were weighed quickly and replaced in the solvent. This procedure was repeated at least four times to ensure the reproducibility of the values. Desorption kinetic measurements were conducted in the procedure for determining the DMSO retention of the polymers in air under ventilation by weighing the swollen polymers as a function of time.

RESULTS AND DISCUSSION

To obtain B-SPEEK, *p*-methyl phenyl sulfonimide was introduced into PEEK by three reaction steps. Scheme 1 outlines the synthesis of B-SPEEK. To remove excess 4-methylbenzenesulfonamide and 3-triethylamine hydrochloride, the mixture was washed successively with CHCl_3 , HCl, and H_2O . The solvent was CHCl_3 instead of 1,2-dichloroethane to obtain a proper boiling point and better solubility.

$^1\text{H-NMR}$ Study

Figure 1 shows the $^1\text{H-NMR}$ spectra of SPEEK, Cl-SPEEK, and B-SPEEK dissolved in DMSO. The $^1\text{H-NMR}$ peak at 4.57 ppm corresponded to the sulfonic acid groups in the pendant side

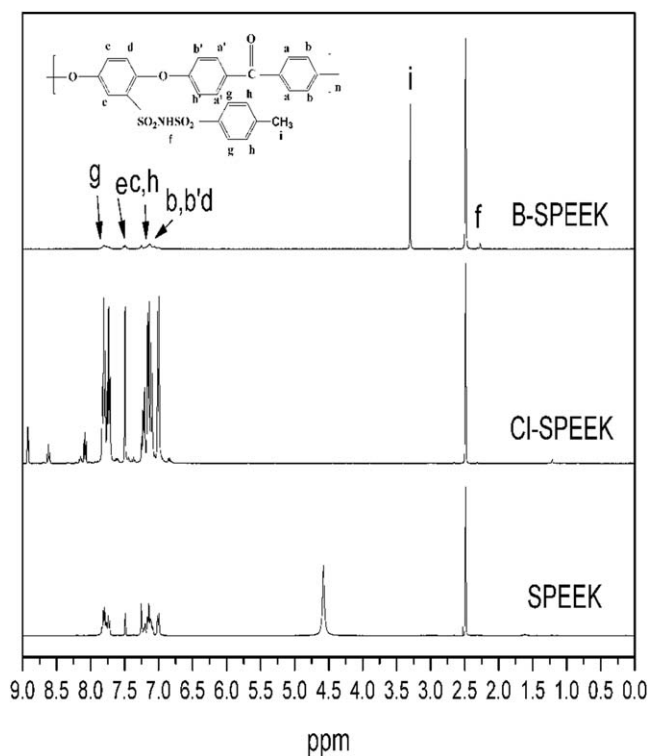


Figure 1. $^1\text{H-NMR}$ spectra of SPEEK, Cl-SPEEK, and B-SPEEK in DMSO.

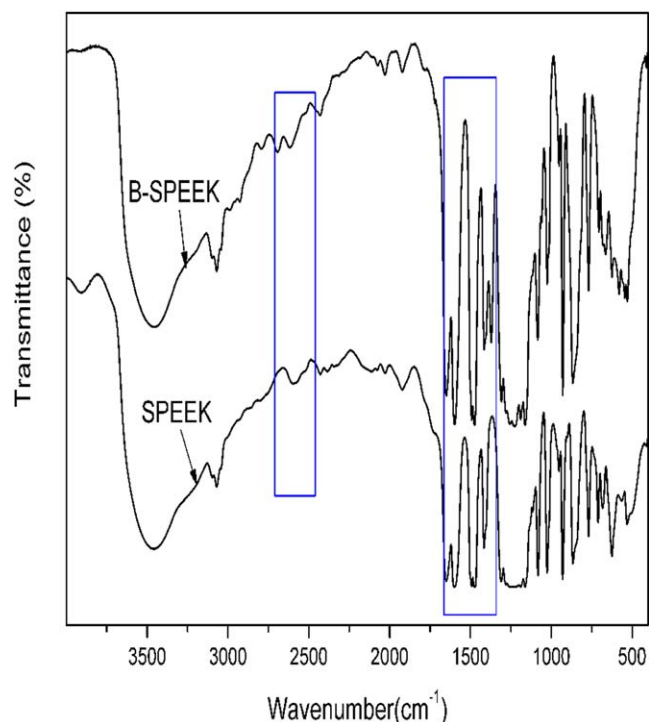


Figure 2. FTIR spectra of the SPEEK and B-SPEEK polymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

