

Perfluoroalkyl-Terminated Star Polymer Electrolyte

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ABSTRACT: A perfluoroalkyl-terminated multiarm star polymer (perfluoroalkyl-terminated hyperbranched polyglycerol) was synthesized and characterized on the basis of perfluorooctanoyl chloride grafting on hyperbranched polyglycerol. The conductivity of a blend of the perfluoroalkyl-terminated star polymer and linear poly(ether urethane) was studied. The results indicated that this blend had better solvating capability in salt and higher ionic conductivity.

The conductivity of the blend was $2.5 \times 10^{-4} \text{ S cm}^{-1}$ at 60°C when the concentration of the perfluoroalkyl-terminated hyperbranched polyglycerol was 30 wt % and the ethylene oxide (EO)/Li ratio was 4 in the blend. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 238–242, 2005

Key words: star polymers; polymer electrolyte; conductivity

INTRODUCTION

Hyperbranched polymers are believed to have great applications in the field of solid polymer electrolytes^{1,2} because of their special advantages, such as their greater number of cavities, high solvating capability in salt, and low glass-transition temperatures (T_g 's). Among hyperbranched polymers, hyperbranched polyglycerol has segments similar to those of poly(propylene oxide), which dissolves salt easily; therefore, it is often used as a polymer electrolyte. In previous studies, hyperbranched polyglycerol and its sulfate were used as polymer electrolytes, and the results showed that hyperbranched polyglycerol has a higher capability to dissolve salt than a linear polymer with the same molar ratio of oxygen atoms to lithium ions.^{3–5} However, terminated hydroxyl groups are electrochemically unstable in hyperbranched polyglycerol used as a polymer electrolyte because the hydroxyl groups can be oxidized or deoxidized when it is charged or discharged in an electric field.

To effectively improve the electrochemical stability of hyperbranched polyglycerol, other compounds are used to react with the terminated hydroxyl groups to form terminated ether or ester groups, which are electrochemically stable in an electric field. In this study, perfluorooctanoyl chloride was used to esterify hyperbranched polyglycerol and produce hyperbranched polyglycerol perfluorooctyrate. This kind of polymer possesses the properties of a hyperbranched polymer but much fewer terminated hydroxyl groups or higher electrochemical stability. On the other hand, the fluo-

rine elements can improve not only its electrochemical and thermal stability but also ionic transfers in hyperbranched polyglycerol perfluorooctyrate. These factors increase the conductivity of the polymer electrolyte. To improve the electrolyte film's dimensional stability, part of linear polyurethane (LPU) is used because the dimensional stability of the hyperbranched polymer film is not good. The polymer electrolyte consists of hyperbranched polyglycerol perfluorooctyrate, LPU, and LiClO_4 .

EXPERIMENTAL

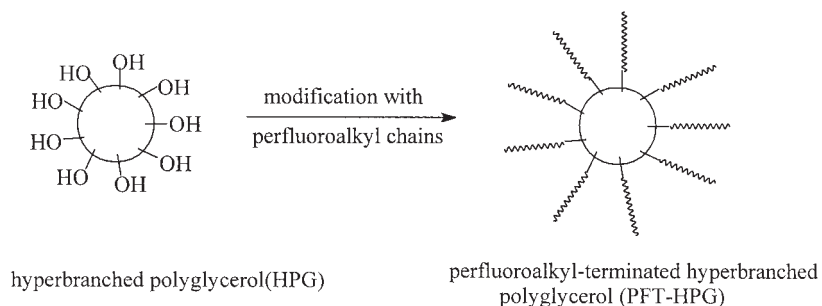
Materials

N,N-Dimethylformamide (DMF) and pyridine from Shanghai Chemical Reagent Co. (Shanghai, China) were dried via refluxing over CaH_2 for 4 h under nitrogen and then were distilled *in vacuo*. Glycidol from Acros (Geel, Belgium) and perfluorooctanoic acid from Shanghai 3F New Materials Co. (Shanghai, China) were used without purification. Perfluorooctanoyl chloride was prepared by the reaction of perfluorooctanoic acid and SOCl_2 . LPU was synthesized from 4,4'-diphenylmethane diisocyanate (MDI), 1,4-butanediol (BD), and poly(ethylene oxide) (PEO; number-average molecular weight = 1000). The MDI/BD/PEO molar ratio was 3:2:1. Hyperbranched polyglycerol was synthesized as described previously.⁵

