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Synthesis of cyclic precursors of poly(ether ether ketone)

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Summary

A novel synthetic route to cyclic PEEK precursors is described. These new cyclic oligomers have been prepared from hydroquinone and N-phenyl(4,4'-difluorodiphenyl) ketimine. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) analysis unambiguously confirmed the cyclic nature.

Introduction

Poly(ether ether ketone)(PEEK) is an important commercial thermoplastics with excellent environmental resistance and good mechanical properties. Due to its semicrystalline structure, the commercial PEEK is prepared through the aromatic nucleophilic substitution reaction of 4,4'-difluorobenzophenone with hydroquinone at very high temperature near its melting point in order to avoid premature crystallization and precipitation. The reaction condition is severe and PEEK dissolves only in some concentrated acids at room temperature. In order to facilitate the synthesis and processing, removable bulky substituents such as tert-butyl[1)], ketal[2)] or Ketimine[3-5)] were introduced to synthesize amorphous PEEK prepolymers. These PEEK prepolymers are soluble in the common polar aprotic solvents like dimethyl sulfoxide, N,N-dimethylformamide and tetrahydrofunan and can be readily transformed to semicrystalline polymer by removal of the substituents.

Our interest is to utilize PEEK in the fabrication of long or continuous fibre reinforced thermoplastic composites. Recently, the use of aromatic macrocyclic oligomers as intermediates for the preparation of high performance thermoplastics has attracted considerable attention since the pioneering work of Brunelle et al. on cyclic carbonates[6)]. The macrocyclics offer a significant advantage over their linear high molecular weight counterparts due to their low melt viscosity and the possibility of undergoing controlled polymerization in the melt without the release of volatile byproducts. The *in situ* transformation of macrocyclic oligomers via ring - opening polymerization to high molecular weight polymers makes them potentially applicable in the area of advanced thermoplastic composites. Up to now, this field has been rapidly extended to cyclic ester[7-9)], cyclic amide[10)], cyclic ether imide[11)], cyclic ether ketone(sulfone)[12-14)] and cyclic thioether[15,16)] system.

However, as to the PEEK, the most widely used material, no one-step procedure for

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synthesis of cyclic precursors from hydroquinone and difluorobenzophenone has been available because of molecular configuration of the conventional monomers. Chen and Gibson et al. have reported the synthesis of macrocyclic precursors of PEEK through a multi-step procedure[17,18]. In the method, long-chain aromatic bisphenols and difluro ketone compound were firstly prepared and then to synthesize large-size cyclic precursors(n = 3, 4, 6, 8). The aim of this paper is to describe a different approach to the synthesis of relatively small-size cyclic precursors of PEEK in which ketimine group was introduced to 4,4'-difluorobenzophenone to increase molecular flexibility of the dihalide and thus provide a strategy for preparation of PEEK cyclic oligomers. In this paper, we disclose the synthesis and characterization of cyclic ether ether ketimine and cyclic ether ether ketone.

Experimental part

Preparation of N - phenyl(4,4' - difluorodiphenyl) ketimine

In a three-necked round bottom flask equipped with a Dean-Stark trap, a condenser, a nitrogen inlet and a thermometer, 21.8 g (0.1 mol) 4,4'-difluorobenzophenone, 13.6 ml aniline (0.15 mol) and 0.08 g *p*-toluenesulfonic acid were dissolved in 120 ml toluene. The mixture was heated to reflux under magnetic stirring over 30 h. The toluene and excess aniline were then removed under reduced pressure. The ketimine product was recrystallized three times from toluene to give 19.0 g (65% yield) yellow crystalline solid with a melting point of 113-115 °C. MALDI - TOF MS (2,5 - dihydroxybenzoic acid as matrix): m/z = 293 Da. ^{1}H NMR (DMSO - d_6): δ = 7.823(2H, dd, J = 8.4, 6.4 Hz); 7.421 (2H, t, J = 8.8 Hz); 7.294 (6H, m); 7.022 (1H, t, J = 7.8 Hz); 6.800 (2H, d, J = 7.8 Hz)ppm.

