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Functionalized poly(ether ether ketone) analogs via reactivity ratio controlled polycondensation

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This manuscript is dedicated to Professor Krzysztof Matyjaszewski on the occasion of his 65th Birthday.

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ABSTRACT

A route for the introduction of functional groups to poly(ether ether ketone) analogs, via a reactivity ratio controlled polycondensation process, has been developed. The reactivity differences, toward nucleophilic aromatic substitution reactions, of the three electrophilic sites in 3,4',5-trifluorobenzophenone, **1**, affords the opportunity to prepare functionalized B₂-type monomers *in situ*, followed by polycondensation with the appropriate bisphenol to prepare the corresponding linear polymer. The reactivity differences in **1** were probed via a combination of ¹³C and ¹⁹F NMR spectroscopy along with model reactions using *m*-cresol as the nucleophile. Reaction of **1** with 1.03 molar equivalents of a series of phenols provided the desired B₂-type monomers in high selectivity. The B₂-type monomers were then converted to the linear polymers by reaction with Bisphenol-A and their structures were confirmed via NMR spectroscopy. The thermal properties were evaluated by a combination of thermogravimetric analysis and differential scanning calorimetry.

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1. Introduction

Poly(arylene ether)s, PAE's, are a class of engineering thermoplastics composed of aromatic rings linked together via ether bonds. The simplest PAE is poly(*p*-phenylene oxide) although it is not commercially available [1]. The more well known poly(2,6-dimethylphenylene oxide) is commonly referred to as PPO and is readily available [1]. Two of the more widely utilized engineering thermoplastic materials are poly(ether ether ketone), PEEK [2,3], and poly(arylene ether sulfone)s, PAES [4]. PAE's are renowned for their thermal and chemical stability making them suitable for a wide variety of end uses. PEEK is a highly crystalline material while PAES systems are completely amorphous.

With the exception of PPO, and its derivatives, which are synthesized via oxidative coupling processes [1], the synthesis of poly(arylene ether)s, PAEs, is typically achieved through nucleophilic aromatic substitution, NAS, reactions of activated aryl halides with phenolate ions [4,5]. A wide variety of activating groups have

been employed such as the strongly electron withdrawing sulfonyl [5–8], carbonyl [2,9,10], and phosphoryl groups [11–16]. In all of these cases, the activating group is located in the *para* position relative to the aryl halide, which activates the electrophilic position by decreasing the electron density at the *ipso* carbon atom. The activating group also serves to stabilize the anionic intermediate, known as a Meisenheimer complex. In most cases, the electron-withdrawing group, EWG, becomes an integral part of the backbone.

One of the long sought after goals in PAE chemistry is the facile introduction of functional groups onto these engineering thermoplastics to modify their properties without sacrificing the backbone. Currently, the NAS conditions required for the synthesis of many PAE's limits access to the desired functional group containing materials.

We have been developing methodology, based on *meta*-activated NAS reactions of 3,5-difluoro aromatic systems as a route to the geometric isomers of typical PAE systems. The activating groups, including sulfone [17], ketone [18], phosphoryl [19], and sulfonamide [20], are incorporated pendent to the backbone and provide an excellent site for the introduction of functional groups, without disrupting the backbone of the polymer.

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1.1. Functionalized PEEK derivatives

The highly crystalline nature of PEEK has been a severe hindrance to the incorporation of functional groups onto its backbone. The synthesis of functionalized PEEK systems generally requires the multistep synthesis of specialty monomers for the “pre” method or the introduction of functional groups directly onto the backbone in a “post” polymerization modification process. The incorporation of functional groups relies heavily on the electron-rich bisphenol component. For example, the incorporation of an aliphatic carboxylic acid, via the corresponding acid-containing bisphenol, was reported by Ritter [21]. A post polymerization sulfonation reaction can introduce the corresponding sulfonic acid groups on the electron rich rings, but also carries the risk of cross-linking [22].

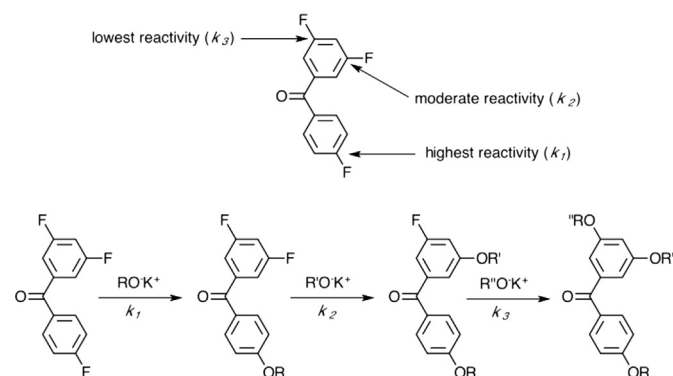
A combination approach has been applied by Roovers et al., in which methyl hydroquinone was used as the bisphenol, followed by subsequent conversion to the bromo methyl group [23]. In turn the bromo methyl group provides access to a host of carbonyl containing functional groups. Other “pre” methodologies have led to PEEKs bearing tertiary amino [24], amino (aniline) [25] and sulfonic acid groups [9,26], while a post polymerization reduction of the carbonyl groups present in the benzophenone moiety results in the formation of secondary alcohols [27,28]. Typically, when the functional groups are present or the specialty monomer is incorporated, the semi-crystalline nature of PEEK is lost.