chain of SPEEK. In the Cl-SPEEK, there was no peak at 3.0–6.0 ppm corresponding to the sulfonic acid groups. The $^1\text{H-NMR}$ signals in the range 6.5–8.0 ppm were due to the aromatic protons in the SPEEK and Cl-SPEEK. In the B-SPEEK, the $^1\text{H-NMR}$ peaks of H_a and H_a' protons appeared downfield because

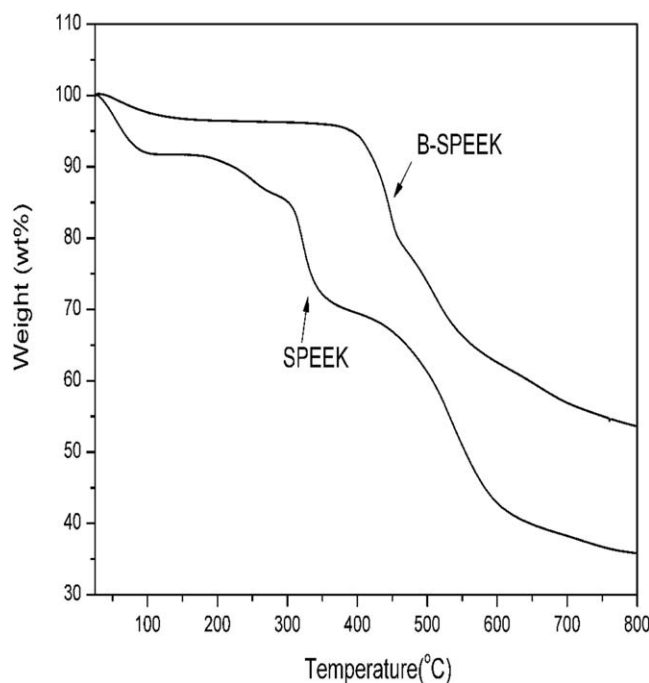


Figure 3. TGA curves of SPEEK and B-SPEEK.

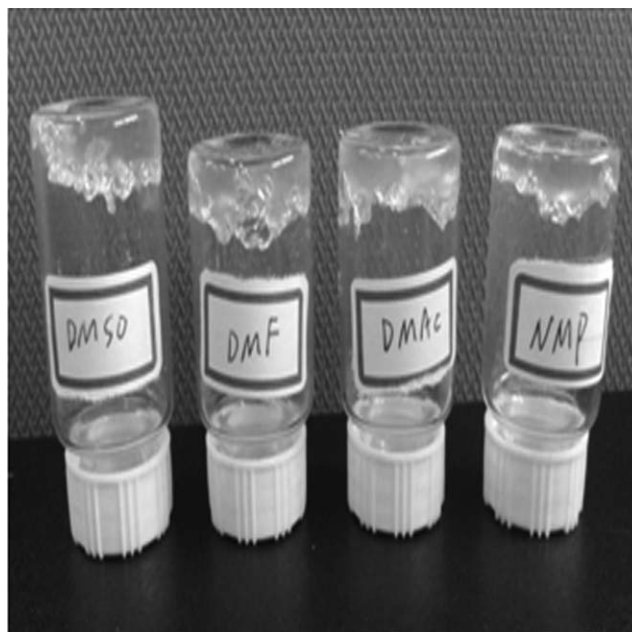


Figure 4. Photos of the gel state of 1 wt % B-SPEEK in 99 wt % DMAc, DMSO, NMP, and DMF.

