

New Synthesis of Poly(arylene ether)s using Masked Bisphenols

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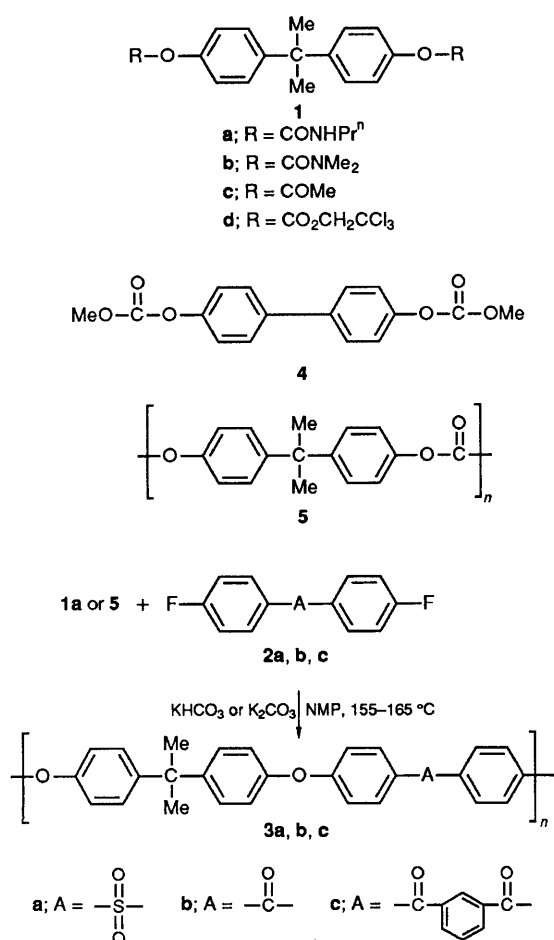
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High molecular weight poly(arylene ether)s are synthesized directly from carbamates of 4,4'-(1-methylethylidene)bisphenol (BPA) or polycarbonate.

Poly(arylene ether)s are a class of high-performance, engineering thermoplastics that have attracted much attention as structural materials in the automobile and electronics industries. They have recently also been evaluated as polymeric matrices for high-performance composites used in the aerospace industry. A great deal of effort has been expended in developing new bisphenols which can be polycondensed with activated dihalogeno aromatic compounds by nucleophilic substitution reactions. Polymerization is conveniently carried out in *N*-methylpyrrolidone (NMP) using potassium carbon-

ate as a base, initially at 130–140 °C for 3–4 h to azeotrope off the resulting water with toluene and then at 160–180 °C to effect the polymer formation.¹ Difficult purification, insolubility of the salt of the bisphenol, or instability of some bisphenols often hampers the polymer synthesis. Silylated bisphenols, as masked bisphenols, have been investigated as starting monomers. The polymerization proceeds at elevated temperatures (*e.g.* 300 °C)² with the elimination of trimethylsilyl fluoride or in an extremely pure solvent.³

We have found that carbamates, which are readily prepared



Scheme 1 Synthesis of poly(arylene ether)s from masked bisphenol

and can be purified by simple recrystallization, can be used as masked bisphenols in the synthesis of poly(arylene ether)s. This new methodology, demonstrated by the synthesis of some known poly(arylene ether)s **3a, b, c** derived from BPA (Scheme 1), relies on the fact that at temperatures (155–165 °C) at which the polymerization occurs the carbamate is rapidly cleaved by potassium hydrogen carbonate to generate potassium phenoxide *in situ*. The volatile by-products, carbon dioxide and alkylamine, are easily removed from the reaction system. High molecular weight polymers are readily formed in a short period of time (e.g. 1–2 h). In comparison, at least a period of 3–4 h¹ is needed to generate the phenoxide by azeotroping off water when a bisphenol is used as a monomer.

