

プロトン導電性芳香族系高分子膜の開発と高分子電解質型燃料電池への応用

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Introduction

Recently polymeric electrolyte fuel cells (PEFC) have attracted great attention as an alternative clean energy source. The key component of PEFC is the polyelectrolyte membrane which serves as proton transport carrier. Nafion, a typical perfluorinated polymer, has been widely used as the polyelectrolyte membrane material due to its high proton conductivity and long term-stability. Unfortunately, however, there are some serious limitations for using this material. These include (1) high cost, (2) low conductivity at low humidity or high temperatures, (3) high methanol permeability. Thus, development of alternative materials without these disadvantages and meanwhile having proton conductivity comparable or higher than that of Nafion is greatly desired. On the other hand, aromatic polyimides, known for their excellent thermal and mechanical properties, have found wide applications in many important industrial fields. A series of sulfonic acid group-containing polyimides (Fig. 1) with fairly high proton conductivity have been developed in our laboratory, and the work will be reported elsewhere.

This presentation will focus on report on synthesis of various star polymers (schematic structure shown in Fig. 2), a class of branched macromolecules which typically consist of a number of linear polymer arms attached to a central core. The unique three-dimensional architecture allows star polymers to have different (improved) physical and mechanical properties from their linear analogues. The core materials are usually multifunctional organic compounds or functional group-terminated spherical oligomers, whereas the linear arms may be mono- or difunctional oligomers. The number of arms of a star macromolecule is dependent on the functionality of the core material. Hyperbranched polymers are globular macromolecules and have a large number of terminal functional groups, which make themselves an ideal class of core materials.

Experimental

The core materials, amine- or anhydride-terminated hyperbranched polyimides, were prepared by condensation polymerization of dianhydride (2,2-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydrides (6FDA) and 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride (DSDA)) and triamine (tris(4-aminophenyl)amine (TAPA)) monomers according to our previously reported method. Anhydride end-capped polyamic acid linear oligomers were prepared by adding diamine to excess amount of dianhydride solution in DMAc or 1-methylpyrrolidone (NMP). The glassy star polyimides were prepared by slowly adding amine-terminated 6FDA-TAPA hyperbranched polyimide or DSDA-TAPA hyperbranched polyamic acid solution in N,N-dimethylacetamide (DMAc) to the as-synthesized linear anhydride end-capped polyamic acid oligomer solutions followed by chemical or thermal imidization. The rubbery star polymers were synthesized by reacting anhydride-terminated 6FDA-TAPA polyimide and poly(ethylene glycol) mono-methyl ether ($M_n = 5000$) or amine end-capped poly(ethylene oxide) oligomer ($M_n = 2000$).

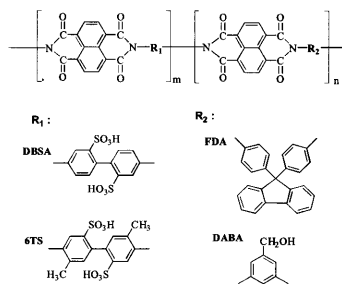


Fig. 1 Sulfonated polyimides

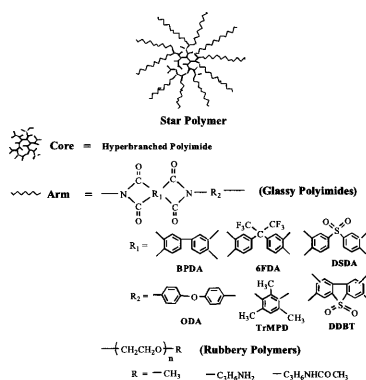


Fig. 2 Schematic structure of various star polymers

Results and discussion

The core materials, hyperbranched polyimides, were synthesized from A2 (dianhydride) + B3(TAPA) monomers. The terminal functional groups (amine- or anhydride) of hyperbranched polyimides are determined to both monomer addition order and monomer molar ratio. When a dianhydride solution was slowly added to the TAPA solution with the monomer molar ratio of 1/1, an amine-terminated hyperbranched polyimide was obtained, whereas the reverse monomer addition order with molar ratio of 2/1 (dianhydride/TAPA) yielded an anhydride-terminated hyperbranched polyimide.

Two types of star polymers were prepared: glassy polymers (fully aromatic polyimides), and rubbery ones. The synthesis of star polyimides is based on the chemical reaction between the terminal amine groups of hyperbranched polyimides and the end anhydride groups of linear polyamic acid oligomers. Hyperbranched polyimide solutions should be slowly added to the linear oligomer solutions. Reactant concentration had great effect on the reaction. Too high concentration caused insoluble gel, whereas too low concentration resulted in no significant reaction. The control of the length of arms was achieved by changing the molar ratio between dianhydrides and diamine

monomers employed for the preparation of the linear polyamic acid oligomers. Similarly, in the case of preparing the rubbery star polymer, the core (anhydride terminated hyperbranched polyimide) solution should also be slowly added to the amine end-capped poly(ethylene oxide) oligomer to avoid gelation. In contrast, there is no such risk when poly(ethylene glycol) mono-methyl ether was used as the arm oligomer because it is mono-functional-group (hydroxy) end-capped.

The resulting star polyimides showed higher inherent viscosity than the corresponding linear oligomers but were soluble in organic solvents, indicating that no crosslinking sites exist in these polymers. In comparison with the corresponding linear polyimides, star polyimides showed significantly enhanced film mechanical strength. BPDA-TrMPD/6FDA-TAPA star polyimide, for example, had a tensile strength at break of 102 MPa, which is larger than that of BPDA-TrMPD linear polyimide (81 MPa). This is also true for the rubbery star polymers, which can form tough films whereas the linear oligomers cannot form films due to their low molecular weight and high crystallinity. Gel permeation chromatography (GPC) measurements revealed that both the glassy and rubbery star polymers displayed broader molecular distribution than the corresponding oligomers. In addition, star polyimides generally showed somewhat lower gas permeation and a little higher ideal selectivity than the corresponding linear ones due to the more compact structure of the former.

Publications

- Jianhua Fang, Hidetoshi Kita, Ken-ichi Okamoto: Synthesis and Properties of Star Polyimides Using a Hyperbranched Polyimide as the Central Core; Polymer Preprints, Japan, p374, 2000. 49. 2.
- Jianhua Fang, Hongyuan Wang, Kazuhiro Tanaka, Hidetoshi Kita, Ken-ichi Okamoto: Synthesis and Properties of Microphase-Separated Star Polymers Using a Hyperbranched Polyimide as the Central Core; Polymer Preprints, Japan, p375, 2000. 49. 2.
- Jianhua Fang, Hidetoshi Kita, Ken-ichi Okamoto: Synthesis and Properties of Star Polyimides Using Hyperbranched Polyimides as the Central Core; 2000 International Chemical Congress of Pacific Basin Societies, Section 7: Macromolecular Chemistry, p727, 2000.

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