of the deshielding effect of the carbonyl group. The H_b protons located at 7.13 ppm were shifted upfield because of the sulfonic groups and the H_b' and H_d protons located at 7.00 ppm. The H_c and H_h protons, respectively, appeared as characteristic singlets at 7.23 and 7.26 ppm. The sulfonic groups were introduced into the hydroquinone ring, which was activated for electrophilic substitution; this caused a significant downfield shift in the H_c , H_d , and H_e signals of the hydroquinone ring. The intensity of the H_e signal at 7.50 ppm corresponded to the hydrogen atoms adjacent to the sulfonic acid groups and equivalent to the sulfonic group content.^{16,17} The H_g protons appeared as characteristic singlets at 7.81 ppm. After the pendent sulfonimide groups were introduced, the presence of $-\text{CH}_3$ and $-\text{NH}-$ groups resulted in distinct proton signals at 3.32 and 2.29 ppm (H_i and H_f , respectively); this indicated that pendent sulfonimide groups were successfully attached to the sulfonic acid groups to form B-SPEEK.^{18,19} Hence, the $^1\text{H-NMR}$ spectrum nicely confirmed the successful synthesis of the B-SPEEK polymer. The $^1\text{H-NMR}$ spectrum nicely confirmed the successful synthesis of SPEEK, Cl-SPEEK, and B-SPEEK.

FTIR Study

The structure of the object product was further confirmed by FTIR study. Figure 2 shows the FTIR spectra of SPEEK and B-SPEEK. The absorptions of the corresponding functional groups were evident. The absorption of a broad band around 3066 cm^{-1} in SPEEK and B-SPEEK was assigned to the stretching vibration of C–H in the aromatic ring. The symmetric stretching vibration due to the sulfonic acid groups in SPEEK and B-SPEEK was evident at 1070 and 1025 cm^{-1} . The four absorptions from 1660 to 1400 cm^{-1} were attributed to the aromatic ring in SPEEK; the corresponding absorptions of the aromatic ring in B-SPEEK were larger at 1653, 1602, 1476, and 1417 cm^{-1} . The peak at 2700 cm^{-1} was due to N–H in B-

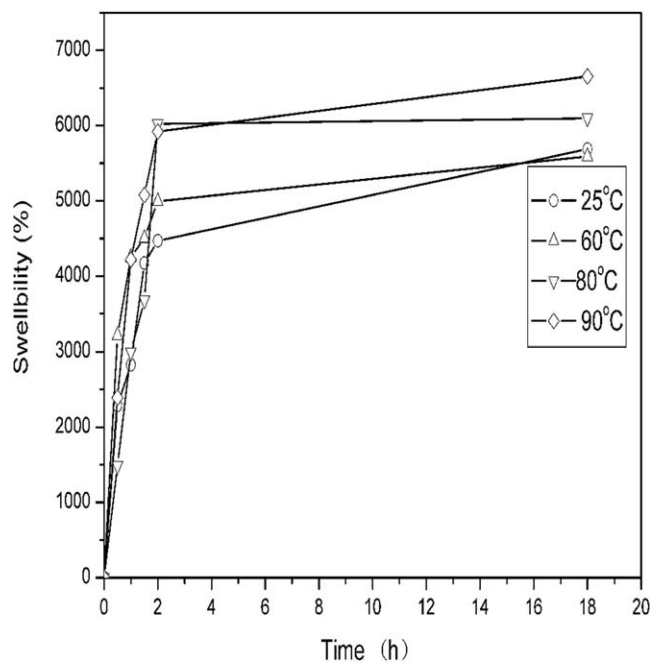


Figure 5. Effects of the time and temperature on the swelling behavior of B-SPEEK in DMSO.