Synthesis of perfluoroalkyl-terminated hyperbranched polyglycerol (PFT-HPG)

In a typical approach, 2.4 mL of perfluorooctanoyl chloride was dropwise added to a solution of 1.5 g of polyglycerol dissolved in 50 mL of anhydrous pyri-

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Scheme 1 Synthesis route of the star polymer.

dine under nitrogen, and then the mixture was heated to 60°C and refluxed for 3 h. In the solution, a deposit appeared. After cooling to room temperature, the mixture was filtered, and the deposit was washed with deionized water three times and dried *in vacuo* at 100°C for 24 h (Scheme 1). A total of 3.9 g of waxy, solid perfluoroalkyl-terminated polyglycerol was obtained, and the yield was 76.3%. The results of an elemental analysis showed that in the polyglycerol about 80% of the hydroxy groups reacted with perfluorooctanoyl chloride.

Preparation of the polymer electrolyte film (PFT-HPG/LPU/Li)

The appropriate amounts of PFT-HPG, LPU, and LiClO₄ were dissolved in DMF, and then the solution was cast onto a Teflon plate. A film formed in an oven at 60°C and was dried in a vacuum oven at 70°C for 48 h.

Instruments

¹H-NMR and ¹⁹F-NMR measurements were carried out on a Bruker 500-MHz NMR spectrometer (Buben-

dorf, Switzerland) with dimethyl sulfoxide-*d*₆ (DMSO-*d*₆) as a solvent. The molecular weight was measured by gel permeation chromatography (GPC) with DMF as a solvent. FTIR spectroscopy and Raman spectroscopy were performed with a Bruker Equinox 55 spectrometer and a BrukerFRA106 spectrometer, respectively (Bruker, Billerica, MA). Differential scanning calorimetry (DSC) studies were conducted under nitrogen with a PE Pyris-1 DSC thermal analyzer (Boston, MA). All samples were heated at a heating rate of 20°C/min from -50 to 100°C. The ionic conductivities of the samples were measured with a Hewlett-Packard HP 4192A LF impedance analyzer (Mt. Palomar, CA). The frequency was varied from 0.1 Hz to 10 MHz. The bulk electrolyte resistance was determined from the width of the high-frequency semicircle in the Cole-Cole plots, and the measurements were taken in a dehumidified room to keep moisture out of the system.

RESULTS AND DISCUSSION

Characterization of PFT-HPG

¹H-NMR spectra show that the number of hydroxyl groups decreased after the esterification reaction be-

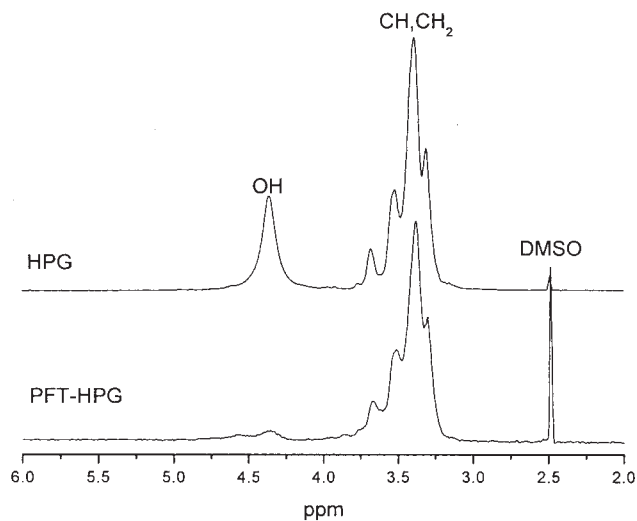


Figure 1 ¹H-NMR spectra of hyperbranched polyglycerol (HPG) and PFT-HPG.

