Linear and Hyperbranched Polymers via Electrophilic Substitution Reaction in Polyphosphoric Acid/PtO₃

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Introduction

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

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

We would like to report a superior polycondensation medium that is non-toxic, relatively less corrosive, and non-retard electrophilic substitution reaction to afford high molecular weight linear and hyperbranched PEK's. It is polyphosphoric acid and (PPA) modified with proper amount of additional phosphorous pentoxide (PtO₃) (Scheme 2).}

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 linear and hyperbranched PEK's, rigid capped rod and coil ABA, triblock copolymers, dumbbell-shaped ABA triblock copolymers, and readily graft copolymers onto carbon nanotube (CNT) or carbon nanofiber (CNF). More interestingly, the reaction medium is highly viscous and thus resultant PEK's display unusual morphology. The reaction medium is hydrophilic and displays reactive solubility to the monomers. By using this characteristic nature, hyperbranched PEK's could be synthesized from commercially available A₃ + Bₚ monomers without network formation.

Experimental

Materials. Monomers, 3-phenylphenolic acid, 4-phenylphenolic acid, trinitro anil, 4-diphenyloxazene, and diphenyl ether, were obtained from Aldrich Co. Ltd. The reaction medium, polyphosphoric acid (PPA, ~93%) and phosphorous pentoxide (PtO₃) were also purchased from Aldrich Co. Ltd. The monomers were re crystallized from proper solvents to have >99.9% purity. Linear and hyperbranched PEK's via electrophilic substitution reactions were synthesized in PPA/PtO₃ as reported.

Results and discussion

Polymerizations. Following the first time reported optimised procedure, all polycondensation of monomers were conducted at 130°C in commercial grade PPA (99.9% purity) with the addition of 25 wt% of PtO₃ to afford corresponding polymers in 5-40% monomer conversions, which are relatively to the amount of PPA used. Interestingly characteristic color and phase changes were monitored as functions of time and temperature for all systems.

As an approach to impact solvent adhesion between a thermoplastic matrix and reinforcing CNT or CNF, we also investigated the possibility of functionalization of CNT or CNF with an acylating precursor in PPA/PtO₃ 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 focused on facile synthesis of high performance linear and hyperbranched PEK's in newly developed mild but less corrosive reaction medium PPA/PtO₃. 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 specific purpose.

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References