SPEEK; this proved that the B-SPEEK was synthesized successfully.²⁰

Thermal Stability

The thermal stabilities of SPEEK and B-SPEEK are evaluated with the TGA test, and the results are presented in Figure 3. The weight loss below 100°C was assigned to the absorbed

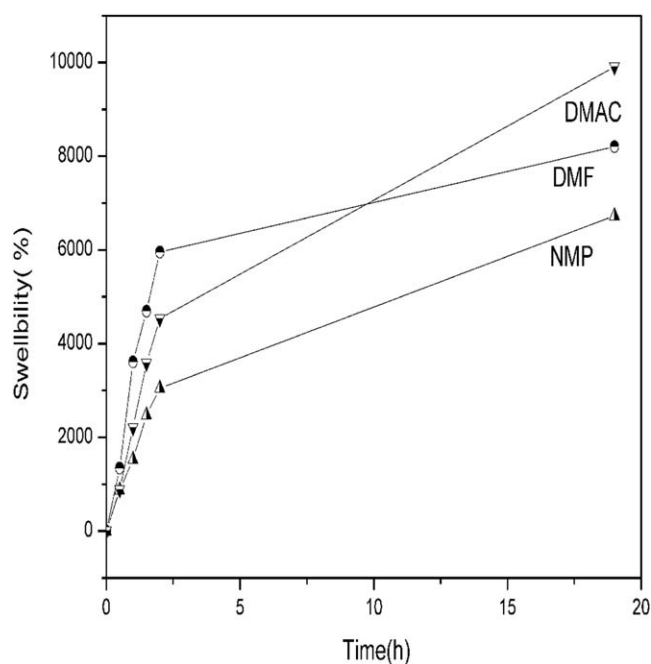


Figure 6. Effects of the time on the swelling behavior of B-SPEEK in DMAC, DMF, and NMP.

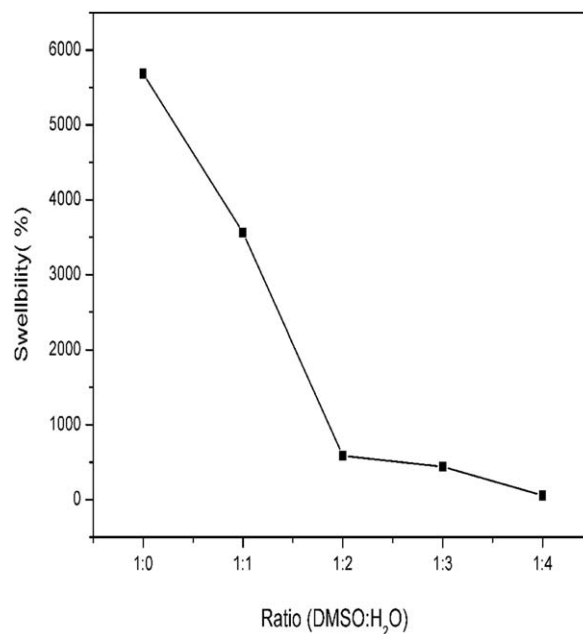


Figure 7. Swelling capacity of B-SPEEK in the DMSO/water mixtures.

water; this was only a little relevant to the thermal stability of SPEEK and B-SPEEK. As for SPEEK, the major weight was lost from about 300°C; this was attributed to the elimination of sulfonic acid groups, and this weight was rapidly lost with increasing temperature. Then, it occurred at about 450°C; this corresponded to the decomposition of the polymer backbone. As for B-SPEEK, the major weight was lost from about 400°C and was lost by two steps with increasing temperature, as shown in Figure 3. The weight loss of B-SPEEK occurred about 400°C, and the thermal degradation that was due to the main-chain decomposition occurred about 500°C. From Figure 3, we found that the thermal stability of B-SPEEK was stronger than that of SPEEK.^{21–23}

Gel Properties of B-SPEEK

In DMAC, DMSO, NMP, DMF, and other common organic solvents, the synthesized B-SPEEK was insoluble, but it gelled in some solvents. To assess the gel properties of B-SPEEK, we investigated it with the tube-inversion method. Figure 4 displays the gels state of 1 wt % B-SPEEK in 99 wt % DMAC, DMSO, NMP, and DMF. In these tubes, 1 wt % dried B-SPEEK was immersed in 99 wt % DMSO, DMAC, DMF, and NMP and then gelled. They had good solvent-uptake abilities in these solvents.

