Preparation and characterization of hyperbranched poly(ether sulfone) and its application as a coating additive for linear poly(ether sulfone)

Bing Han, Dong Sun, Xiujie Li, Cong Gao, Shuling Zhang

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, People's Republic of China
Correspondence to: S. L. Zhang (E‑mail: zsl@jlu.edu.cn)

ABSTRACT: Hyperbranched poly(ether sulfone) (HPES), a suitable coating additive for improving the rheological properties of linear poly(ether sulfone) (LPES), was easily produced via polymerization of commercially available bisphenol S (A_2 monomer, BPS) and synthesized 2,4′,6-trifluoro-phenylsulfone (BB_2' monomer, TF). During this reaction, fluoro- or phenolic-terminated HPES (F-HPES or OH-HPES) could be facilely obtained by controlling the feed mole ratios of the two monomers. The polymerization mode $A_2 + BB_2'$ was confirmed by analyzing the model compounds and the degree of branching (DB) was calculated systematically. In addition, the synthesized polymers' chemical structures were exhibited by FTIR, ^{1}H NMR as well as ^{19}F NMR spectroscopy. Notably, the addition of 1 wt % HPES reduced the melt viscosity and improved the high temperature liquidity of LPES because of its unique spherical shape. Furthermore, the addition of HPES did not have a negative impact on the performance of LPES, which was attributed to the good miscibility between HPES and LPES. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43892.

INTRODUCTION

In recent years, common and engineering plastics have been unable to meet the demands of some high-end products. Thus, the development of high performance engineering plastics, such as linear poly(ether sulfone) (LPES), is receiving a lot of attention.[1,2] Nowadays, LPES is undergoing extensive research because of its excellent heat, hydrolysis, creep, impact, and chemical resistance as well as nontoxicity, which have inspired its use in electronic, electrical, aerospace, aviation, and medical fields.[3–5] In particular, LPES shows strong adhesion to metals and high hardness of the coating. All of these advantages make it very suitable as a chemical and corrosion resistant, nonstick coating. However, unfortunately LPES must undergo a curing and sintering process when applied as a coating. In this process, because of the high melt viscosity and poor rheological properties of LPES, the surface of the coating becomes defective, affecting the overall performance. In recent years, chemical and physical modifications have been performed to solve the above problem, but chemical modification has not been widely adopted in industry because of the complex synthetic process and high cost. Physical modification can be achieved by simply blending polymers of low viscosity at relatively low cost, retaining the excellent properties of LPES.

Hyperbranched polymers have attracted considerable attention in the past 20 years because of their fascinating unique physical and chemical properties, as well as their potential wide range of applications in coatings, additives, drug-delivery, and supramolecular science compared to their linear analogues.[6–9] In brief, research has mainly focused on strategies to prepare hyperbranched polymers, especially the facile one-step polymerization of AB_x monomers.[10–12] Nevertheless, most AB_x monomers are not available commercially, which does not meet the requirements of convenience and low-cost. Consequently, some convenient synthetic methods have been developed, such as the polymerization of A_2 and BB_2' monomers.[13–15]

Hyperbranched polymers have been proven to be effective in rheology modification because of their globular shape, resulting in low hydrodynamic volume and melt viscosity.[16,17] For coating additives with low molecular weight, hyperbranched polymers with high molecular weight can be used to avoid surface migration, which is very important for the long-term use of materials. For example, Kim and Webster[16] reported that the melt viscosity of polystyrene (PS) decreased after the addition of a small amount (ca. 5%) of bromo-terminated hyperbranched polyphenylene, without affecting the thermal stability of PS. Furthermore, hyperbranched polymers with similar molecular structures to

---

Additional Supporting Information may be found in the online version of this article.

their corresponding linear polymers and facile preparation procedures are more suitable as rheology modifier. Jiang et al. incorporated hyperbranched poly(ether ether ketone) (HPEEK) into poly(ether ether ketone) (LPEEK) as a rheology control agent to improve the melt processability and mechanical properties of LPEEK.[17] However, the incorporation of hyperbranched polymers into LPES for modification of its rheological properties has not yet been reported.

Herein, we report a novel, facile method to prepare hyperbranched poly(ether sulfone) (HPES) using commercially available bisphenol S (A$_2$ monomer) and synthesized 2,4′,6-trifluorophenylsulfone (TF, BB$_2'$ monomer). During this reaction, F- and HO-terminated HPES could be conveniently obtained by adjusting the feed ratio of the two monomers. The polymerization process and chemical structure of HPES were characterized systemically. Moreover, highly branched, low melt viscosity HPES was blended with LPES in order to effectively modify its rheological properties while solving levelling problems at high temperature without sagging. Furthermore, the effects of adding HPES on the properties of LPES are discussed in detail.

EXPERIMENTAL

Materials

Following substances were got from commercial sources and used directly without further treatment: 2,6-Difuorobenzenesulfonyl chloride (Yanji Chemical Works), bisphenol S (BPS, Nantong Huayi Import & Export), fluorobenzene (Shanghai Tainuo Chemical), ferric chloride (Shanghai Meixin Chemical), dimethyl sulfoxide (DMSO, Tianjin Tiantai Chemical), N,N-dimethylformamide (DMF, Shanghai Chemical), and N,N-dime-
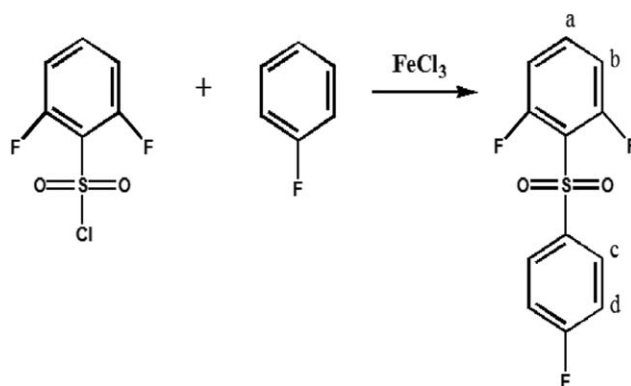
**Scheme 1.** Synthesis of BB$_2'$ monomer.

thylacetamide (DMAc, Shanghai Chemical). Furthermore, before using sodium carbonate (Na$_2$CO$_3$) and potassium carbonate (K$_2$CO$_3$), they were dried for 24 h at 120 °C and LPES (melt flow index, 30 g/10 min; $T_g = 229$ °C) was received from Changchun Jilin University Super Engineering Plastics Research.