Synthesis of cyclic ether ether ketimine oligomers

The cyclization reaction was conducted in a 500 ml round - bottom flask which was fitted with a nitrogen inlet, thermometer, Dean-Stark trap and condenser. The flask was charged with 300 ml of DMF, 40 ml of toluene and 4.0 g anhydrous potassium carbonate. The solution was mechanically stirred vigorously and heated to reflux. The temperature range was 146 - 150 °C. A solution of N - phenyl(4,4' - difluorodiphenyl) ketimine 2.198 g(7.5 mmol) and hydroquinone 0.825 g(7.5 mmol) in 50 ml of DMF was added into the flask over 8 h. After addition, the resulting solution was stirred for another 8 h to ensure complete reaction and then cooled and filtered to remove the salt. The solvent was then evaporated under reduced pressure to 20 ml and then added into distilled water. The precipitate was filtered and dried in a vacuum oven (70 øC). The yield was 2.8 g(93%).

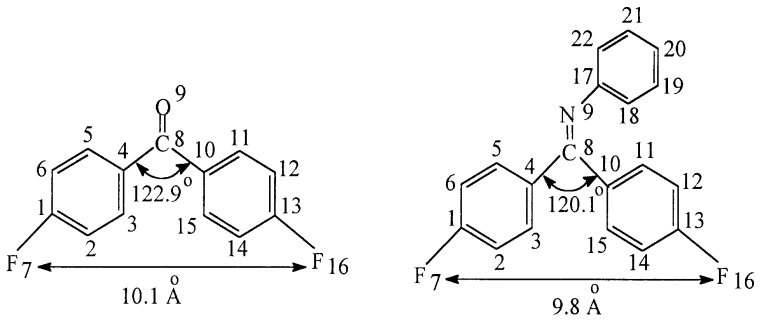
Synthesis of cyclic ether ether ketone oligomers

The cyclic ether ether ketimine oligomers 1.5 g was dissolved in 20 ml THF, and 5.0 ml HCl was added into the solution. After stirring for 5 h, the solution was filtered to remove linear product. and then poured into 30 ml methnol. The precipitate was filtered and dried in a vacuum oven (70 °C). The yield was 0.4 g(34%). ^{1}H NMR ($CDCl_3$): δ = 7.816(4H, m); 7.162(4H, m); 7.075(4H, m)ppm.

Results and discussion

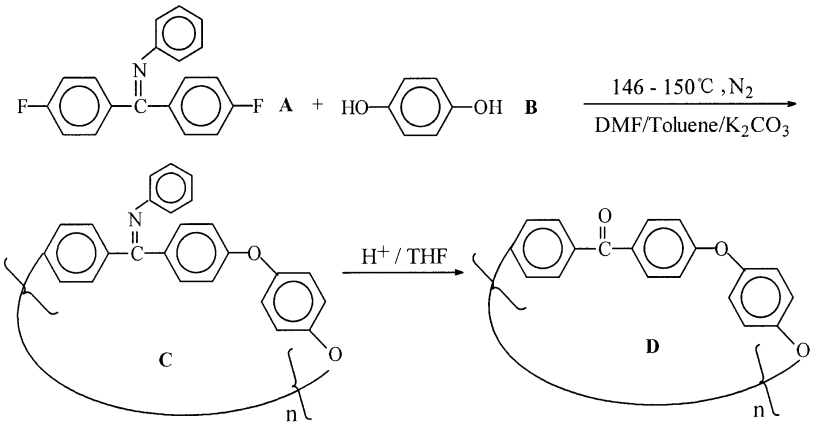
Synthesis of macrocyclic oligomers is very complicated by the formation of linear