As such, a methodology that affords the possibility of introducing functionality while maintaining some level of crystallinity would provide a significant advancement to the field. We have previously described the preparation of semi-crystalline, soluble PEEK derivatives based on 3,5-difluorobenzophenone [29]. The result is a PAE-type material that carries a pendent benzoyl group, which is an ideal site for the introduction of functional groups.

1.2. Reactivity ratio controlled polycondensation, RRCP

During the course of investigations dealing with the synthesis of hyperbranched PAEs from $A_2 + B_3$ systems we observed considerable differences in the reactivity of the three aryl fluoride moieties in some B_3 monomers, such as 3,4',5-trifluorobenzophenone, **1**, as illustrated in Scheme 1 [30]. The *para*-fluoride was considerably more reactive than the *meta*-positions and, while initially the two *meta*-fluorides are of equivalent reactivity, upon reaction of one *meta*-fluoride, the last one became significantly less reactive.

If the differences in reactivity are sufficient, a B_3 -type monomer, more aptly described as a $BB'B''$ monomer, provides the opportunity to install a functional group *in situ*, followed by polymerization



Scheme 1. Reactivity ratios of 3,4',5-trifluorobenzophenone, **1**, a potential B_3 ($BB'B''$) type monomer for the synthesis of functional poly(arylene ether)s, PAE, via a reactivity ratio controlled polycondensation, RRCP.

to the desired, linear poly(arylene ether). This report will describe our initial efforts to prepare functional PEEK analogs via a “one-pot”, reactivity ratio controlled polycondensation (RRCP) process, based on **1**.

2. Experimental

2.1. Materials

All reactions were carried out under a nitrogen atmosphere. Reagent-grade anhydrous potassium carbonate powder (K_2CO_3) and calcium chloride ($CaCl_2$) were dried at 130 °C in an oven before use. Anhydrous aluminum chloride ($AlCl_3$), 4-*tert*-butyl phenol, 3-aminophenol, ethyl-4-hydroxybenzoate, and 4-methoxyphenol were purchased from Sigma Aldrich Chemical Co. and used as received. Bisphenol-A was purchased from Sigma Aldrich Chemical Co., recrystallized from toluene and dried under vacuum prior to use. *N*-Methylpyrrolidinone (NMP) was purchased from Sigma Aldrich Chemical Co., dried and distilled over CaH_2 under nitrogen prior to use. Phenol and *p*-cresol were purchased from Sigma Aldrich Chemical Co. and distilled under vacuum prior to use. 4-bromophenol was purchased from Sigma Aldrich Chemical Co., recrystallized from hexanes and dried under vacuum prior to use. Fluorobenzene and 3, 5-difluorobenzoyl chloride were purchased from Oakwood Products and used as received.

2.2. Instrumentation

GC/MS analyses were carried out using a Hewlett–Packard (HP) 6890 Series GC with auto injection and a HP 5973 Mass Selective Detector/Quadrupole system.

1H and ^{13}C NMR spectra were acquired using an AVANCE 300 MHz instrument operating at 300, and 75.5 MHz, respectively. Samples were dissolved in appropriate deuterated solvents ($DMSO-d_6$ or $CDCl_3$), at a concentration of (~30 mg/0.6 mL). ^{19}F NMR spectra were obtained using a Bruker AVANCE 400 MHz instrument operating at 376.5 MHz using 10% $CFCl_3$ as an external standard with the instrument set relative to the lock signal.

Size Exclusion Chromatography (SEC) analysis was performed using a system consisting of a Viscotek Model 270 Dual Detector (viscometer and light scattering) and a Viscotek Model VE3580 refractive index detector. Two Polymer Laboratories 5 μm PL gel Mixed C columns (heated to 35 °C) were used with tetrahydrofuran/5% (v/v) acetic acid as the eluant and a GPCmax VE-2001 with pump operating at 1.0 mL/min. Number average molecular weights, M_n , and the dispersity were determined with the RI signal (calibrated with polystyrene standards).

DSC and TGA analysis were carried out under nitrogen (or air) on TA Instruments DSC Q200 and TGA Q500, respectively, at a heating rate of 10 °C/min. Melting points were determined on a MEL-TEMP apparatus and are uncorrected. Elemental analyses were obtained from Midwest Microlabs, Inc., Indianapolis, IN.

2.3. Synthesis of 3,4',5-trifluorobenzophenone, **1**

In a 100 mL RB flask, equipped with an addition funnel, condenser, a stir bar, a nitrogen gas inlet and a $CaCl_2$ drying tube were placed 9.10 g (68.0 mmol) of $AlCl_3$ and 25 mL of fluorobenzene. 3,5-difluorobenzoylchloride (6.5 mL, 55.0 mmol) was measured under a nitrogen blanket and added to the addition funnel containing 28 mL of fluorobenzene. The resulting mixture was added to the flask, drop wise, over 1 h at room temperature and maintained with stirring for 24 h. The reactant mixture was precipitated into an excess of acidified deionized water (300 mL) and extracted into chloroform (150 mL). The organic layer was

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