Characterization

A Nicolet Impact 410 Fourier transform infrared spectrometer was applied to the measurement of the IR spectra (KBr); a Bruker 510 NMR spectrometer (500 MHz) was adopted so that the ^{1}H NMR could be performed on it; and an AXIMA-CFR MALDI-TOF spectrometer (COMPACT) was also employed to carry out the mass spectrometry (MS). Furthermore, the gel permeation chromatography (GPC) was carried out on a Waters 410 apparatus, in which PS was taken as a standard and DMF was used as the eluent. Under the conditions that the heating
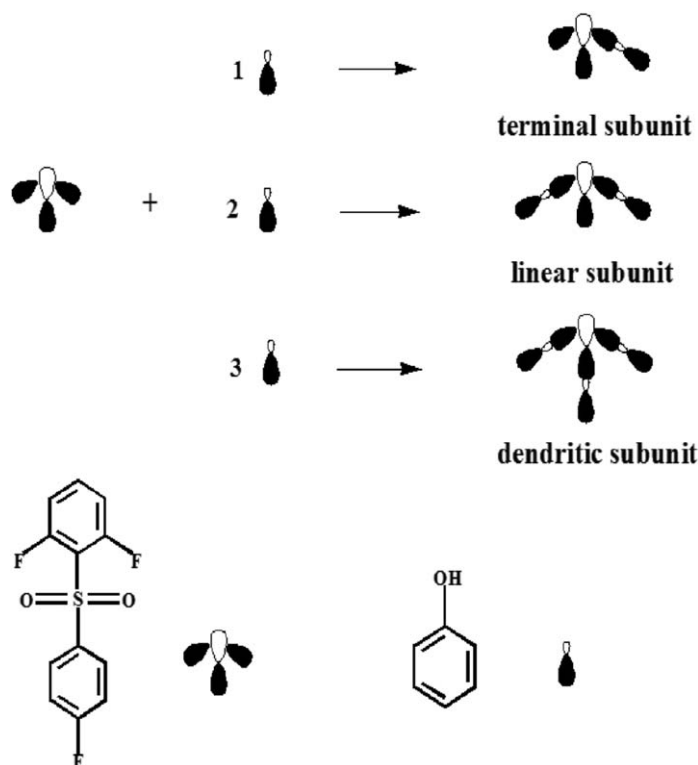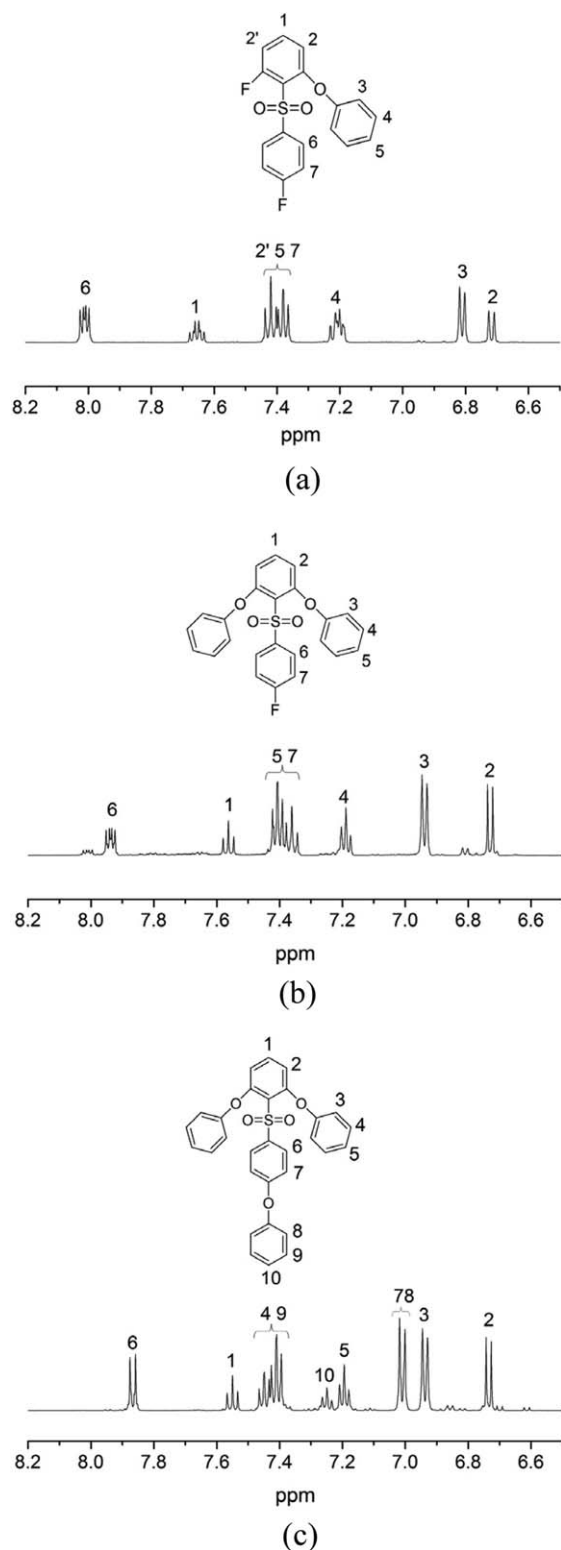

**Scheme 2.** Synthesis of model compounds.

Figure 1. ^{1}H NMR spectra of model compounds. (a) Terminal model compound, (b) linear model compound, and (c) dendritic model compound.

rate was 10 °C/min and a nitrogen atmosphere existed, a Mettler Toledo DSC821[e] apparatus was used to conduct the differential scanning calorimetry (DSC), while a Perkin Elmer TGA-7 was also adopted to carry out the thermal gravimetric analysis
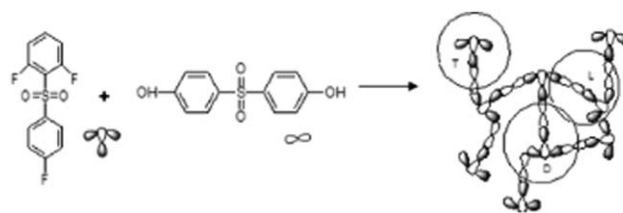
Scheme 3. Synthesis of hyperbranched polymer (L, linear; D, dendritic; T, terminal).

(TGA) under the same conditions. In addition, a Perkin Elmer 2400 instrument was applied so as to perform the elemental analysis and an America Dynisco test LCR7001 capillary rheometer was also used to measure the rheological properties at 330 °C. The morphologies of the samples were analyzed with the application of the scanning electron microscopy (SEM, SSX-550 SHIMADZU).

