

NOTES

Synthesis of Arenesulfonated Hyperbranched Polyimide from A₂ + B₃ Monomers

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Hyperbranched polymers have drawn considerable attentions in recent years for their unique physical and chemical properties due to their dendritic structure.^{1–5} The dendritic polymers were thought to have similar properties as the perfectly branched dendrimers, such as low viscosity, good solubility, thermal property, and chemical reactivity. Therefore, hyperbranched polymers might be an alternative and cost-effective substitute for dendrimers under certain conditions, and would be promising candidates for industrial applications, because one-step polymerizations are suitable for mass production.⁴ Up to now, some attempts have been reported on their applications as novel functional polymers, such as encapsulation micelles for dye molecules,^{6,7} crosslinking agents,^{8,9} and nonlinear optical materials.^{10–12}

The large number of reactive groups at the periphery of hyperbranched polymers offers an easy way for further modification and special applications.^{1–4} Functionalization can be performed by the reaction of the end groups with materials containing certain functional groups. The resulting functional polymers were thought to have high functionality because of the decreased chain entanglement and the peripheral location of the functional groups.^{3,4}

In previous work,¹³ we reported the synthesis and characterization of a series of hyperbranched polyimides (HBPIs) based on a new tramine (B₃), 1,3,5-tris(4-aminophenoxy)benzene (TAPOB), and conventional dianhydrides (A₂). Different monomer addition methods and monomer molar ratios resulted in HBPIs with amino- or anhydride-terminated groups. The amino-terminated HBPIs had degrees of branching

(DB) in the range of 0.62–0.67, while the anhydride-terminated and chemically modified HBPIs gave a DB value of 1 according to ¹H NMR analysis with the help of model compounds. In present paper, we describe our initial results on the synthesis of arenesulfonated HBPI (S-HBPI) from 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) and TAPOB, which may be potentially applied as proton conducting polymer. Sulfonation of the polymer was directly fulfilled during the course of polymerization of poly(amic acid) precursor, by modification of the terminal anhydride groups with sulfanilic acid, and then the precursor was chemically imidized in the presence of acetic anhydride and triethylamine.

EXPERIMENTAL

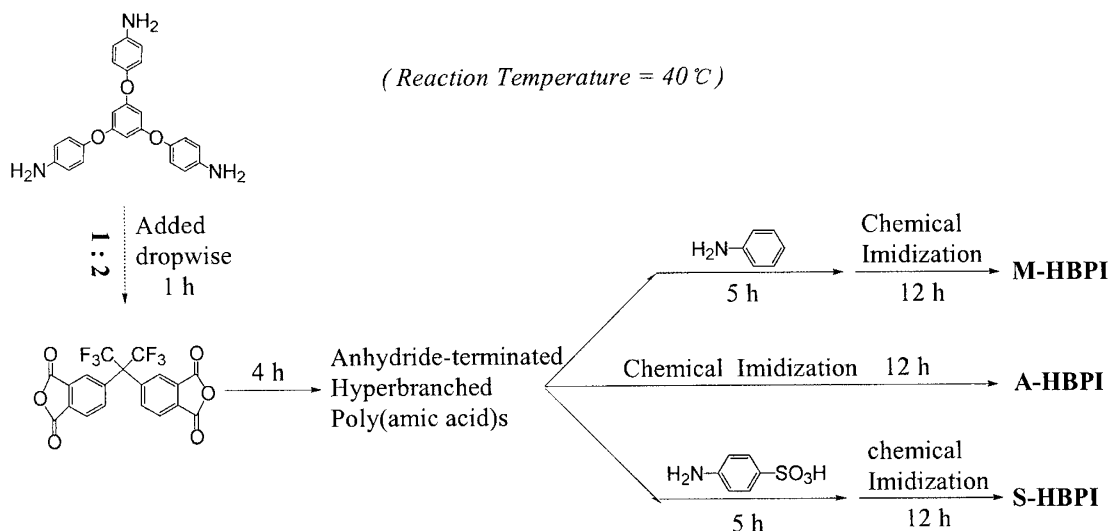
Chemicals

N-Methyl-2-pyrrolidone (NMP) was distilled from calcium hydride under reduced pressure. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA) was obtained commercially, and purified by recrystallization from acetic anhydride before use. 1,3,5-Tris(4-aminophenoxy)benzene (TAPOB) was synthesized in our lab.¹³ Other solvents and reagents were used as received.