The carbamate **1a** (m.p. 133–134 °C)[†] was synthesized from BPA and *n*-propyl isocyanate in diethyl ether in the presence of a catalytic amount of pyridine at room temperature and purified by recrystallization from ethanol. Polycondensation of **1a** with difluorides **2b** and **2c** in NMP at 160–165 °C gave the corresponding polymers **3b** and **3c**, respectively, with intrinsic viscosities of 0.61 and 0.90 dl g^{−1} (CHCl₃), in greater than 90% yields. A high molecular weight polymer **3a** (inherent viscosity: 0.47 dl g^{−1} in CHCl₃) was readily formed in two hours even when the less reactive bis(4-chlorophenyl) sulphone was used.

Also explored were other types of masking groups such as *N,N*-dimethylcarbamate, acetate, methyl carbonate and trichloroethyl carbonate. They were easily prepared from BPA from the chlorocarbamate, acetic anhydride or the chloroform-

ates, respectively, according to known procedures.⁴ It was found that BPA dimethylcarbamate **1b** (m.p. 160–61 °C) could not be cleaved by potassium carbonate in NMP at reflux temperature during 24 hours. The formation of high molecular weight polymers by polycondensation of the acetate ester **1c** (m.p. 165–166 °C) with dihalogeno aromatic compounds proved to be difficult, even though the phenoxide was readily generated. It was found that if BPA acetate **1c** was first treated with potassium carbonate in distilled NMP at 80–90 °C for 30 min to effect complete cleavage of the acetate, and then bis(4-chlorophenyl) sulphone was added in portions during a period of one hour while the reaction temperature was raised rapidly to 160 °C, the polymer **3a** was obtained with inherent viscosity of 0.38 dl g^{−1} in chloroform. However, gel permeation chromatography indicates the polymers are bimodal in molecular weight distribution probably owing to side reactions with the resulting potassium acetate which would terminate the polymerization reaction. In the case of **1d** (m.p. 81–82 °C), it was readily deprotected under the usual polymerization conditions (potassium hydrogen carbonate in NMP); however, only low molecular weight polymers were obtained owing to competitive side reactions with the resulting potassium trichloroethoxide. Cleavage of the carbonate **1d** with an excess of zinc did not yield the reactive phenoxide and as a result no polymer was formed. Since both methyl or ethyl carbonates of BPA are viscous oily compounds and are obtained in high purity with difficulty, the carbonate **4** (m.p. 148–149 °C) derived from 4,4'-biphenol which is a crystalline solid was used in the polymer synthesis. Polycondensation of **4** with the difluoride **2a** gave only a low molecular weight polymer. The ¹H NMR spectrum of the polymer shows a methoxy peak at δ 3.95, indicating that the polymerization is terminated during the reaction by the resulting potassium methoxide since the polymer contains a methoxy end group.

Polycarbonate **5**, commercially available under the trade name of Lexan[®] resin, is another form of masked bisphenol A. It has been found that heating polycarbonate **5** and dihalides **2a, b, c** at 150–165 °C in NMP in the presence of potassium carbonate (Scheme 1) affords in <2 h the corresponding polymers **3a, b, c** with inherent viscosities ranging from 0.33 to 0.53 dl g^{−1} in chloroform. Cleavage of the carbonate group is promoted by the action of potassium carbonate in NMP at about 130 °C and facilitated by loss of carbon dioxide. Although the reaction is usually run in NMP as a solvent, other solvents such as dimethylacetamide, dimethylformamide and dimethyl sulphoxide can be used.

Advantages of this 'carbamate method' over the conventional one or the 'silyl method' are that (i) monomers can be purified by simple recrystallization; (ii) no water is generated during polymerization; (iii) high molecular weight polymers are readily formed in a short period of time under mild conditions. This methodology also offers a unique route to convert polycarbonate completely to polysulphone upon treatment with potassium carbonate in NMP.

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- 5 Lexan[®] 135-A obtained from the General Electric Company: *M*_w 41 000, *M*_w/*M*_n 2.7, *η*_{int} 0.59 dl g^{−1} in chloroform.

[†] All monomers were characterized by spectroscopic means.