oligomers and high molecular weight polymers via competing polycondensation reaction. The factors that influence the relative proportion of cyclics vs linear products include molecular configuration of reaction monomers, reaction rate and high dilution condition etc. Among them, molecular configuration of monomers is intrinsic factor to the cyclization reaction. It is critical to understand the relationship between molecular configuration and cyclooligomer formation. Hydroquinone exhibits a rigid linear structure; it easily reacts with 4,4'-difluorobenzophenone to form a folded chain. Thus it is very difficult to obtain PEEK cyclics although under optimum condition. As we know, the incorporation of ketimine substituent can suppress premature crystallization of polymerization and activate the fluoride atom to undergo a nucleophilic aromatic substitution. In order to determine which of monomers is favorable to cyclization, molecular models of 4,4'-difluorobenzophenone and N-phenyl(4,4' - difluorodiphenyl) ketimine were set up using MOPAC program on a SGI (Silicon Graphics Indy) workstation with IRIX 5.2 operation system. The bond angles and bond lengths were calculated for each of them (see Scheme 1). The angles of C4 - C8 - C10 are 122.9ø for the ketone monomer and 120.1 ° for the ketimine monomer, the distance of F7 - F 16 are 10.1 Å and 9.8 Å respectively. From the data above, ketimine molecule may show a much more "bent" configuration and prefer cyclization.



Scheme 1

Under pseudo-high-dilution condition, PEEK cyclic precursor was prepared with N-phenyl(4,4'-difluorodiphenyl) ketimine and hydroquinone as initial monomers as shown in Scheme 2.



Scheme 2

Gel permeation chromatographic (GPC) analysis of the crude product indicates that the reaction generated a mixture of low molecular weight oligomers with a negligible amount of high molecular weight product. The most direct determination of composition of the reaction product is matrix-assisted laser desorption/ionization time-of-flight mass spectrometry(MALDI-TOF MS). Recently, MALDI-TOF MS has become a very powerful technique for the detection and identification of macrocyclic oligomers. A positive MALDI spectrum of cyclics **C** (Figure 1) using dithranol as matrix gives seven groups of peaks which are composed of two part with excellent signal to noise ratio. In each group, the peak to peak mass increment is 70 Da. The expanded scale of the MS spectrum shows the signals for cyclic tetramer. For example, the signals of two peaks are located at 1383.6 and 1453.8 Da. The signal at 1453.8 Da corresponds to the protonated molecular ion peak of cyclic tetramer. The higher peak represents linear oligomer with difluoro end groups. It is interesting to find that most of the linear oligomers are ended with ketimine monomer. This may be attributed to oxidization of hydroquinone to quinoid structure, thus resulting in stoichiometric imbalance. On the basis of MS and ^{1}H NMR analysis, the yield of cyclic ether ether ketimine oligomers is 40%.

Pure cyclic ether ether ketone oligomers can be isolated by hydrolysis of cyclic ether ether ketimine oligomers since the linear PEEK oligomers are totally insoluble in tetrahydrafunan. The MALDI-TOF MS spectrum of cyclic ether ether ketone oligomers is shown in Figure 2. It reveals the presence of the cyclic dimer (n = 2, m/z = 576.8) to cyclic tetramer (n = 4, m/z = 1154.5). Therefore, the PEEK cyclic precursors were successfully prepared via the ketimine route, this will extend applications of PEEK in the high performance thermoplastic composites.

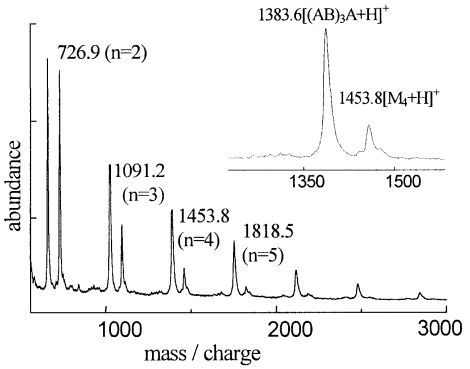


Figure 1. MALDI-TOF MS spectrum of cyclic ether ether ketimine oligomers

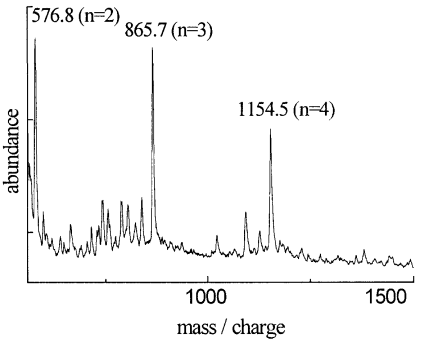


Figure 2. MALDI-TOF MS spectrum of cyclic ether ether ketone oligomers

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