Measurements

Infrared spectroscopic (IR), differential scanning calorimetric (DSC, at a heating rate of 10 °C min⁻¹ in nitrogen) and thermogravimetric (TGA, at a heating rate of 10 °C min⁻¹ in nitrogen) analyses were performed on FT-IR Paragon 1000, DSC Pyris 1 and

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TGA-7 of PerkinElmer, respectively. ^1H NMR spectra were recorded on a Mercury 400-MHz spectrometer. Elemental analysis was conducted on an Elementar Varioel apparatus. Molecular weights were determined by gel permeation chromatography (GPC) using polystyrene as a standard on a PerkinElmer Series 200 apparatus equipped with Waters Styragel column. The eluant was *N*-dimethylformamide (DMF) containing 0.01 mol L^{-1} lithium bromide with a flow rate of 1.0 mL min^{-1} at 40°C . Polymer solution was filtered through a Whatman $0.45 \mu\text{m}$ PTFE filter before injected into the column. The reduced viscosities of the polymer were determined as a function of polymer concentration by Ubbelohde viscometry in *N,N*-dimethylacetamide (DMAc) at 30°C .

Synthesis of Arenesulfonated Hyperbranched Polyimide (S-HBPI) (Scheme 1)

In a 150 mL thoroughly dried three-neck flask equipped with a nitrogen inlet and a magnetic stirrer, 5 mmol of 6FDA was dissolved in 30 mL of NMP. A 2.5 mmol of TAPOB in 30 mL of NMP was dropwise added to the mixture through a syringe over 1 h at 40°C . An excess amount of sulfanilic acid (3 mmol) was added to the mixture 4 h later, and the reaction was further conducted for 5 h at 40°C . Then a mixture of 5 g of triethylamine and 15 g of acetic anhydride was added, and the reaction mixture was stirred at 40°C for 12 h. After cooling to room temperature, the mixture was precipitated from 700 mL ethanol. The polymer was collected by filtration and dried *in vacuo* at 80°C for 24 h.

Determination of the Ion-Exchange Capacity (IEC)

A 1.0 g of dry S-HBPI powder was immersed in 50 mL of saturated NaCl aqueous solution, and the sus-