A Tu 4 cup was designed by GB/T1732-93 to measure the viscosity of the samples. Records time (s) that a certain amount of
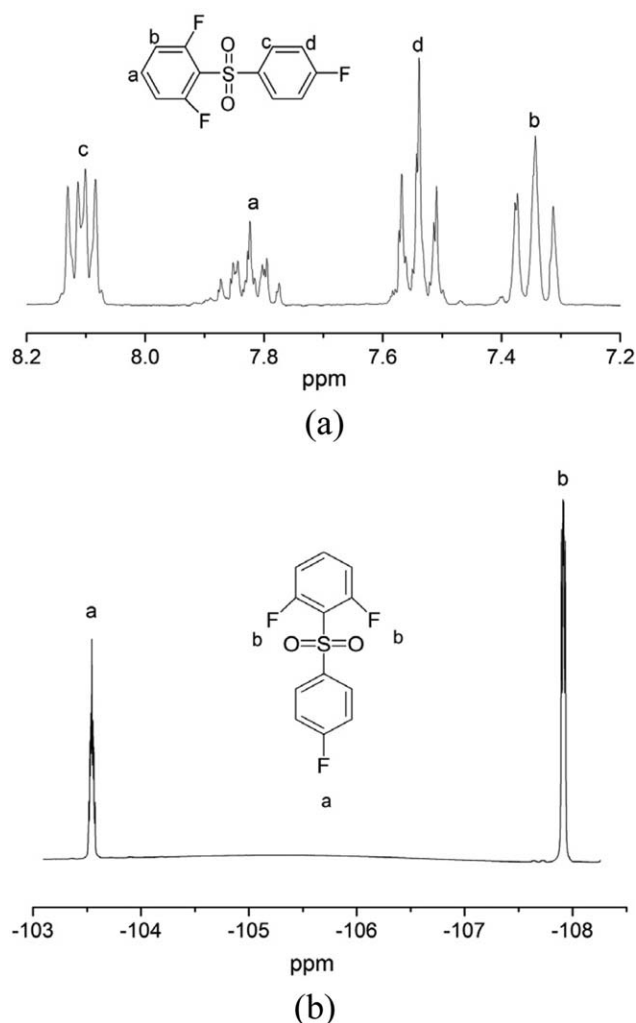

Figure 2. (a) ^{1}H NMR spectrum and (b) ^{19}F HMR spectrum of the BB_2' monomer.

Table I. Reaction Conditions and Polymerization Results

Method	OH : F (mol/mol)	M_w[a]	M_n[b]	PDI[c]	T_g (°C)[d]	$T_{d5\%}$ (°C)[e]
A$_2$ + BB$_2'$	0.55	29,761	16,795	1.77	198	464
	0.60	82,127	27,667	2.97	209	449
	0.63	96,048	28,988	3.21	231	476
	1.40	38,237	20,472	1.87	219	410
	1.45	15,881	12,182	1.30	197	396
	1.50	15,498	11,630	1.33	197	397
	1.55	14,453	11,824	1.22	195	394

[a] Molecular weight.
[b] Number average molecular weight.
[c] Polydispersity index.
[d] Glass transition temperature.
[e] Thermal decomposition temperature (5% loss of weight).

samples are flowing out from a hole with the required diameter at a certain temperature.

Adhesion tests were carried out according to GB/T1720-79(89): the film was fixed on a platform that could move back and forth, with a needle moving above the film surface. The level of adhesion can be determined through observation of the fracture position of the film on the overlapping circle lines.

The impact properties were identified using a GB/T1732-93 Impact Instrument. The sample size for impact tests of the coatings is 50 mm × 120 mm × 20 um, which was sprayed onto a specified plate and cured completely.

Pencil hardness was evaluated according to GB/T6739-1996, using a QHQ Coating Pencil Scratch Hardness Tester.

Acid, alkaline, and salt resistance tests were measured according to GB1763-1976(88). Aluminium plates were sprayed with different amounts of paint and then placed in 5 wt % HCl, 5 wt % NaOH, and 5 wt % NaCl solutions. The appearance of the films was investigated after 48 h.

Flexibility was measured in accordance with GB 1748-1976(88), by observing the cracks and shedding after bending the films.

Synthesis

2,4′,6-Trifluoro-Phenylsulfone (TF, BB$_2'$ Monomer, Scheme 1). The addition of anhydrous ferric chloride (89.4 g, 0.55 mol) in 500 mL of fluorobenzene into 2,6-difluorobenzene sulfonyl chloride (106.25 g, 0.5 mol) in 500 mL of fluorobenzene was carried out drop by drop with stirring. Then under the condition of reflux, the reaction mixture was heated in the atmosphere of nitrogen for 10 h, followed by pouring it into 1000 mL of acidic water. When the fluorobenzene evaporated, cool the residue until 25 °C was reached and then the solid was filtrated. At last, purification of the crude product was from ethanol and water conducted through recrystallization for providing 2,4′,6-trifluoro-phenylsulfone as a needle-like solid.

$$MS: m/z = 272.$$

Elem. anal. calcd for $C_{12}H_7O_2F_3S$: C, 52.84%; H, 2.59%; S,12.6%. Found: C, 52.79%; H, 2.6%; S, 12.6%.

$$IR \left(KBr, \ cm^{-1} \right): 3079 \ (Ar-H), \ 1148 \ and$$
$$1102 \ (Ar-F), \ 1068 \ (O=S=O).$$

^{1}H NMR (DMSO-d$_6$, δ in ppm): 7.77–7.89(m, 1H, Ha); 7.31–7.38(t, 2H, Hb); 8.08–8.13(d, 2H, Hc); 7.51–7.57(t, 2H, Hd).

Model Compounds. *Terminal model compound [Scheme 2, Figure 1(a)].* Phenol (0.94 g, 10 mmol) was added to a mixture of TF (2.72 g, 10 mmol), DMAc (40 mL) and K$_2$CO$_3$ (1.449 g, 10.5 mmol). Then under the condition of reflux, the reaction mixture was heated in nitrogen until the temperature of 160 °C was reached for 3 h. Subsequently, after pouring the reaction mixture into 500 mL of water, the precipitate was gathered and finally hot deionized water was used to wash the precipitate.

$$MS: m/z = 346.$$

^{1}H NMR (DMSO-d$_6$; δ, ppm): 7.63–7.68 (1H, H(1)); 6.71–6.73 (1H, H(2)); 7.37–7.44 (1H, H(2)); 6.80–6.81 (2H, H(3)); 7.19–7.23 (2H, H(4)); 7.37–7.44 (1H, H(5)); 8.00–8.03 (2H, H(6)); 7.37–7.44 (1H, H(7)).

Linear model compound [Scheme 2, Figure 1(b)]. Phenol (1.88 g, 20 mmol) was added to a mixture of TF (2.72 g, 10 mmol), DMAc (40 mL), and K$_2$CO$_3$ (2.898 g, 20.1 mmol). The procedure was the same as how the terminal model compound was synthesized.

$$MS: m/z = 420.$$

^{1}H NMR (DMSO-d$_6$; δ, ppm): 7.55–7.58 (1H, H(1)); 6.72–6.74 (2H, H(2)); 6.93–6.95 (2H, H(3)); 7.17–7.20 (2H, H(4)); 7.34–7.42 (1H, H(5)); 7.92–7.95 (2H, H(6)); 7.34–7.42 (2H, H(7)).