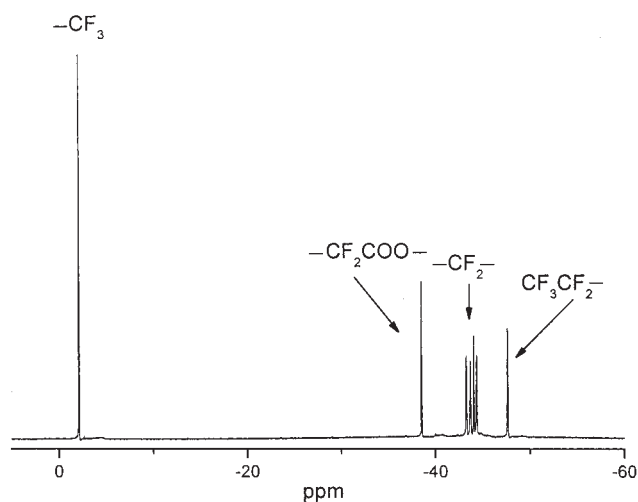


Figure 2 ¹⁹F-NMR spectrum of PFT-HPG.

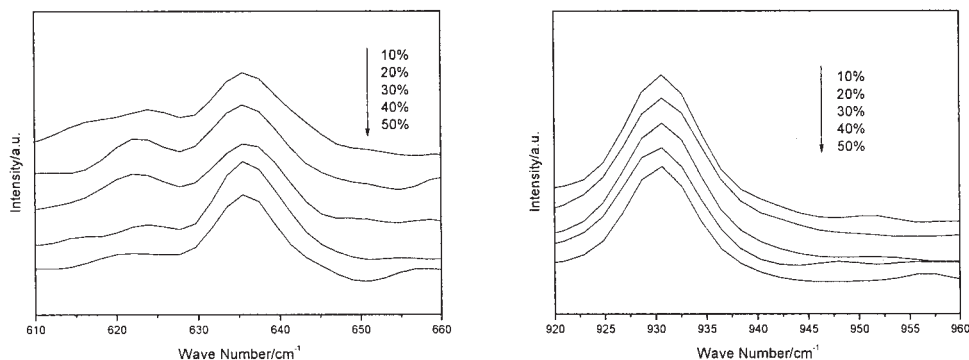


Figure 3 Raman spectra of films at different star polymer concentrations.

cause the hydroxyl groups reacted with perfluorooctanoyl chloride (Fig. 1). There were two kinds of hydroxyl groups in the hyperbranched polyglycerol: outer and inner hydroxyl groups located on the surface and core of the spherical hyperbranched polyglycerol molecule, respectively. In the esterification reaction, the outer hydroxyl groups reacted much more easily with perfluorooctanoyl chloride than inner hydroxyl groups because the inner hydroxyl groups were concealed in the core, and this resulted in lower activity. In the $^1\text{H-NMR}$ spectrum, the peak of the hydroxyl groups (ca. 4.3 ppm) is small and broad because the inner hydroxyl groups easily formed hydrogen bonds in the molecular core. In the $^{19}\text{F-NMR}$ spectrum, various peaks of the fluorine element can be detected at -2.16 (CF_3) and -38.56 (CF_2COO) in $\text{DMSO-}d_6$, and this indicates that the perfluoroalkyl chain was successfully grafted onto polyglycerol (Fig. 2). Its molecular weight and polydispersity, measured by GPC, were about 2.5×10^4 and 1.8, respectively.