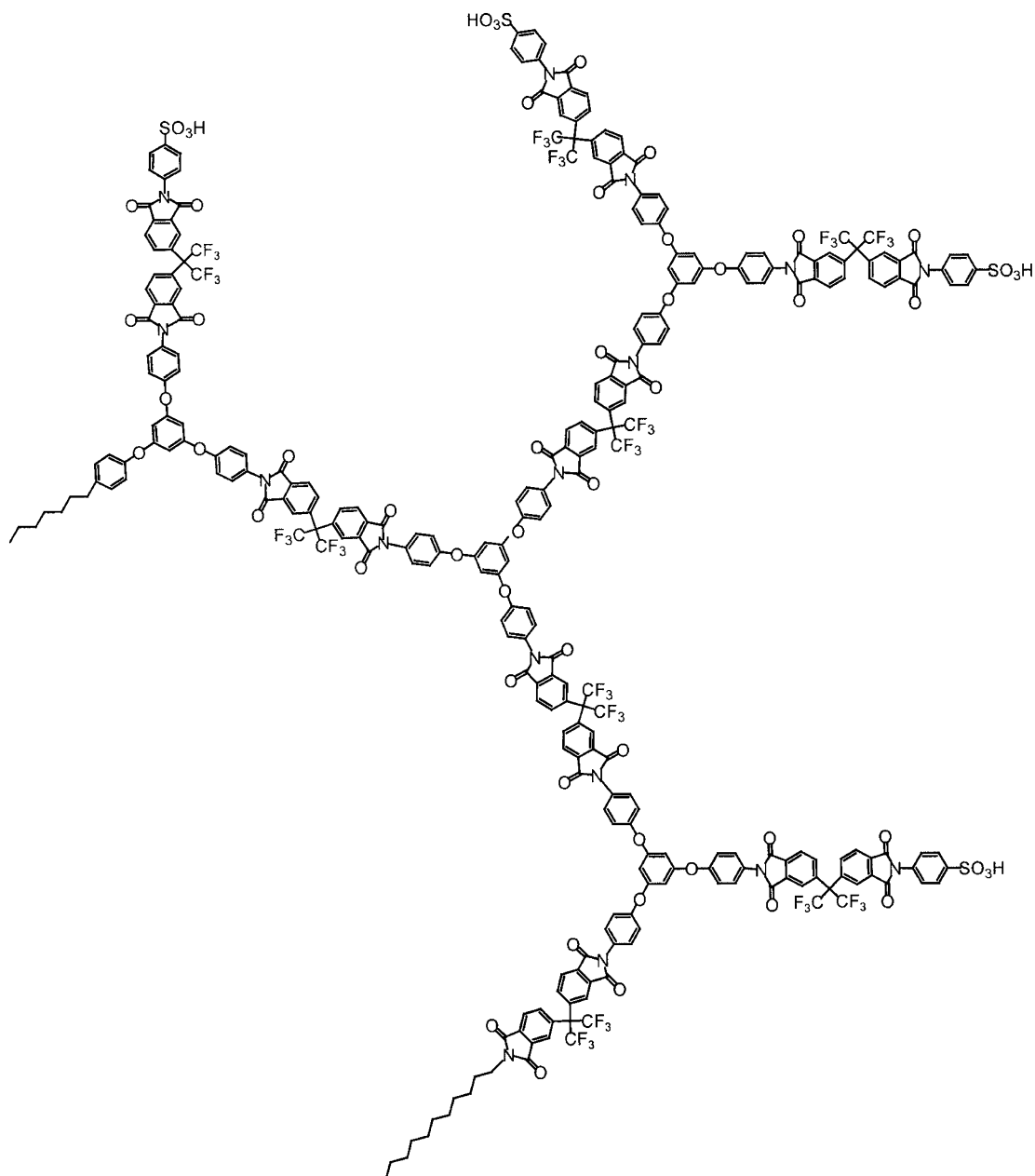
pension was vibrated at 30°C for 24 h. The H^+ ions of the polymer were released by excessive amount of Na^+ ions. Then the solution containing the powder was titrated with 0.1 N NaOH solution.

RESULTS AND DISCUSSION

Polymerization and Characterization.

A series of hyperbranched polyimides (HBPIs) based on 1,3,5-tris(4-aminophenoxy)benzene (TAPOB) (B_3) and conventional dianhydrides (A_2) have been prepared recently in our lab, and showed rather good solubility and thermal stability.¹³ HBPIs with amino- or anhydride-terminated groups were obtained through different monomer addition methods and molar ratios of monomers. When the triamine solution was added to a dianhydride solution with the monomer molar ratio of 1:2, anhydride-terminated HBPIs were obtained. Whereas the addition of a dianhydride solution to the triamine solution with the molar ratio of 1:1 yielded amino-terminated HBPIs. The degrees of branching (DBs) of HBPIs were estimated by ^1H NMR analysis with the help of model compounds. The amino-terminated HBPIs had DBs in the range of 0.62–0.67, while the anhydride-terminated and chemically modified HBPIs gave a DB value of 1. Here, the 6FDA-based anhydride-terminated HBPI was modified at the periphery with sulfanilic acid during the course of polymerization of the poly(amic acid) precursor, which was then imidized by chemical method.

As shown in Scheme 1, a solution of TAPOB was added dropwise over 1 h to the reaction system containing 6FDA using NMP as the solvent in a monomer molar ratio of 1/2 (molar ratio of amino and anhydride groups: 3/4) to afford an anhydride-terminated hyperbranched poly(amic acid). Subsequently, an ex-



Scheme 2. Chemical structure of arenesulfonated hyperbranched polyimide (S-HBPI).