Dendritic model compound [Scheme 2, Figure 1(c)]. Phenol (2.829 g, 30.1 mmol) was added to a mixture of TF (2.72 g, 10 mmol), DMAc (40 mL) and K$_2$CO$_3$ (4.347 g, 30.15 mmol). The procedure was also the same as how the terminal model compound was synthesized.

$$MS: m/z = 494.$$

^{1}H NMR (DMSO-d$_6$; δ, ppm): 7.53–7.57 (1H, H(1)); 6.73–6.74 (2H, H(2)); 6.93–6.95 (4H, H(3)); 7.39–7.57 (4H, H(4)); 7.18–7.21 (2H, H(5)); 7.86–7.88 (2H, H(6)); 7.00–7.02 (2H, H(7));
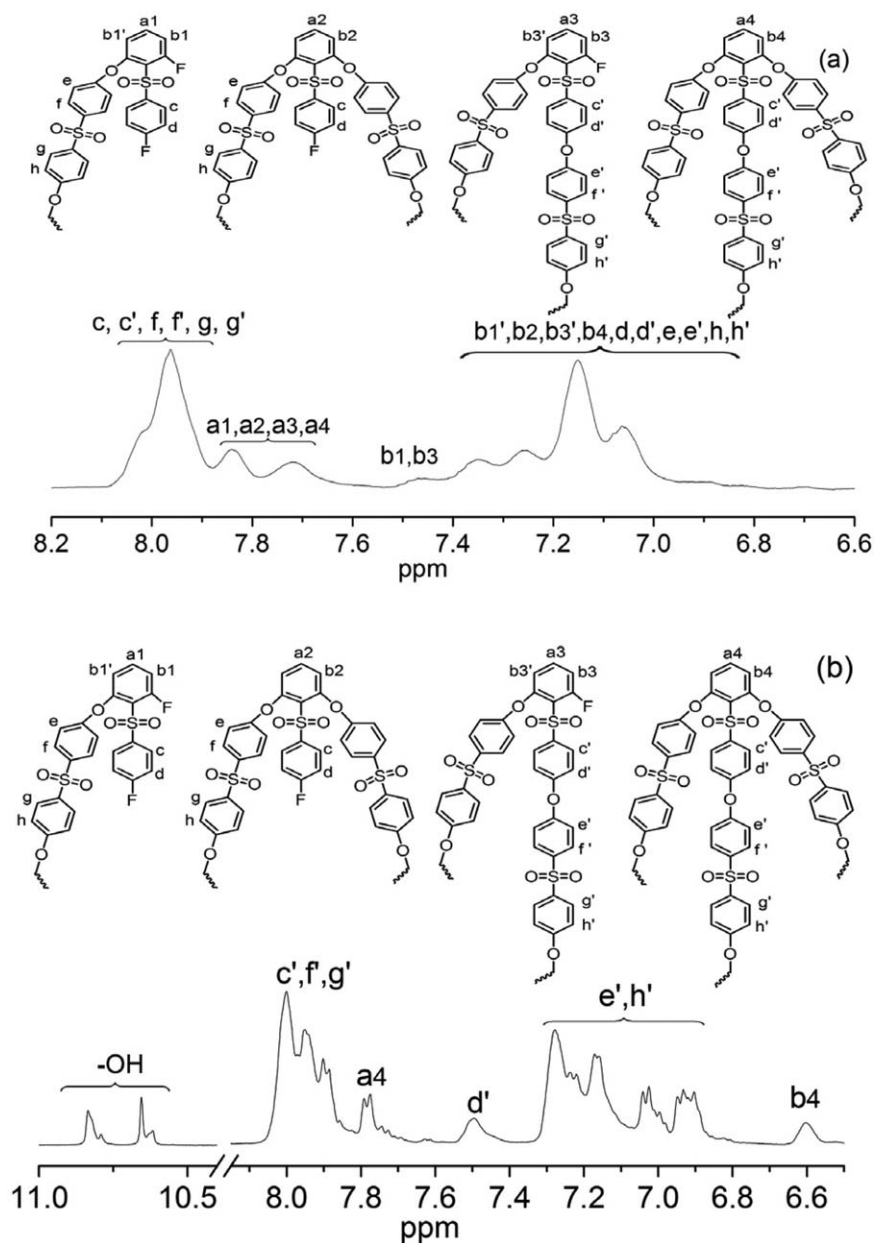
Figure 3. ^{1}H NMR spectra of (a) F-HPES and (b) HO-HPES.

7.00–7.02 (2H, H(8)); 7.39–7.47 (2H, H(9)); 7.23–7.26 (1H, H(10)).

Fluoro-Terminated Hyperbranched Poly(ether sulfone). Following typical steps of experiment was carried out on condition that the feed mole ratio of A_2 to BB'_2 was equal to or smaller than 1 (OH:F = 0.63 in Table I): firstly, a nitrogen inlet along with a thermometer, a Dean-Stark trap as well as a mechanical stirrer was used to dissolve bisphenol S (2.50 g, 10 mmol), TF (2.72 g, 10 mmol), K_2CO_3 (0.483 g, 3.50 mmol) as well as Na_2CO_3 (0.7430 g, 7 mmol) in 27 mL of NMP and 16 mL of toluene in a three-necked flask fitted (100 mL) and then the purification of the apparatus was conducted with the application of nitrogen. Subsequently, in order to make sure that the reaction mixture was dehydrated completely, it was heated under the

condition of reflux for 2 h. When the toluene was cleared, the reaction mixture was heated again under the condition of nitrogen until the temperature reached about 190 °C for 8 h. Then after pouring the resultant mixture into 500 mL of deionized water, a precipitate was formed and collected through filtration. Finally, triple precipitation was conducted on the crude product from water into ethanol so that Fluoro-Terminated Hyperbranched Poly(ether sulfone) (F-HPES, Scheme 3) could be provided.

$$\text{IR } \left(\text{KBr, cm}^{-1}\right): 3078 \text{ (Ar−H)}, 1239 \text{ (−O−)},$$
$$1148 \text{ (O=S=O)}, 1236 \text{ and } 1296 \text{ (Ar−F)}.$$

Phenolic-Terminated Hyperbranched Poly(ether sulfone). Following typical steps of experiment was carried out on condition that the feed mole ratio of A_2 to BB'_2 was equal to or larger than

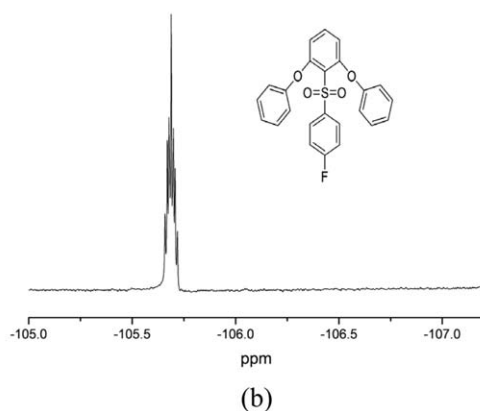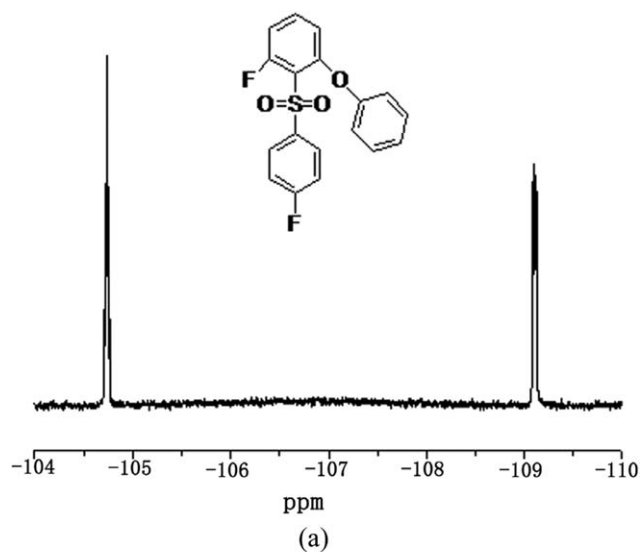**Figure 5.** ^{19}F NMR spectrum of F-HPES (OH:F = 0.63).