From previous solvents, DMSO was selectively used to characterize the solvent-uptake abilities of B-SPEEK and the kinetics measurement. In the temperature range from 25 to 90°C, we investigated the solvent-uptake ability variation in the DMSO solution of the complex. Figure 5 shows the swelling capacities of the synthesized B-SPEEK in DMSO. According to the diagram, two obvious tendencies could be determined. With increasing temperature and extended times, a rapid increase in the solvent-uptake ability of B-SPEEK in DMSO was

obvious. When B-SPEEK was immersed in aqueous DMSO, the solvent absorbency increased rapidly up to around 6600% and then plateaued. To verify this abnormal behavior, we repeated the swelling experiments and rechecked the results several times at different temperatures. The unusual behavior of B-SPEEK was found to be reproducible. Maybe the sulfonimide groups of B-SPEEK were well dissociated and formed hydrogen bonds with the molecules of DMSO; this caused gel to expand extremely. The DMSO retention of the polymers was followed over time by examination of the weight loss of the swollen polymer in air. The study indicated that the absorbed DMSO of gels was released very fast (50%) under ventilation at room temperature within an average of 180–200 min.

We also examined the gel in DMAC, DMF, and NMP, and the results similar were similar to those in DMSO. Figure 6 shows the swelling capacities of the synthesized B-SPEEK in DMAC, DMF, and NMP at 80°C. According to the diagram, one obvious tendency could be determined. With the extension of time, a rapid increase in the solvent-uptake ability of B-SPEEK in DMAC, DMF, and NMP was obvious. When B-SPEEK was immersed in aqueous DMAC, DMF, and NMP, the solvent absorbency increased rapidly and then plateaued. To verify this abnormal behavior, we repeated the swelling experiments and rechecked the results several times. Maybe the sulfonimide groups of B-SPEEK were well dissociated and formed hydrogen bonds with the molecules of DMAC, DMF, and NMP; this caused the gel to expand extremely.

The gel swelling was further examined in binary mixtures of DMSO with varied water contents. We observed that water could cause B-SPEEK to shrink. Figure 7 shows the swelling capacity changes in various DMSO/water media. We found that gel collapse was first observed in lieu of increasing fractions of water in the binary mixture obviously. The binary mixture solvents' absorbency decreased quickly from 3560% to around 580% and then gentled. To explain the strange behavior of the higher swelling of B-SPEEK in DMSO compared to that in the mixed solvent, we preliminarily focused on DMSO and its properties in aqueous media. DMSO was a polar molecule with two hydrophobic CH₃ groups and one S=O group. The nonpolar sites caused effects of the hydrophobic hydration and hydrophobic dissociation of DMSO molecules. The polar sites were expected to interact with water to form strong hydrogen bonds.

Many researchers have disclosed that different associations of $m\text{DMSO}-n\text{H}_2\text{O}$ ($m = 1$ and 2 and $n = 1-3$). B-SPEEK is a polar macromolecule with a high potential of solvation in polar solvents.²⁴⁻²⁶ Among the polymer-solvent interactions engaged here, those involved with the sulfonic acid groups were major. Without water, the sulfonyl imide groups from the polymer chains tended to interact with the sulfonyl groups in DMSO via hydrogen bonding and polar interaction to form stable gel networks. A very significant ionic interaction was sulfonate-sulfonate ionic repulsive forces between the polymer chains, which led to the gel network expansion.²⁴ When water molecules were added to the system, they tended to replace the sulfonimide

groups from the polymer chains in the gel; this led to the precipitation of B-PEEK and the shrinkage of the gel.

CONCLUSIONS

In conclusion, B-SPEEK was prepared by PEEK, sulfuric acid, thionyl chloride, *para*-toluene sulfonate, and pyridine. B-SPEEK was successful synthesized, as proven by FTIR spectroscopy and ¹H-NMR. This polymer was found to be thermally stable by TGA, and it possessed rapid and good organic-solvent-uptake abilities. The swelling of the gels was examined in DMAC, DMF, NMP, DMSO, and DMSO/water mixture. We found that the gel showed extremely high swelling in DMSO, DMF, DMAC, and NMP. In these solvents, the solvent uptake of B-SPEEK rapidly grew up to above 6600%. Further study clearly showed that B-SPEEK could be applied as absorbents for organic solvents.

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