Analysis of the polymer electrolyte

Raman spectroscopy analysis

Raman spectroscopy was used to investigate the ion-ion interactions. In Figure 3, the band between 610 and 660 cm^{-1} is associated with the anion bond mode,

which can be separated into two contributions. The lower frequency component can be attributed to free perchlorate anions, and the higher frequency component can be assigned to ion pairs. The ratio of free anions increased with an increase in PFT-HPG and reached a maximum when the concentration was 30%. On the other hand, the band between 920 and 960 cm^{-1} is associated with the anion symmetric stretching mode. In this band, a free perchlorate anion peak (931 cm^{-1}) can be found, but ion pairs (938 cm^{-1}), ionic aggregations (945 cm^{-1}), and salt crystals (957 cm^{-1}) cannot be found. These results indicate that the perchlorate anions were almost like free ions in the polymer electrolyte and enhanced the conductivity.

FTIR spectroscopy analysis

FTIR spectroscopy was employed to study the interaction behavior between the ion and the polymer host. A Gaussian function was used to deal with the different peaks and to study the relative intensity of the coordination between $\text{C}=\text{O}$ or $\text{C}-\text{O}-\text{C}$ and lithium ions, as previously reported.⁶⁻⁸ Figure 4 illustrates that the intensity of the coordination increased with the increase in PFT-HPG and was maximum at a concentration of 30%; this means more salt dissolved in the polymer matrix. It was helpful for the polymer

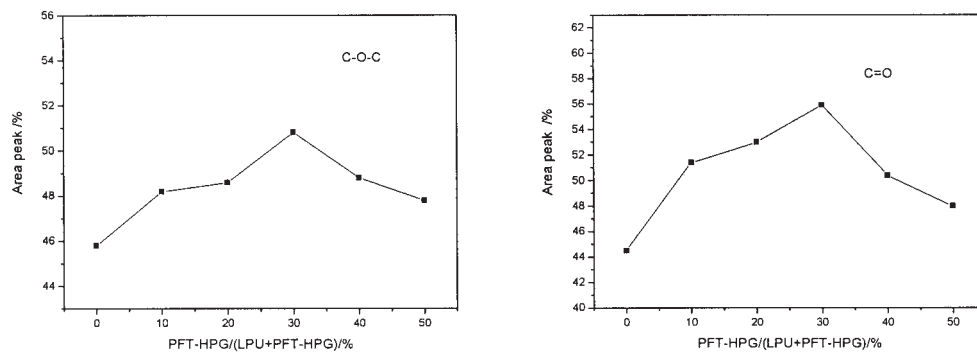


Figure 4 Star polymer concentration dependence of the relative intensity of coordinative $\text{C}-\text{O}-\text{C}$ and $\text{C}=\text{O}$ bands.

TABLE I
 T_g at Star Polymer Different Concentrations

Film	12-0%	12-10%	12-20%	12-30%	12-40%	12-50%
T_g (°C)	3.1	-0.2	-19.2	-23.7	-23.1	-17.2

electrolyte to increase the salt solubility when PFT-HPG was mixed in the matrix. The results agree with the Raman spectral analysis.

DSC

Table I shows that T_g decreased with an increase in PFT-HPG, especially at a 20% concentration of the perfluoroalkyl-terminated star polymer. However, T_g was not influenced by PFT-HPG when the concentration of PFT-HPG was greater than 30%. It is possible that the star polymer acted as a plasticizer, and this resulted in a decrease in T_g when the PFT-HPG content was lower; however, the compatibility of the polymer electrolyte was bad, so PFT-HPG did not act effectively as a plasticizer when the PFT-HPG content was greater than 30%.