Figure 4. ^{19}F-NMR spectra of (a) terminal model compound and (b) linear model compound.

2 (OH:F = 1.33 in Table I): firstly, a nitrogen inlet along with a thermometer, a Dean-Stark trap as well as a mechanical stirrer was used to dissolve the bisphenol S (4.9875 g, 19.95 mmol), TF (2.72 g, 10 mmol), K_2CO_3 (0.9636 g, 7 mmol) as well as Na_2CO_3 (1.4803 g, 13.97 mmol) in NMP (29 mL) and toluene (15 mL) in a three-necked flask fitted (100 mL) and then the purification of the apparatus was conducted with the application of nitrogen. It can be seen that these steps were the same as how F-HPES was synthesized, with the exception that after mixing 800 mL of deionized water with 50 mL of hydrochloric acid, the pouring of the crude product into it was completed by stirring vigorously. Finally, for the purpose of providing phenolic-terminated hyperbranched poly(ether sulfone) (HO-HPES, Scheme 3), triple precipitation was conducted from water on the crude product into ethanol under an atmosphere of nitrogen.

$$IR\left(KBr, cm^{-1}\right): 3419\,(-OH),\ 3078\,(Ar-H),$$
$$1239\,(-O-),\ 1150\,(O=S=O).$$

Blend Preparation

The blends were prepared by solution blending as follows: HPES (0, 0.5, 1, 2, and 3 wt %) and LPES were completely dis-

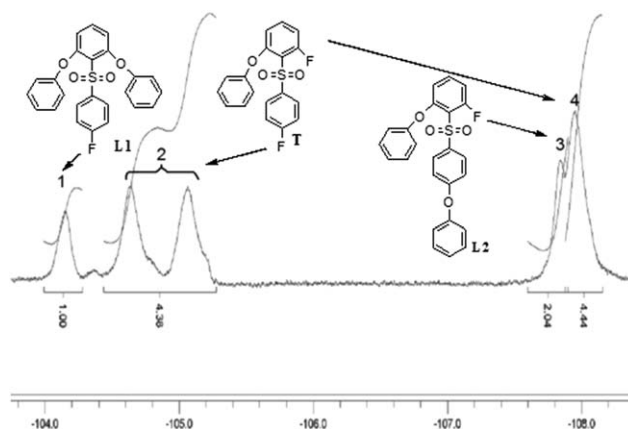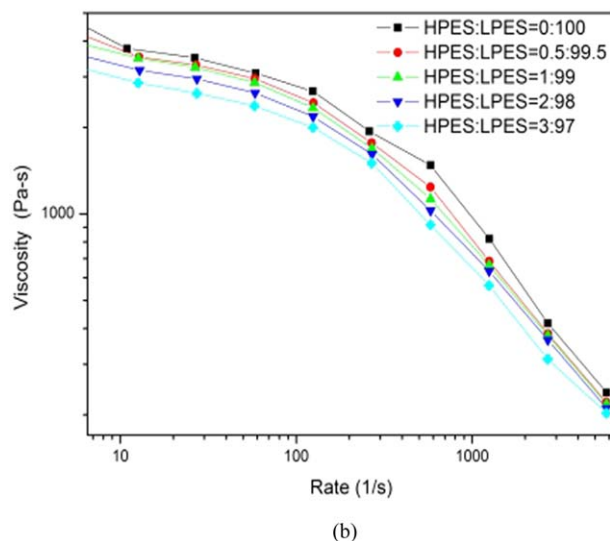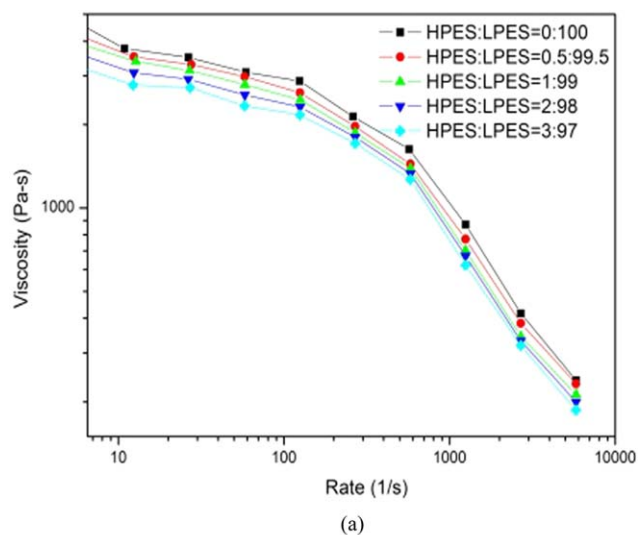**Figure 6.** Plots of shear viscosity versus shear rate for (a) LPES and F-HPES/LPES blends and (b) LPES and OH-HPES/LPES blends. [Color figure can be viewed in the online issue, which is available at wileyonline-library.com.]

Table II. Viscosity Data Measured by Tu 4 cup for LPES and HPES/LPES Blends

Sample	Weight (g)	Amount of solvent (mL)	Time (s)
LPES	1	5.714	28
F-HPES/LPES = 0.5/99.5	1	5.682	28
F-HPES/LPES = 1/99	1	5.618	28
F-HPES/LPES = 2/98	1	5.556	28
F-HPES/LPES = 3/97	1	5.464	28
OH-HPES/LPES = 0.5/99.5	1	5.682	28
OH-HPES/LPES = 1/99	1	5.650	28
OH-HPES/LPES = 2/98	1	5.556	28
OH-HPES/LPES = 3/97	1	5.495	28

solved in DMAc, then poured into distilled water slowly and smashed into a powder after solidification. Finally, the residual impurities and solvent were removed by recrystallization from water and ethanol, and then dried at 170 °C for 24 h.

Coating Preparation

In accordance with the coating preparation method (GB1729-92), the specimen was sprayed into a uniform coating on the specified plate (aluminium plate or glass). The sprayed plate was placed into a high temperature oven at 120 °C for 15 min to dry the coating. Then, the sample was sprayed and dried again using the same procedure. Subsequently, the sample in the oven was heated to 380 °C at the heating rate of 2 °C/min and maintained for 10 min to cure the coating completely.

