

새로운 Hyperbranched Polyimides and Polyamides: 합성, 말단기 변형, 경화 연구, 그리고 물리적 성질

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New Hyperbranched Polyimides and Polyamides: Synthesis, Chain-End Functionalizations, Curing Studies, and Some Physical Properties

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Key Words: Hyperbranched Polymers, Polyimides, Polyamides, Curing, Rheology, Physical Properties

ABSTRACT

While aromatic polyimides and polyamides have found widespread use as high performance polymers, the present work addressed the need for organosoluble materials through the use of a hyperbranching scheme. The AB₂ monomers were prepared. The AB₂ monomers were then polymerized via aromatic fluoride-displacement and Yamazaki reactions to afford the corresponding hydroxyl-terminated hyperbranched polyimides (**HT-PAEKI**) and amine-terminated hyperbranched polyamides, respectively. **HT-PAEKI** was then functionalized with allyl and propargyl bromides as well as epichlorohydrin to afford allyl-terminated **AT-PAEKI**, propargyl-terminated **PT-PAEKI**, and epoxy (glycidyl)-terminated **ET-PAEKI**, in that order. All hyperbranched poly(ether-ketone-imide)s were soluble in common organic solvents. **AT-PAEKI** was blended with a bisphenol-A-based bismaleimide (**BPA-BMI**) in various weight ratios. Thermal, rheological, and mechanical properties of these blend systems were evaluated. Two characteristic hyperbranched polyamides, which the one has para-electron donating groups to the surface amine groups and the other has para-electron withdrawing groups to the surface amine groups, were selected to compare BMI curing behaviors. The electron rich polymer displayed ordinary Michael addition type exothermic reaction, while electron deficient polymer did display unusual curing behaviors. Based on analytical data, the later system provided the strong evidences to support room temperature curing of BMI by reactive intermediates instead of reactive primary amine groups on the macromolecule surface.

1. Introduction

Hyperbranched polymers have received considerable attention over the past decade due to their unusual properties such as large numbers of end groups, low melt and solution viscosities, and three-dimensional structures.

Aromatic polyimides (PIs) and aromatic polyamides (PAs) are well-known, high-performance materials with widespread applications in the aerospace and electronics industries due to their excellent thermomechanical and dielectric properties.¹

This paper describes the application of high performance hyperbranched polymers to utilize the combined characteristics of hyperbranched polymers and

high performance polymers. Recently, Manson et al.² have demonstrated the usefulness of an epoxy-modified hyperbranched aliphatic polyester to improve the critical energy release rate (G_{IC}) of carbon fiber/epoxy composite from 1400 to 2500 J m⁻². However, the use temperature of aliphatic polymers as additives to high temperature resins is questionable. There have been only few reports on both synthesis of high performance hyperbranched polymers³ and their utilization.⁴

We are interested in developing the potential of functionalized hyperbranched polymers as property enhancers for high temperature thermosets, e.g. bismaleimide (BMI) resin, and particularly, the toughening aspect without compromising the thermal and thermomechanical properties of BMI.

Thus, an objective of this research was to synthesize self-polymerizable AB₂ monomers and functionalize the resulting hyperbranched polymer with reactive chain ends. Such reactive hyperbranched polymers may be useful as toughening additives for high-temperature thermosets.

2. Experimental

2.1 Monomer synthesis

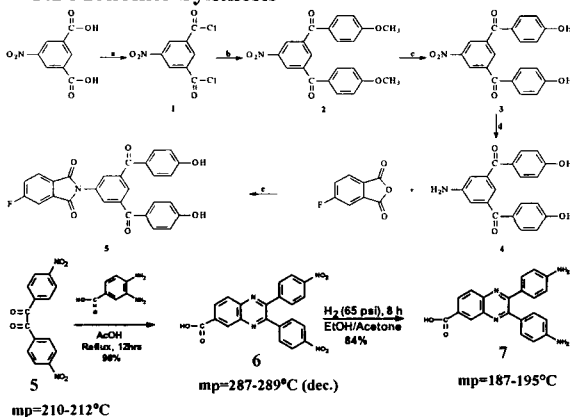
The AB₂ monomers were synthesized according to Scheme 1 and the identity and purity were ascertained by conventional organic characterization prior to polymerization experiments, including FT-IR, NMR, HPLC, elemental analysis, and mass analysis. Polymerizations carried as described in literature.

2.2 Solution Blending of Hyperbranched Polymers with BMI

Basically, hyperbranched polymers were soluble in molten BMI. However, the stock solutions of hyperbranched polymers were first prepared in DMAc and then added to the vials containing predetermined amounts of BMI so as to minimize experimental error. Each vial was then diluted with additional solvent until the mixture became homogeneous. The solvent was then removed under reduced pressure at 70-80 °C for 72h prior to analysis.

3. Results and Discussion

3.1 Monomer Synthesis



Scheme 1

Experimental details are described in the literature.^{3,9}

3.2 Polymerization

To prepare hyperbranched polyimide, the AB₂ monomer **5** was self-polymerized in an NMP/toluene mixture in the presence of potassium carbonate to afford the hydroxyl-terminated hyperbranched poly(aryl-ether-ketone-imide) (HT-PAEKI) after acidic work-up. Different functional groups such as allyl-, propargyl-, and epoxy- were introduced onto HT-PAEKI by corresponding reactions.

Hyperbranched polyamides were prepared by using direct polycondensation via Yamazaki reaction with AB₂ monomers was conducted following literature procedure.^{3,5}

3.3 Mechanical Properties

Allyl-terminated hyperbranched poly(aryl-ether-ketone-imide) (AT-PAEKI) and BPA-BMI were solution blended and evaluated that hyperbranched polymer might be useful as additives for high-temperature thermosets. For example, AT-PAEKI played excellent additive to BPA-BMI without compromising thermal, rheological, and mechanical properties.⁴

Based on evaluation results of AT-PAEKI, hyperbranched polymer could be the best additive to the high temperature resins. For the coating application, a system certainly would be ideal when hyperbranched polymer can initiate curing reaction at low temperature (ambient temperature). Fortunately, the system has been found and the results are to be mainly discussed.

4. Summary

Various high performance hyperbranched polymers were synthesized and evaluated as additive to high temperature resin. Based on evaluation results, it can be concluded that hyperbranched polymers are excellent candidate for the resins.

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