cess amount of sulfanilic acid was added in one pot to introduce sulfonic acid groups at the periphery. The arenesulfonated hyperbranched polyimide (S-HBPI) (Scheme 2) was obtained through chemical imidization of the precursor at 40 °C in the presence of acetic anhydride and triethylamine. Preparation and property of the anhydride-terminated HBPI (A-HBPI) and its terminally modified counterpart by aniline (M-HBPI) based on 6FDA and TAPOB were also shown in this paper for comparison.¹³

FT-IR spectra of HBPIs (A-HBPI, M-HBPI, and S-HBPI) were shown in Figure 1. The bands at 1786–1789 cm^{-1} , 1727–1729 cm^{-1} , and 720–723 cm^{-1} can be attributed to the absorption from imide carbonyl groups, and the bands at 1377–1381 cm^{-1} from imide

C–N groups for all polymers, which are the characteristic absorption bands of polyimides. The absence of the characteristic band of poly(amic acid) (around 1680 cm^{-1}) clarifies that the precursors were fully imidized by chemical method. The peak at 1035 cm^{-1} in S-HBPI (c) resulted from the vibration absorption of the sulfonic acid groups at the periphery of the global polyimide backbone.^{14,15} The disappearance of the band at 1859 cm^{-1} for S-HBPI (c), which is from the C=O stretching absorption of the terminal anhydride groups in A-HBPI (a), indicates that the modification of the terminal anhydride groups by sulfanilic acid was achieved completely.

Figure 2 showed ¹H NMR spectra of M-HBPI and S-HBPI in DMSO-*d*₆. The absorption peaks in the range

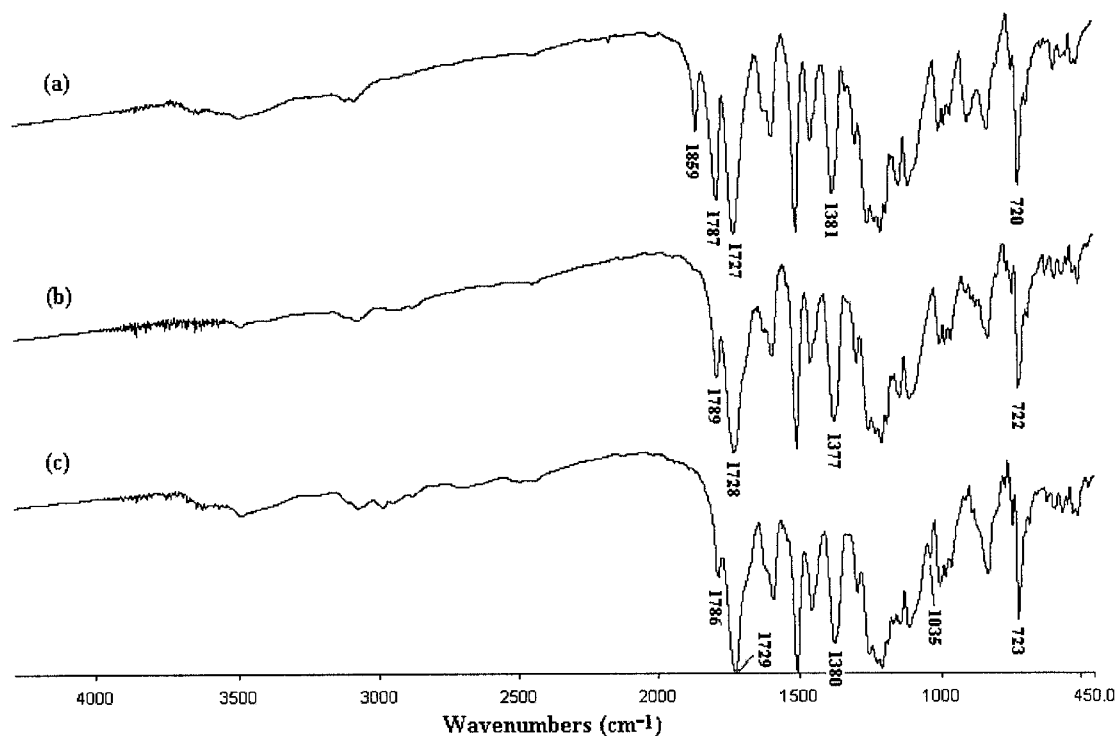


Figure 1. FT-IR spectra of HBPIs. (a) A-HBPI, (b) M-HBPI, and (c) S-HBPI.