RESULTS AND DISCUSSION

Design and Synthesis of HPES

The BB_2' monomer that contained three fluoro groups (TF) was synthesized with great success. The fluorine situated at the *para* position to the O═S═O group has distinct activity with the fluorines situated at the *ortho* position. According to Scheme 1, the synthesis of TF was completed through a Friedel-Crafts acylation reaction. In addition, the MS, IR, ^{1}H NMR as well as ^{19}F NMR spectroscopy confirmed its chemical structure, which was shown in Figure 2.

With regard to the HPES synthesized by the method of $A_2 + BB_2'$, distinct types of HPES were obtained by the distinct feed molar ratios between the A_2 (BPS) and BB_2' (TF) monomers. F-HPES was achieved on condition that the feed molar ratio of A_2 to BB_2' was equal to or smaller than 1 (A_2:$BB_2' \leq 1$ or OH:F ≤ 0.63); while HO-HPES was realized on condition that the feed molar ratio of A_2 to BB_2' was equal to or larger
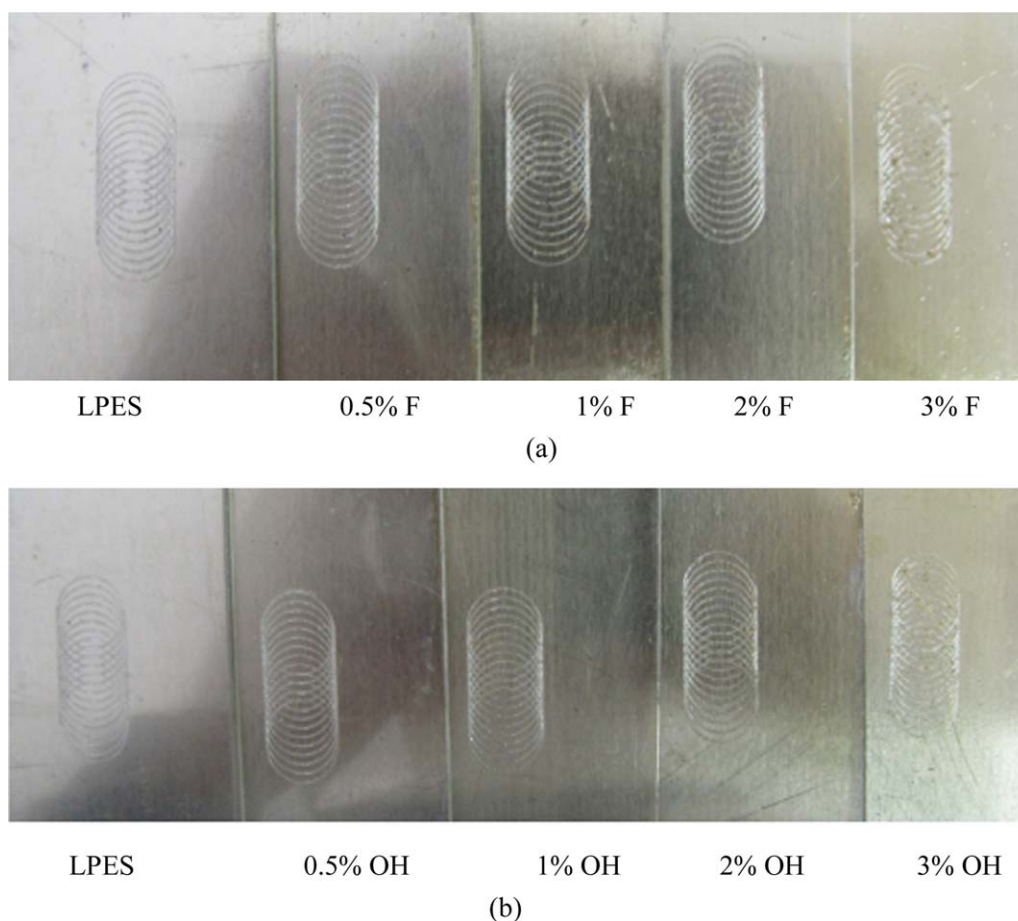

Figure 7. Adhesion tests for (a) F-HPES/LPES and (b) HO-HPES/LPES blends. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
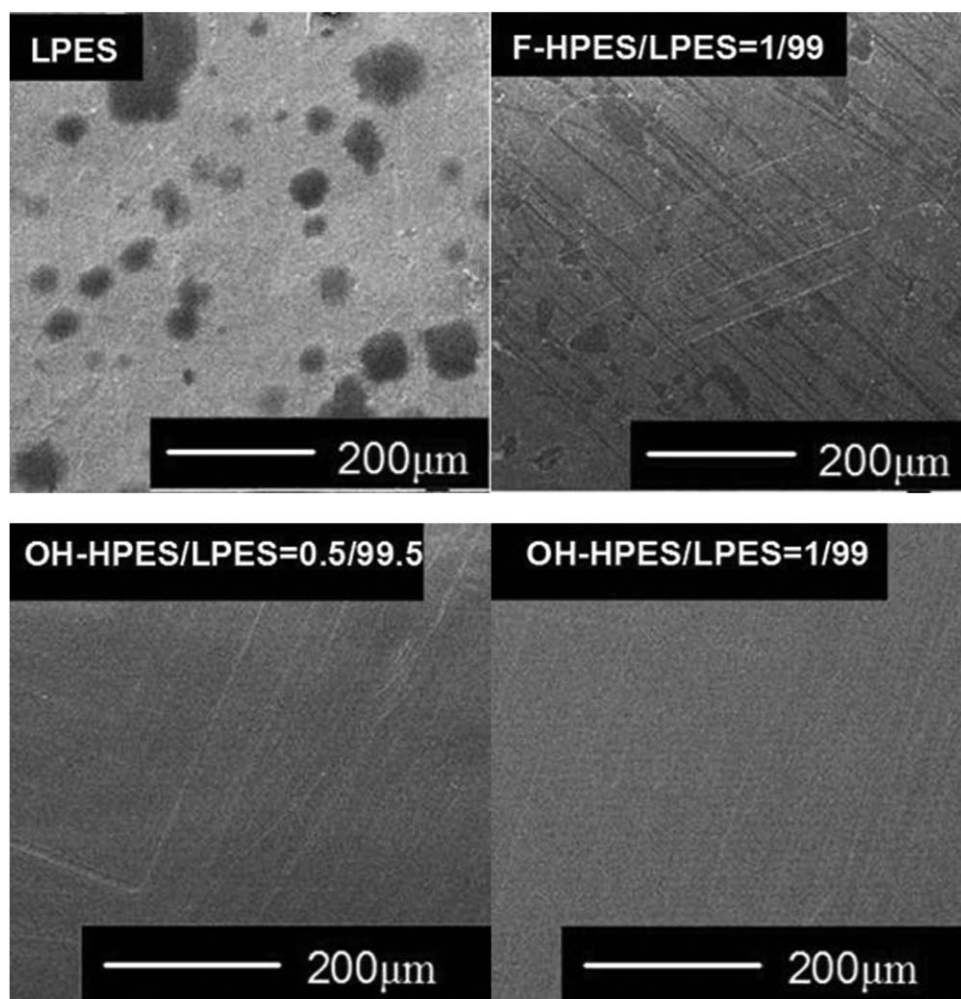
Figure 8. SEM images of LPES and HPES/LPES blend films.

than 2 (A_2:$BB'_2 \geq 2$ or OH:F ≥ 1.4). Compared to the $A_2 + B_3$ approach (OH:F ≤ 0.48 or OH:F ≥ 2.02), the phenolic and fluoro groups' molar ratio was nearer to 1 and HPES with higher molecular weight was able to be yielded. Moreover, it can be seen from Table I that the molecular weight increased to 96,048 for F-HPES and 38,237 for HO-HPES.