Scanning electron microscopy (SEM)

SEM pictures show that the compatibility of the polymer electrolyte was improved with an increase in the star polymer and was best at a 30% concentration of PFT-HPG (Fig. 5). However, the compatibility of the polymer electrolyte was not good when the concentration of PFT-HPG exceeded 30%, and obvious phase separation could be observed at a 40% concentration of PFT-HPG. The results illustrate that a suitable con-

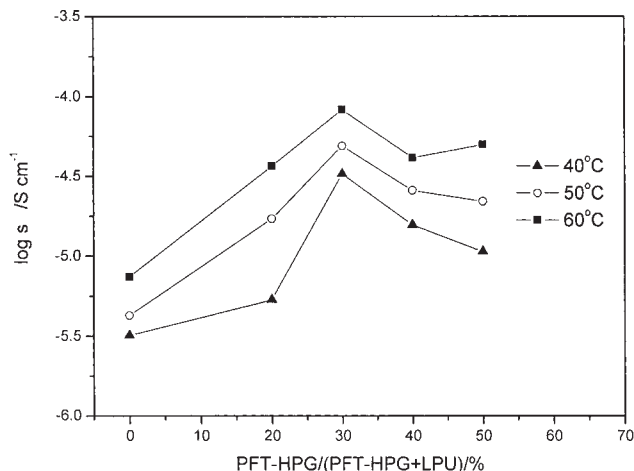


Figure 6 Star polymer concentration dependence of the conductivity (s).

centration of the star polymer facilitated salt dissolution in the blend, but more star polymer resulted in worse compatibility between PFT-HPG and LPU and decreased the ionic conductivity.

Conductivity measurements

Generally, the conductivity increased with increasing temperature because ionic transfer was easier.^{9,10} Figure 6 shows that the star polymer concentration affected the conductivity at 40, 50, and 60°C. At room temperature (25°C), the conductivity was $1.8 \times 10^{-5} \text{ S cm}^{-1}$. The ionic conductivity was maximum when the concentration of the star polymer was 30%, and the optimum conductivity at 60°C was $2.5 \times 10^{-4} \text{ S cm}^{-1}$.

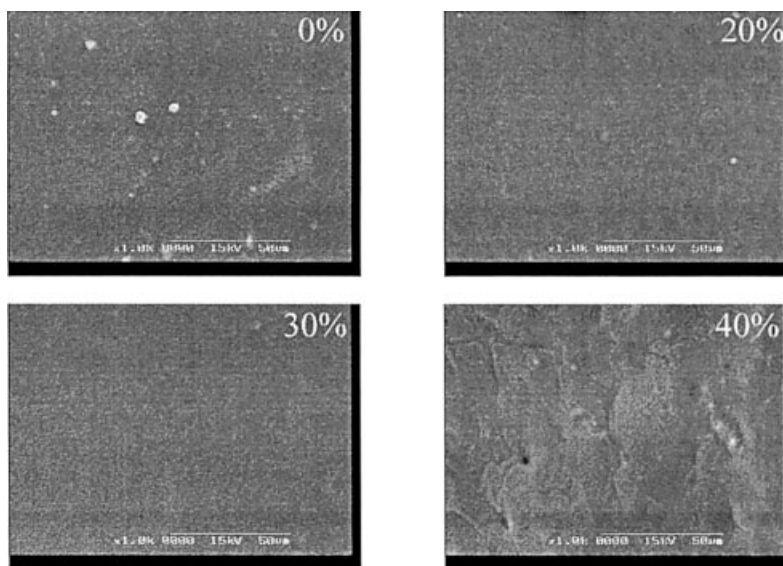


Figure 5 SEM pictures at different star polymer concentrations.

when the EO/Li molar ratio was 4. This result is in agreement with the previous results.

CONCLUSIONS

A perfluoroalkyl-terminated star polymer was prepared, characterized, and used as a part of solid polymer electrolytes. PFT-HPG in the polymer electrolyte improved the solubility of salt, enhanced the ionic transfer ability by decreased entanglement of polymer chains, and resulted in higher ionic conductivity. When the concentration of PFT-HPG was 30% and the EO/Li molar ratio was 4, the polymer electrolyte showed the maximum solubility of salt and conductivity, and the optimum conductivity at 60°C was $2.5 \times 10^{-4} \text{ S cm}^{-1}$. However, the conductivity decreased

because phase separation occurred, and a loss of properties was observed when the concentration of PFT-HPG was up to 30%.

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