Communications to the Editor

Novel Poly(aryl ether)s from Bis(4-fluorophenyl)acetylene

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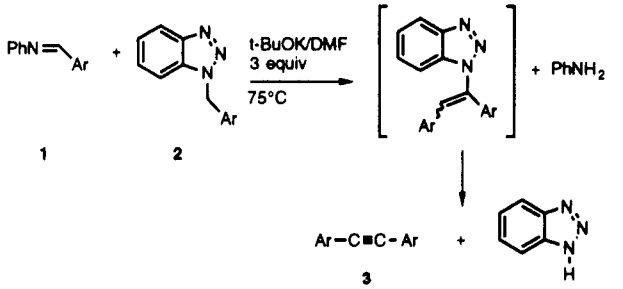
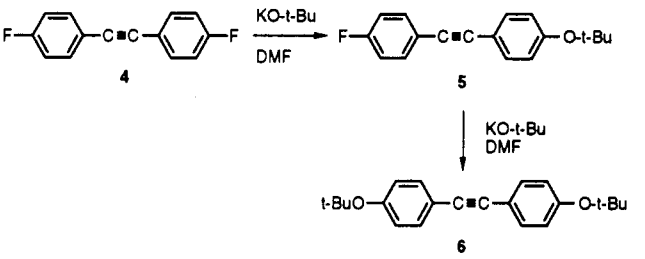
Introduction. The incorporation of acetylenic moieties into polymers has been studied extensively. Polyimides containing acetylene groups have been recently reviewed.[1] The most common approach has been to introduce the acetylenic groups as end caps on oligomers which can then be molded into the final shape and subsequently cross-linked by heating. For example, in polyimides (3-aminophenyl)phenylacetylene[2,3] has been used for the end-capping of oligomers. For use as matrices for advanced composites the low molecular weight of the prepolymer facilitates molding of the resin. Polymers with pendent acetylenic groups along the chain have also been synthesized,[4–6] and attempts have been made to design polymers where the predominant reaction that occurs on heating is an intramolecular cyclization which would result in an increase in the glass transition of the cured polymer without concomitant cross-linking of the polymer.[7] A third approach, which has been explored to a lesser extent, is the incorporation of the acetylene groups into the backbone of polymers. Polyimide copolymers have been synthesized by using bis(3-aminophenyl)acetylene to replace some of the diamines,[8] and eneyne moieties have been introduced into polyimides.[9] When all of these polymers are heated, a strong exothermic reaction takes place with the resulting cross-linking of the polymers. The position of the exotherm peak varies with the structure of the acetylene moiety. Ethynyl groups cross-link at a much lower temperature (ca. 250 °C) than phenylethynyl groups (ca. 350 °C).

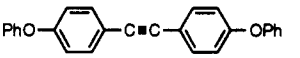
Results and Discussion. We have recently demonstrated a new, facile synthesis of diarylacetylenes (**3**) by the reaction of an aromatic imine **1** with the *N*-benzyl derivatives of benzotriazole **2** (Scheme I).[10] When we attempted to synthesize bis(4-fluorophenyl)acetylene (**4**) by this route, we found that the fluorines are readily displaced by a *tert*-butoxide anion in quantitative yield to yield bis(4-*tert*-butoxyphenyl)acetylene (**6**; Scheme II).[11] This is a sequential reaction, and the intermediate monodisplaced product **5** can also be isolated under the proper conditions. We found, furthermore, that upon reaction of **4**[11] with phenol in the presence of potassium carbonate in a dipolar aprotic solvent, under conditions that are generally used for the synthesis of poly(aryl ether)s, bis(4-phenoxyphenyl)acetylene (**7**) is formed in quantitative yield. Reaction with bisphenols under these conditions yields high molecular weight linear polymers which contain the acetylene moiety in the backbone of the polymers. High molecular weight linear polymers **9a** and **9b** are obtained from 4,4′-(1-methylethylidene)bisphenol (BPA) (**8a**) and 9,9-bis(4-hydroxyphenyl)fluorene (**8b**; Scheme III) which are readily soluble in solvents like chloroform and methylene chloride at room temperature.