Scheme 3 shows the process how HPES is synthesized. IR and ^{1}H NMR verify the chemical structures of F-HPES and HO—HPES (Figure 3). The bands at around 3078 (Ar–H), 1148 (O$=$S$=$O), and 1239 cm^{-1} (—O—) are the representative absorption bands of HPES. In addition, the terminal fluoro and phenolic groups' stretching in F-HPES and HO-HPES can, respectively, explain the bands at 1236, 1296 (Ar–F), and 3419 (—OH) cm^{-1}. As a result, the successful synthesis of F-HPES and HO-HPES can be seen from these data.

Figure 3(a) displays ^{1}H NMR spectrum of F-HPES, in which the resonance absorption of the phenyl hydrogen *ortho* or *para* to the S$=$O groups is the reason for the bands' range from 7.56 to 8.08 ppm, while the phenyl hydrogen *ortho* to —O— or —F is the reason for the bands' range from about 6.65 to 7.51 ppm. In the ^{1}H NMR spectrum of HO-HPES [Figure 3(b)], the —OH hydrogen is observed as peaks at around 10.59–10.88

ppm, apart from the phenyl hydrogen's resonance absorption situated at the *meta* position to the —OH groups and *ortho* or *para* to the S$=$O groups in the range 7.56–8.08 ppm, as well as the resonance absorption of the phenyl hydrogen situated at *ortho* to the —OH and —O— groups in the range 6.56–7.55ppm. Therefore, the chemical structures of F-HPES and HO-HPES can be further verified by these data.

The conditions and results of reaction are summarized in Table I. In terms of F-HPES (OH:F ≤ 0.63) and HO-HPES (OH:F ≥ 1.4), both M_n, polydispersity index (PDI), and glass transition temperature (T_g) gradually increased while the molar ratio of OH to F was close to 1. No significant difference was found between the T_g of HPES and LPES. The TGA results also showed the same trend. Moreover, when heated under nitrogen, the rate of which was 10 °C/min, high thermal stability could be observed and over 95% of their weight maintained as high as 394 °C.

Mode of Reaction

In order to explore the reaction modes of the polymers, terminal, linear, and dendritic model compounds were synthesized and confirmed by ^{1}H NMR (Figure 1). According to the data, the fluorine located *ortho* to the O$=$S$=$O group has a higher

activity compared with the fluorine located *para* to the O=S=O group. In other words, the fluorine located *ortho* to O=S=O reacted earlier than the fluorine located *para* to O=S=O with the phenolic group. Moreover, the fluorine located *ortho* to O=S=O gradually disappears in the terminal and linear model compounds' ^{19}F NMR spectra shown in Figure 4 compared to the BB$_2'$ monomer's ^{19}F NMR spectra shown in Figure 2(b), which further supports the above statements.

The phenolic group (A) along with the fluorine located *para* to the O=S=O group (B) as well as the fluorine located *ortho* to the O=S=O group (B′) exists in the reaction system. As previously demonstrated, B′ reacts quite faster than B with A for the reaction mode A$_2$ + BB$_2'$ (A$_2$: bisphenol S; BB$_2'$: 2,4′,6-trifluoro-phenylsulfone).

Degree of Branching

The evaluation of the degree of branching (DB) of HPES can be realized through the ^{19}F NMR spectra. Under the condition of a 100% DB, dendritic polymers are completely branched; nevertheless, the structure of hyperbranched polymers is far more irregular. Despite of defining their irregular structure unambiguously is difficult, the DB is adopted to measure the irregularity, as what the following equation has defined[18,19]:

$$DB = \frac{D+T}{D+T+L} \quad (1)$$

where D, T, and L stand for dendritic, terminal, and linear units, respectively.

Hölter *et al.* proposed that T will become the same as D in large hyperbranched molecules. Thus, the following equation is proposed so as to estimate the branching degree[20]:

$$DB = \frac{2T}{2T+L} \quad (2)$$

Regarding HPES, three distinct types of units are displayed with regard to its overall structure, including "dendritic," D that is without any fluoro group; "terminal" T that is with two fluoro groups as well as "linear" L that is with one fluoro group. The evaluation of the percentage of D, T, and L can be realized with the application of NMR spectra because of their large differences among the chemical environments of D, T, and L's trisubstituted aromatic rings. In order to distinguish the three subunits, the synthesis of the model compounds was conducted (Scheme 2). Comparing the model compounds' ^{1}H NMR spectra shown in Figure 1 with those of F-HPES and HO-HPES shown in Figure 3, it is difficult to identify the three subunits since each peak cannot be obviously discriminated.

As a result, the ^{19}F NMR spectra were used to evaluate the DB of HPES. In Figure 5, it can be seen that the terminal and linear subunits exhibit distinct differences to the ^{19}F NMR spectrum of F-HPES (OH:F = 0.63). Additionally, there were two types of linear units (L1 and L2 in Figure 5). This phenomenon might be explained by the fact that the synthesis temperature of the polymers was higher than that of the model compounds, which resulted in little difference between the reaction activity of fluorine located at *para* and *ortho* positions. Consequently, the DB for F-HPES (OH:F = 0.63) was evaluated as 74.6% using eq. (2), according to the peak area given in Figure 5. The same ana-

lytical procedure was applied to HO-HPES (OH:F = 1.40). However, there were no peaks in the ^{19}F NMR spectrum of HO-HPES, which suggested that there were no terminal or linear units. That is to say, DB of HO-HPES was 100%.

Influence of HPES Addition on the Rheological Properties of LPES

In order to solve the problem of the high melt viscosity of LPES coatings, F-HPES (A$_2$:BB$_2'$ = 1 or OH:F = 0.63) and HO-HPES (A$_2$:BB$_2'$ = 2 or OH:F = 1.40) were chosen as rheology control agents because of their hyperbranched structures and higher molecular weight. It should be noted that hyperbranched polymers with higher molecular weight can avoid surface migration more effectively, which is very important for the long-term use of materials. Furthermore, an elementary study on the effects of HPES addition on the rheological properties of LPES was carried out.

Figure 6 shows the shear viscosity of LPES and HPES/LPES blends versus shear rate. It is obvious that the addition of hyperbranched polymers can indeed reduce the linear polymer's melt viscosity. Moreover, the LPES/HPES blends' shear viscosity shows a trend of gradual decline as the HPES content increases. As can be seen in Figure 6, F-HPES and HO-HPES show the same trend.

