Synthesis of Wholly Aromatic Polyketones Using 2,2′-Dimethoxybiphenyl as the Acyl-Acceptant Monomer

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Aromatic polyketones are recognized as high-temperature thermoplastics with high chemical stability and excellent mechanical strength.[1] These polymers tend to be semicrystalline and to show complex thermal behavior. The control of their crystallizability is one of the most significant issues for aromatic polyketones. To avoid precipitation of oligomer crystals during the polymerization which reduces the molecular weight of the isolated polymers, bulky substituents,[2] protective groups of the ketone linkage,[3] and some solvent/condensing agent systems [liquid hydrogen fluoride/trifluoroborane (HF/BF_3)[4] or phosphorus pentoxide/methanesulfonic acid (P_2O_5/CH_3SO_3H)[5]] were reported to be effective. Introduction of 1,3-phenylene or biphenyl units was shown to be effective in reducing the polymer skeleton crystallinity.[6] Nevertheless, almost all of the aromatic polyketones so far reported have ether linkages in the main chain; i.e., they are aromatic poly(ether ketone)s, with few exceptions.[7] Thus, the properties and synthetic feasibility of "aromatic polyketones" depend on the diaryl ether moiety to a considerable extent. For the exact evaluation of the features of aromatic polyketones, the synthesis of a polymer without an ether linkage in the main chain is essential.

Preparation of aromatic polyketones by nucleophilic aromatic substitution inevitably places ether linkages into the polymer main chain. By alternative Friedel–Crafts type polycondensations, ether linkages are not necessarily incorporated into the polymer main chain, but the required polymerization conditions often cause irregular chain structures. Pertinent design and modification for high activation of the monomers and the intermediates are required to propagate successive formations of aromatic ketone linkages by attack of an acyl cation on acyl-acceptant aromatic rings.

Recently, we found that 2,2′-dimethoxybiphenyl (**1**)[8,9] is highly effective as an acyl-acceptant monomer (nucleophilic monomer) in electrophilic aromatic substitution polymerization. By using **1**, the synthesis of wholly aromatic polyketones was achieved. A typical reaction procedure is given in Scheme I and is as follows: Equimolar amounts (1 mmol) of **1** and terephthaloyl chloride (**2a**) were dissolved in 1,2-dichloroethane (5 mL for 1 mmol of monomers). Then 2.7 molar amounts of anhydrous aluminum chloride were gradually added for 30 min with gentle stirring to the ice-cooled mixture under a nitrogen stream. The temperature was gradually raised to 20 °C for 1 h, followed by stirring at 20 °C for 24 h. The precipitated polymeric materials were ground, filtered off, and washed with aqueous 5% hydrogen chloride and hot water. The obtained solid was dried in vacuo at 120 °C overnight.

Scheme I

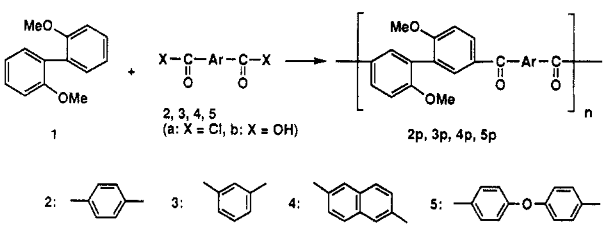

Table I. Syntheses of Aromatic Polyketones from 1 and Diacyl Compounds

diacyl compd	solvent/condensing agent	η_{inh} (dL/g)[a]	T_g (°C)[b]
2a	$CH_2ClCH_2Cl/AlCl_3$[c]	0.71	217
2a	$CH_2Cl_2/AlCl_3$[c]	0.16	
2a	$CHCl_3/AlCl_3$[c]	0.19	
2a	$PhNO_2/AlCl_3$[c]	0.10	
3a	$CH_2ClCH_2Cl/AlCl_3$[c]	0.24	200
4a	$CH_2ClCH_2Cl/AlCl_3$[c]	0.24	217
2b	P_2O_5/CH_3SO_3H[d]	0.23	
3b	P_2O_5/CH_3SO_3H[d]	0.23	
5b	P_2O_5/CH_3SO_3H[d]	0.49	
5b	CF_3SO_3H[d]	0.28	
5b	poly(phosphoric acid)[d]		