Scheme I

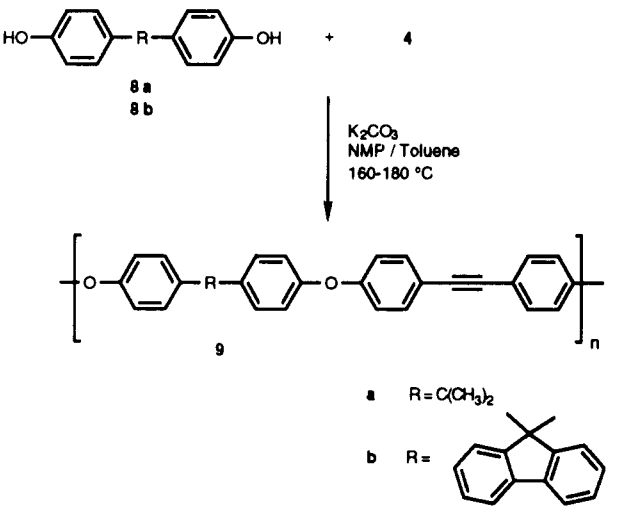


Scheme II





Scheme III



Presumably reaction proceeds due to activation from the acetylene moiety by induction and stabilization of the Meisenheimer complex intermediate. The activation of the fluorines by the acetylene functionality is considerably less than that by a carbonyl group or a sulfone group, but it is sufficient so that the reaction can be carried to completion in several hours.

The properties of the poly(aryl ether)s **9a** and **9b** are shown in Table I. Both polymers have relatively high molecular weights ($\eta_{inh} > 0.5$), and the molecular weight distributions of polymers **9a** and **9b** as determined by gel permeation chromatography (GPC) are narrow and a low

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Table I
Properties of Polymers 9

polymer	η_{inh}[c]	T_g[a,d]	exotherm[a,d] max (°C)	TGA[a,b] (°C) air	TGA[a,b] (°C) N_2	solubility
9a	0.69	163	380	512	510	$CH_2Cl_2/CHCl_3$
9a[e]		nd[e]	nd[f]	501	505	insoluble
9b	0.59	264	388	529	534	$CH_2Cl_2/CHCl_3$
9b[e]		nd[f]	nd[f]			insoluble

[a] Heating rate 10 °C/min. [b] Values correspond to the temperature at which a 10% weight loss occurs. [c] 0.5 g/dL in *sym*-TCE at 25 °C. [d] By DSC [e] After heating to 420 °C in the DSC. [f] nd = not detectable.

molecular weight fraction is not present. The polymers appear to be amorphous, and films of the polymers cast from solution are tough, transparent, and creasable. Preliminary thermomechanical studies using thin films (0.075 mm) show that these materials maintain good mechanical properties to temperatures close to their glass transition temperatures, 163 and 264 °C, respectively. Thermogravimetric analyses of these polymers in air show 10% losses above 500 °C. High molecular weight polymers cannot be prepared from bis(4-fluorophenyl)acetylene and hydroquinone or 4,4′-biphenol since the resulting products are crystalline and highly insoluble and precipitate from the reaction mixture during polymerization.

When polymer **9a** is heated in the DSC from 25 to 420 °C under nitrogen, a T_g is observable at 163 °C, followed by an exotherm at 380 °C, corresponding to the reaction of the diphenylacetylene moiety (Figure 1). When the same sample is reheated to 420 °C, a T_g and an exotherm are no longer observable (Table I). The cured sample is now insoluble and brittle and does not swell when stirred in refluxing $CHCl_3$ or *sym*-tetrachloroethane (*sym*-TCE). Polymer **9b** behaves in the same manner after heating to 420 °C.

We are currently involved in preparing a series of other poly(aryl ether)s as well as copolymers of poly(ether sulfone)s and poly(ether ketone)s containing varying amounts of the acetylene moiety. In addition, using the fluoro displacement reaction, we can also synthesize end-capped polymers as well as polymers containing pendent arylethynyl groups.

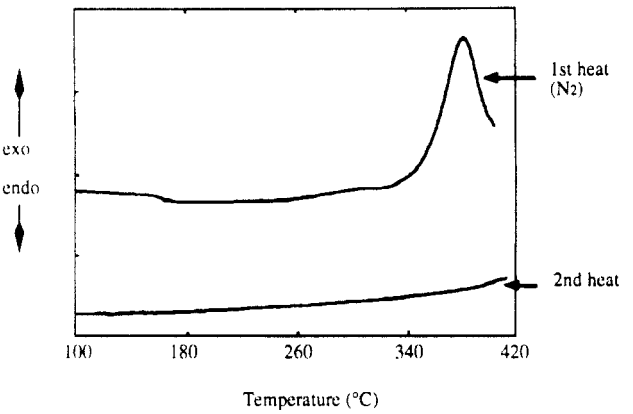

Figure 1. DSC thermogram of polymer **9a**.

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References and Notes

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