Communications to the Editor

Applications of Arene–Iron Chemistry to Polymer Synthesis: Preparation and Polymerization of Novel Triaryl Diether Monomers

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Fully aromatic polyesters are an important class of compounds with many desirable mechanical and thermal characteristics. Aromatic homopolyesters, however, are quite undistinguished with regard to processibility due mostly to very high melting transitions (T_m) and very narrow temperature ranges, above the T_m but below the decomposition point, within which the polymer may be manipulated.

The traditional solutions to this problem include copolymerization of the aromatic hydroxy acid (or diacid and diphenol) with kinked[1] or flexible spacers[2] to lower the symmetry and raise the melting entropy of the polymer, the introduction of bulky pendant groups to disrupt packing,[3] and the incorporation of carbonyl,[4] phenyl ether,[5] or other disruptor linkages to reduce the rigidity of the polymer.

The conventional routes to the incorporation of phenyl ether linkages either employ 3,4′- or 4,4′-dicarboxydiphenyl ether in a copolymerization with an aromatic diacid and a diphenol or require the presence of one of a limited array of electron-withdrawing groups on the ring.[6] The first arrangement constrains the polymer to an ether/ester ratio of no more than 1:2, and the second is inconvenient unless the additional functionality is desired for another purpose. Also, it is well-known that the physical properties of a polymer depend not only upon the overall composition but upon the comonomer sequence,[7] and it is recognized that ordered sequence copolyesters undergo rapid sequence randomization above their melting points, even without a catalyst.[7a,8] Much information regarding the positional effect of a diaryl ether disruptor must therefore remain unassessed as the relative locations of the disruptors in the chain are neither regular nor able to be pinpointed. The same may be said for the effect of any structural modification that may be repositioned *via* transesterification or any similar randomization process.

We report herein methodology, based upon the synthesis of triaryl diethers *via* transition-metal-activated sequential nucleophilic aromatic substitution,[9] which allows access to polymers with compositions and geometries that are inaccessible by traditional routes (Figure 1; triaryl diethers, with an aryl ether/aryl ester ratio of 2:1) and which ensures that any high-temperature transesterification which occurs *results in a polymer of identical sequence*, thus introducing a technique for the synthesis of isoregic, wholly aromatic, poly(ether–esters) and for studying the effects on polymer properties of strategically located disruptors.

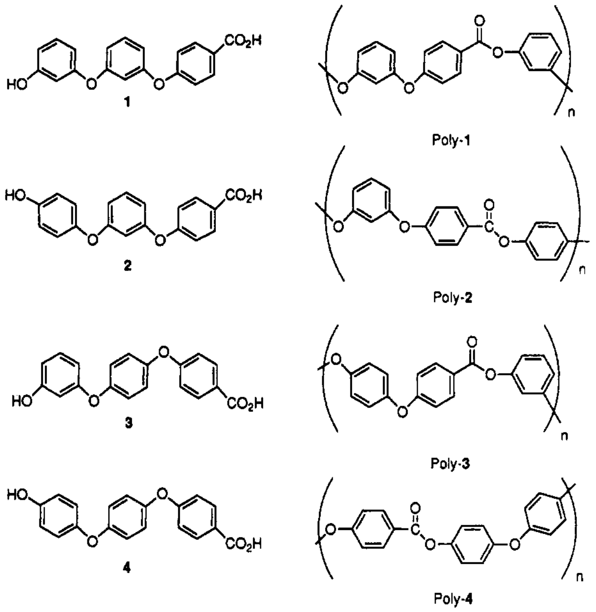
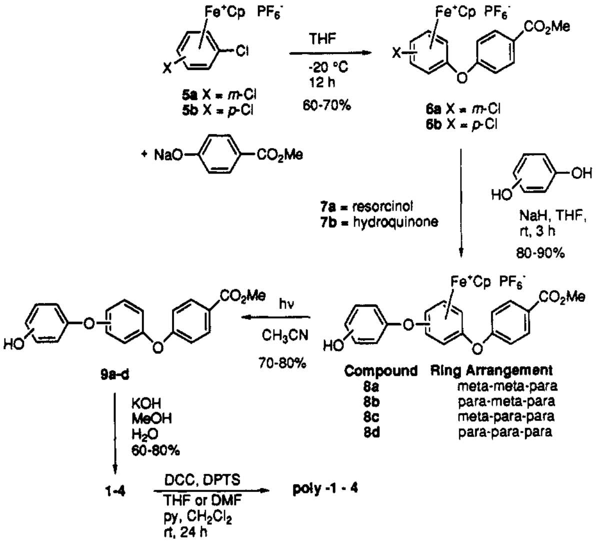


Figure 1. Structures of triaryl diether monomers and their polymer repeat units.

