

Linear and Hyperbranched Polymers via Electrophilic Substitution Reaction in Polyphosphoric Acid/P₂O₅

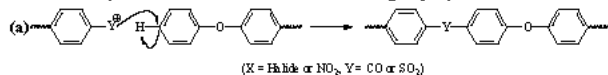
Ja-Young Choi,¹ In-Yeop Jeon,¹ Loon-Seng Tan,² Jong-Beom Baek^{*1}

¹School of Chemical Engineering, Chungbuk National University, Cheongju, Chungbuk, 361-763 Korea

²Polymer Branch, Materials & Manufacturing Directorate, AFRL/MLBP, Air Force Research Laboratory, WPAFB, Ohio, 45433-7750 USA
jbaek@chungbuk.ac.kr

Introduction

Aromatic polyetherketones (PEK's) and polyethersulfones (PES's) are a unique class of high-performance engineering polymers because of their excellent thermal and mechanical properties.¹ Both aromatic electrophilic substitution (Friedel-Crafts acylation reaction) and aromatic nucleophilic substitution reactions are versatile methods to synthesize PEK's and PES's (Scheme 1). The latter base-promoted polymer-forming reaction is preferred route because of the availability of monomers, non-corrosive reactive reaction media, and easiness of synthesis. In some cases, however, it fails to yield high-molecular weight polymers due to the position of substituent on aromatic ring and the solubility of resultant polymer, especially in the case of semi-crystalline material.^{2,3} Even worse, acid-promoted polymer-forming aromatic electrophilic substitution reaction were unsuccessful in producing high molecular weight polymers because of the limited solubility of growing polymer chains in chlorinated solvents such as dichloromethane,⁴ the utilization of superacid systems such as boron trifluoride in anhydrous hydrofluoric acid was able to afford high molecular weight polymers.^{5,6} The key to achieving high molecular weight polymer via electrophilic substitution even in the case of semi-crystalline material is by protonation of carbonyl or sulfonyl groups.⁷ As a result, the solvation by strong acid makes it possible to retain polymer in solution even at low temperatures, preventing premature precipitation. Unfortunately, the superacid systems are relatively expensive as well as hazardous to handle because of their volatility, corrosiveness, and toxicity. Thus, the uses of these systems are limited and only for lab-scale preparation. Furthermore, most of these systems can still only afford moderate molecular weight polymers.

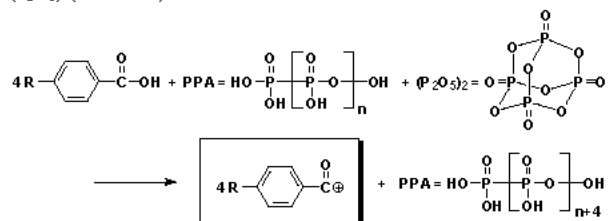


(X = H, alk or NO₂, Y = CO or SO₂)



Scheme 1. Synthetic routes to PEK's and PES's: (a) nucleophilic substitution reaction; (b) electrophilic substitution reaction

We would like to report a superior polycondensation medium that is non-toxic, relatively less corrosive, and non-volatile electrophilic substitution reaction to afford high molecular weight linear and hyperbranched PEK's. It is polyphosphoric acid (PPA) modified with proper amount of additional phosphorous pentoxide (P₂O₅) (Scheme 2).^{8,9}



Scheme 2. The reaction aromatic benzoic acid in polyphosphoric acid and phosphorous pentoxide medium

The system has very strong driving force to give extra ordinary high molecular weight linear¹⁰ and hyperbranched PEK's,¹¹ rigid coil-rigid rod-rigid coil ABA triblock copolymers¹² dumbbell-shaped ABA triblock copolymers,¹³ and covalently grafted polymers onto carbon nanotube (CNT) or carbon nanofiber (CNF).^{14,15,16} More interestingly, the reaction medium is highly viscous and thus resultant

PEK's display unusual morphology.¹⁷ The reaction medium is hydrophilic and displays selective solubility to the monomers. By using this characteristic nature, hyperbranched PEK's could be synthesized from commercially available A₃ + B₂ monomers without network formation.^{18,19}

Experimental

Materials. Monomers, 3-phenoxybenzoic acid, 4-phenoxybenzoic acid, trimesic acid, 1, 4-diphenoxybenzene, and diphenyl ether, were obtained from Aldrich Co. LTD. The reaction medium, polyphosphoric acid (PPA, ~83%) and phosphorous pentoxide (P₂O₅) were also purchased from Aldrich Co. LTD. The monomers were recrystallized from proper solvents to have >99.9% purity. All linear and hyperbranched PEK's via electrophilic substitution reactions were synthesized in PPA/P₂O₅ as reported.¹⁰

Results and discussion

Polymerizations. Following the first time reported optimized procedure,¹⁰ all polycondensations of monomers were conducted at 130°C in commercial grade PPA (83% assay) with the additional 25 wt% of P₂O₅ to afford corresponding polymers in 5 wt% monomer concentrations, which are relative to the amount of PPA used.¹⁰ Interesting characteristic color and phase changes were monitored as functions of time and temperature for all systems.

As an approach to impart covalent adhesion between a thermoplastic matrix and reinforcing CNT or CNF, we also investigated the possibility of functionalizing CNT or CNF with an acylium precursor in PPA/P₂O₅ and *in-situ* polymerization of PEK with various amount of CNT or CNF. The results on the synthesis and characterization of the linear or hyperbranched PEK grafted CNT or CNF nanocomposites are to be presented.

Conclusions

This work was focus on facile synthesis of high performance linear and hyperbranched PEK's in newly developed a mild but less corrosive reaction medium PPA/P₂O₅. The reaction condition was utilized in various synthetic approach and further extended it to the functionalization of carbon nanomaterials such as CNT and CNF for the application on specific purpose.

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