The reduction of melt viscosity might be attributed to following reasons. Compared with linear polymers, the melt viscosity of hyperbranched polymer molecules is lower, which is caused by their three-dimensional structures that are highly branched and have less entangled molecular chains; hence the obvious difference between the inherent melt viscosities of LPES and HPES. In addition, HPES/LPES blends exhibited good miscibility, because these two components are similar in terms of their chain structure. Consequently, the melt viscosity of LPES can be decreased prominently by blending only a little HPES with LPES. What's more, other systems like HPEEK/LPEEK have also identified similar influences.[17]

Influence of HPES Addition on the Adhesion Properties of LPES

The blends were adjusted to engineering-required viscosity by Tu 4 cup, as shown in Table II. It was found that the addition of hyperbranched polymers can reduce the amount of solvent required at room temperature. In other words, a small amount of HPES could improve the solubility of LPES. It was also suggested that as the amount of hyperbranched polymer was increased, the amount of solvent required decreased. This reduced solvent evaporation and is thus more environmentally friendly.

After spraying the coating, a series of adhesion tests were carried out. The results are presented in Figure 7, which shows that the addition of a small amount of hyperbranched polymer has little effect on aluminium adhesion. However, the adhesion of the film was beyond the scope of use when more than 3 wt % hyperbranched polymer was added. Meanwhile, compared to the blends with the same amount of additive, the adhesion of the HO-HPES/LPES blend was superior to that of the F-HPES/LPES blend.

In order to further confirm the aforementioned results, it was necessary to obtain scanning electron micrographs of LPES and the HPES/LPES blends. As shown in Figure 8, although the addition of F-HPES could improve the liquidity of the film, the appearance of the film was not good. In contrast, the same amount of HO-HPES not only improved the liquidity of the film, but also smoothed the appearance. In other words, when only a small amount of HO-HPES was added to LPES, the cavity formed during solvent evaporation could no longer be seen.

Moreover, comparing the HO—HPES/LPES = 0.5/99.5 blend to the HO—HPES/LPES = 1/99 blend, as shown in Figure 8, it can be seen that the amount of hyperbranched polymer added does not have a significant effect, although the liquidity properties are improved to some extent when the amount added is small. We could also observe the place where the liquidity effect was not ideal. Additionally, the film with added HPES showed great performance, meaning that the incorporation of HPES did not have a negative impact on the properties of LPES (see Supporting Information).

CONCLUSIONS

The polymerization of bisphenol S (A_2 monomer) and 2,4′,6-trifluoro-phenylsulfone (BB'_2 monomer) with Na_2CO_3 and K_2CO_3 was achieved by a new strategy of $A_2 + BB'_2$ to prepare higher molecular weight HPES. In the reaction system, the fluorine located *ortho* to the O=S=O group had a higher activity compared with the fluorine located *para* to O=S=O, i.e., the fluorine located *ortho* to O=S=O reacted with the phenolic group prior to the fluorine *para* to O=S=O. When the feed molar ratio of A_2 to BB'_2 was less than or equal to 1 (A_2:$BB'_2 \leq 1$ or OH:F ≤ 0.63), F-HPES was obtained. HO-HPES was obtained when the feed molar ratio of A_2 to BB'_2 was greater than or equal to 2 (A_2:$BB'_2 \geq 2$ or OH:F ≥ 1.4). The melt viscosity of LPES can be reduced and its high temperature liquidity can be improved effectively by the addition of hyperbranched polymers as rheology additives because of their spherical structure. Moreover, the performance of HO-HPES was better than that of F-HHPES, with an optimized addition value of 1 wt %. Furthermore, the addition of HPES did not negatively affect the properties of LPES, which is attributed to their good miscibility. In summary, HPES improved the rheological properties and liquidity of LPES, and could therefore be used as an effective modifier.

ACKNOWLEDGMENTS

REFERENCES

1. Zhang, S. L.; Yin, S. B.; Rong, C. R.; Huo, P. F.; Jiang, Z. H.; Wang, G. B. *Eur. Polym. J.* **2013**, *49*, 3125.
2. Wang, H. S.; Wang, G. B.; Li, W. L.; Wang, Q. T.; Wei, W.; Jiang, Z. H.; Zhang, S. L. *J. Mater. Chem.* **2012**, *22*, 21232.
3. Wang, Z. G.; Chen, T. L.; Xu, J. P. *Macromolecules* **2001**, *34*, 9015.
4. Li, F.; Liu, Y.; Qu, C. B.; Xiao, H. M.; Hua, Y.; Sui, G. X.; Fu, S. F. *Polymer* **2015**, *59*, 155.
5. Rao, V. L. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **1999**, *39*, 655.
6. Frechet, J. M. *Science* **1994**, *263*, 1710.
7. Xu, Y. Y.; Gao, C.; Kong, H.; Yan, D. Y.; Jin, Y. Z.; Watts, P. C. P. *Macromolecules* **2004**, *37*, 8846.
8. Wang, J. L.; Zhang, K. J.; Ye, Z. B. *Macromolecules* **2008**, *41*, 2290.
9. Matsumura, S.; Hlil, A. R.; Lepiller, C.; Gaudet, J.; Guay, D.; Shi, Z. Q.; Holdcroft, S.; Hay, A. S. *Macromolecules* **2008**, *41*, 281.
10. Miller, T. M.; Neenan, T. X.; Kwock, E. W.; Stein, S. M. *J. Am. Chem. Soc.* **1993**, *115*, 356.
11. Hawker, C. J.; Chu, F. K. *Macromolecules* **1996**, *29*, 4370.
12. Shu, C. F.; Leu, C. M. *Macromolecules* **1999**, *32*, 100.
13. Mu, J. X.; Zhang, C. L.; Chen, J.; Jiang, Z. H.; Kireev, V. V. *Polym. Sci. Ser. A* **2006**, *48*, 1035.
14. Wang, D.; Zhang, S. L.; Zhang, Y. H.; Wang, H.; Mu, J. X.; Wang, G. B.; Jiang, Z. H. *Dyes Pigments* **2008**, *79*, 217.
15. Li, X. J.; Zhang, S. L.; Wang, H.; Pang, J. H.; Sun, D.; Mu, J. X.; Wang, G. B.; Jiang, Z. H. *Polym. Int.* **2010**, *59*, 1360.
16. Kim, Y. H.; Webster, O. W. *Macromolecules* **1992**, *25*, 5561.
17. Li, X. J.; Zhang, S. L.; Wang, H.; Zhang, C. F.; Pang, J. H.; Mu, J. X.; Wang, G. B.; Jiang, Z. H. *Polym. Int.* **2011**, *60*, 607.
18. Hawker, C. J.; Lee, R.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.
19. Gao, C.; Yan, D. *Prog. Polym. Sci.* **2004**, *29*, 183.
20. Holter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30.