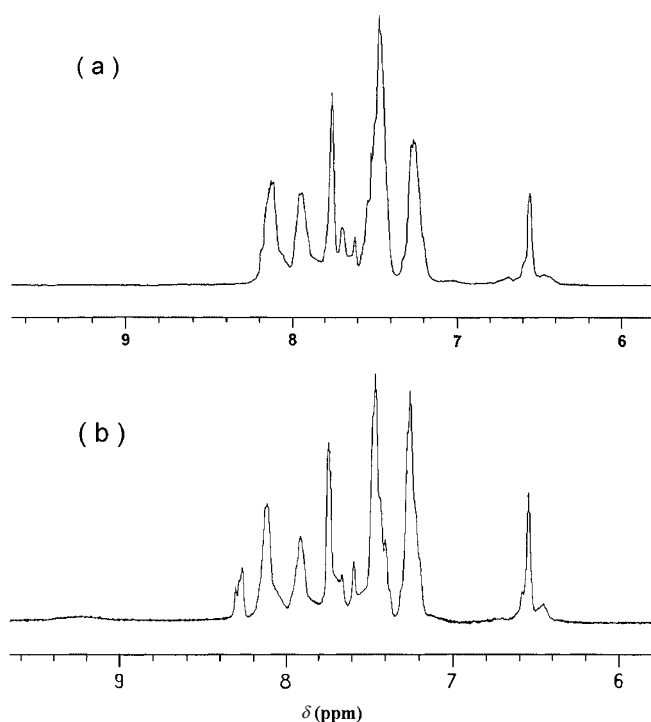


Figure 2. ^1H NMR spectra of M-HBPI (a) and S-HBPI (b).

of 6.4–8.2 ppm belong to the protons of 6FDA and TAPOB residues, and the peak at 8.2–8.4 ppm range can be attributed to the resonance absorption of *ortho*- and *meta*-hydrogen to sulfonic acid groups.¹³ The proton absorption of sulfonic acid groups was found in the range of 9.0–9.4 ppm, a very broad peak, which is in agreement with that of sulfonic acid in chemical shift and peak profile.

Molecular weights of HBPIs were determined by GPC using DMF containing 0.01 mol L^{-1} LiBr as the eluent. The results of the GPC analysis on the basis of linear polystyrene standards were summarized in Table I. All polymers had moderate molecular weights with broad distributions, as expected for HBPIs based on the anhydride-terminated HBPI.^{13,16} By comparison with the molecular weights of different HBPIs, it can be found that the GPC data from various polymerization procedures were not the same, even if the feed ratios of the monomers were identical, as indicates that it is rather difficult to control the polymerization behaviors of hyperbranched polymers from $A_2 + B_3$ monomer systems.

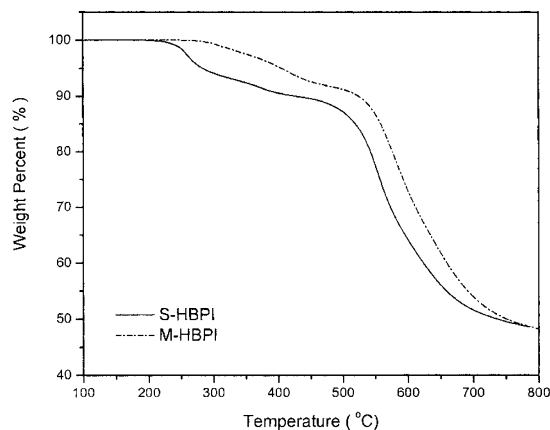
Polymer Properties

Polymer electrolyte membranes that exhibit fast proton transport at elevated temperatures are needed for electrochemical devices operating in the 100–200°C range, and so the thermal stability of proton conducting polymer electrolyte membranes is a very important factor for fuel cell applications.^{17,18} The thermogravimetric analysis (TGA) on S-HBPI was carried out in nitrogen, taking M-HBPI as the comparison (Figure 3). A quick weight loss in the range of 250–350°C was observed. The margin of the weight loss of S-HBPI versus M-HBPI at 350°C is about 5.2%, which could be attributed mostly to the loss of sulfonic acid groups (calculated value for the content of sulfonic acid groups in S-HBPI is 6.1 wt%; found value by elemental anal-