Scheme 1



The starting point for the monomer synthesis was η^6-1,3- or 1,4-dichlorobenzene-η^5-cyclopentadienyliron hexafluorophosphate (**5a**,**b**, Scheme 1), both of which are readily prepared by standard methods *via* a Lewis acid promoted ligand-exchange reaction with ferrocene.[10] The yellow microcrystalline salts are stable, 18-electron complexes which can be stored in the dark indefinitely.[11] The cyclopentadienyliron moiety is electron withdrawing and thus activates the arene ring to nucleophilic substitution *via* an addition–elimination pathway, by stabilizing the incipient dienyl anion. When a dichloroarene is employed, the second chloride is less easily displaced owing to the presence of an electron-rich substituent on the ring which moderates the influence of the metal. This selectivity can be exploited in the construction of unsymmetrical triaryl diethers. Depending on the nature of the nucleophile, the first substitution can be accomplished at temperatures as low as −78 °C and the second at temperatures ranging from 0 °C to room temperature. With most organic ligands,

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the metal can then be cleanly removed by photolysis of an acetonitrile solution of the complex.[9]

Sodium 4-(methoxycarbonyl)phenoxide is a weaker nucleophile than either diphenol monophenoxide (**7a** or **7b**); thus, it was chosen as the first nucleophile, in order to maximize the selectivity. The beige microcrystalline salts (**6a,b**) isolated after this step were subjected to a second substitution reaction using either hydroquinone or resorcinol monophenoxide to give **8a–d**. Photolytic (sunlamp or room-lighting) decomplexation, followed by flash chromatography gave **9a–d**. Hydrolysis of the liberated organic ligands to the corresponding acids afforded the isomeric monomers 1–4 in Figure 1.

A typical S_NAr reaction on these complexes involves generation of the phenoxide (NaH, THF, rt, 15 min) followed by cooling the reaction to the appropriate temperature and adding the organometallic species. After the reaction times indicated in Scheme 1, the reaction is quenched with dilute acid, the mixture is diluted with dichloromethane and washed (H_2O), and the product is isolated by precipitation from a concentrated dichloromethane solution by addition of diethyl ether. While temperature control in the selective substitutions is critically important to ensure complete chemoselectivity, reagent stoichiometry is not. The first substitution is quite chemoselective at −20 °C, even in the presence of 2–3-fold excesses of the nucleophile. It is likewise important to note that, with the exceptions of the synthesis of the dichlorobenzene complexes and the nucleophilic substitution with the diphenol, *it is not necessary to exclude oxygen during these transformations*. No special handling techniques are required, save the necessity of excluding light if complexes are to be stored for prolonged periods.[11]

Polymerization of these units proceeding *via* the acid chloride (thionyl chloride/pyridine/DMAP, sealed tube, 120 °C, 36 h) gave fibrous, but very insoluble and difficult to characterize, high molecular weight polymers; thus, we chose to restrict our initial efforts to the synthesis of lower molecular weight homologs (M_w *ca.* 8000, M_n *ca.* 6000, M_w/M_n *ca.* 1.3, relative to polystyrene standards) which we could more effectively and completely characterize. We found these to be easily accessible using a modification of literature methods for carbodiimide-mediated polyesterifications (Scheme 1).[12] The polymers were isolated as white solids by precipitation from methanol and reprecipitated from THF/methanol until they were free of dicyclohexylurea by GPC.

The signals in the proton NMR spectra of the polymers (THF-d_8 or DMF-d_7) are quite sharp, which is indicative of both the isoregic orientation of the subunits and of the relatively low molecular weights of the polymers, although end-group analysis by either FTIR or ^{13}C NMR spectroscopy was not productive, indicating a chain length sufficient to render the end group undetectable by our instrumentation (≤5% of signal).

Thermal gravimetric analysis (TGA) shows the onset of weight loss in the range 390–450 °C with final weight retentions of 30–40% at 700 °C (Table 1). This compares favorably with analogous polyester and poly(ether–ester) systems,[5] which indicates that, as expected, the additional phenylene oxide linkage is not detrimental to thermal stability.

The monomers were designed especially with an eye toward assessing the effects of the ordered sequencing on liquid crystallinity relative to the existing ordered systems employing long aliphatic flexible spacers.[13] The results of hot-stage microscopy (HSM) studies are somewhat encouraging. As expected, poly-3 forms an isotropic melt. Poly-4 seems to form a nematic phase but decomposes very close to its T_m (*ca.* 295 °C). Poly-1 displays some shear-induced ordering, albeit very weakly. Poly-2 also displays shear-induced ordering, possibly characteristic of a nematic phase. The results of DSC concur with the HSM results. Poly-3 displays only one endotherm (Table 1).[14] Poly-1 does not display a repeatable second endotherm on cooling or a second heating. Poly-2 shows endotherms at 110 and 160 °C. Our immediate goal is to fine tune the monomer units in order to obtain more strongly liquid crystalline systems and to begin investigation of the properties of the higher molecular weight homologs, possibly by investigating melt-phase polymerizations or reinvestigating the acid chloride system.

Table 1. Characterization Data for Poly(ether–esters)

polymer	GPC data			TGA, onset of dec (°C)	DSC (°C)	
	M_w	M_n	M_w/M_n		T_m	$T_{lc \to i}$
1	7300	6100	1.2	431	132	
2	8300	3900	2.2	426	110	160
3	5000	2500	2.0	393	170	
4	NA[a]			448	295 (hot-stage microscopy)[a]	

[a] Differential scanning calorimetry data could not be obtained for poly-4 because it decomposed close to the melting point, and GPC data could not be obtained due to the insolubility of this compound in common solvents.

Additional studies are underway to extend the generality of this method. It is important to recognize that this approach is in no way limited to aryl ether/aryl ester polymers, as the haloarene–metal complexes are susceptible to nucleophilic displacement by a variety of alkoxide, amine, and carbon nucleophiles.[9] Various ordered monomer sequences are available by judicious nucleophile selection, as is the isoregic introduction of side-chain disruptors. Current attention is also being given to the possibility of conducting the polymerizations prior to removal of the metal in anticipation of obtaining solubility enhancements similar to those which have been observed in polymerizations of arene–ruthenium[14] and arene–chromium[15] complexes.[16]

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