Table I. Preparation of HBPIs

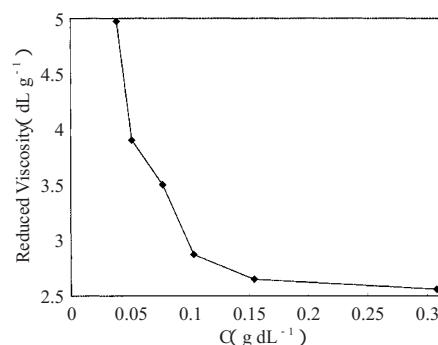
	M_w	M_n	Yield (%)	PDI M_w/M_n	T_{10} °C	T_g °C	IEC _{calc} ^a (meq g ⁻¹)	IEC _{meas} ^b (meq g ⁻¹)
A-HBPI	140700	26200	95	5.4	505	228	—	—
M-HBPI	153900	27900	94	5.5	517	217	—	—
S-HBPI	103800	23000	94	4.5	428	235	0.704	0.685

^aCalculated ion-exchange capacity of S-HBPI on the basis of the sulfur content obtained by elemental analysis. ^bMeasured ion-exchange capacity of S-HBPI by titration.

**Figure 3.** Thermal gravimetric curves of S-HBPI and M-HBPI in nitrogen at a heating rate of 10 °C min⁻¹.

ysis is 5.7 wt%). Under 200 °C, no detectable weight loss was found. The substitution of sulfonic acid groups on the phenyl ring, which attached to the electron withdrawing imide units, might contribute to the high thermal stability of the C–S bonds.^{17, 19} Since the high thermal stability of sulfonic acid groups is the desired property of sulfonated polymers for practical applications as polymer electrolytes,^{17, 18} the arenesulfonated HBPI might be a promising candidate to be used in polymer electrolyte fuel cell systems. The bulk degradation of polyimide backbone began at around 480 °C for both polymers. The 10% weight loss temperatures (T_{10}) and glass transition temperatures (T_g) were summarized in Table I. T_g of S-HBPI is greater than those of A-HBPI and M-HBPI. This is due to the difference in the end-group polarity of the polymers, that is, higher polar end groups lead to greater T_g values.^{1, 20}

S-HBPI showed good solubility in NMP, DMF, DMAc, and DMSO, and even in low boiling point solvents, such as tetrahydrofuran, chloroform, and acetone; and it is partly soluble in methanol, but insoluble in ethanol. The dry polymer dissolved slowly at room temperature in 5 wt% Na₂CO₃ aqueous solution. After dissolution, the aqueous solution exhibited a reversible dissolution and precipitation process according to the change in pH value of the solution. When the solution was shifted to acidic condition (pH < 6) by the addition of hydrochloric acid, the polymer precipitated immediately; and when the pH value was elevated to 9 again,

**Figure 4.** Dependence of the reduced viscosity of S-HBPI on the polymer concentration in DMAc.

the precipitation disappeared quickly. This is due to the conversion of the sulfonic acid groups at the macromolecular periphery of the polymer to sulfonate sodium salts in alkaline condition.

Figure 4 showed that the reduced viscosity of S-HBPI increased with the decrease in the polymer concentration. As is the characteristic of the polymer electrolyte in polar solvents.²¹

Ion-exchange capacity (IEC) of the arenesulfonated HBPI is summarized in Table I. The IEC of the polymer electrolyte determined by titration is in agreement with the calculated value on the basis of the sulfur content obtained by elemental analysis.

CONCLUSIONS

A kind of arenesulfonated hyperbranched polyimide (S-HBPI) was prepared using the anhydride-terminated hyperbranched polyimide as the polymer backbone. The negatively charged groups, sulfonic acid groups, were introduced by the reaction of the terminal anhydride groups with the amino groups of sulfanilic acid during polymerization of the poly(amic acid) precursor, which was then chemically imidized. S-HBPI exhibited rather good thermal stability and high organosolubility. Further studies on the polymer electrochemical properties, including the water uptake property and proton conductivity, are under way.

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