[a] Measured at 30 °C on a 0.3 g/dL solution in 96% sulfuric acid. [b] T_g was determined by DSC (heating rate 10 °C/min, under nitrogen). [c] Reaction conditions were described in the text. [d] Reaction conditions: monomers, 1 mmol; condensing agent, 3 g; reaction time, 24 h; reaction temp, 60 °C (100 °C for poly(phosphoric acid)).

When **2a** was used as the acyl cation source, high molecular weight polymer **2p** with an inherent viscosity of 0.71 dL/g[10] was obtained, which afforded a flexible cast film (see Table I). The polymerization of **1** with isophthaloyl chloride (**3a**) or 2,6-naphthalenedicarbonyl chloride (**4a**) gave medium molecular weight aromatic polyketones **3p** and **4p** with an inherent viscosity of 0.24 dL/g. These aromatic polyketones are fully amorphous[11] and have high glass transition temperatures (T_g's 200–217 °C)[12] compared to that of poly(ether ether ketone) (153 °C),[1a] and they are soluble in 1,2-dichloroethane. The full amorphism thus achieved in these polyketones has been seldom observed for polyketones prepared by Friedel–Crafts type polycondensation.

Direct polycondensation of **1** and aromatic dicarboxylic acids was also attempted. The direct polycondensation of **1** and 4,4′-oxybis(benzoic acid) (**5b**) in P_2O_5/CH_3SO_3H[5] gave the polymer **5p** with an inherent viscosity of 0.49 dL/g.[10] Other polyketones (**2p** and **3p**) prepared by the same method from **1** and terephthalic acid (**2b**) or isophthalic acid (**3b**) have medium molecular weights. Polymerization of **1** and **5b** in trifluoromethanesulfonic acid[13] also gave a polymer with a satisfactory molecular weight (inherent viscosity 0.28 dL/g[10]). No polymeric material was obtained from the reaction of **1** and **5b** in poly(phosphoric acid),[14] because of the insolubility of **1**.

The successful synthesis of wholly aromatic polyketones having no ether linkage in the main chain proved the high potency of **1** as a bisfunctional acyl-acceptant monomer in electrophilic aromatic substitution polymerizations. It evidences complete transfer of the electrically enhanced reactivity of **1**, without a decrease by bond formation, to the intermediate oligomers. The nucleophilicity of the 5,5′-positions of **1** was enhanced by introduction of the electron-donating methoxy groups in the para positions. The reactivity of the methoxyphenyl group attached at

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the end of the polymer chain is retained when the adjacent aromatic ring is acylated. This substitution also causes an additional and adequate twist of two aromatic planes of biphenyl "kink" units 1, which prevents the crystallization of the intermediate oligomers and the polymers. These electrical and structural properties of the repeating unit of 1 in the polymer skeleton are responsible for the amorphous nature and high T_g's of the wholly aromatic polyketones.

These results demonstrate a novel approach to aromatic polyketones by a conventional method of electrophilic aromatic substitution.

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(8) 2,2′-Dimethoxybiphenyl (1) was synthesized as follows: 2,2′-Dihydroxybiphenyl was methylated by dimethyl sulfate in an aqueous sodium hydroxide solution. The crude product precipitated was washed thoroughly with water, dried, and dissolved in dichloromethane. The thus obtained dichloromethane solution was washed with an aqueous sodium hydroxide solution to exclude mono- and unsubstituted biphenyl compounds, and the solution was dried over anhydrous sodium sulfate, followed by evaporation and recrystallization from acetone. Mp: 152.5–153.5 °C (lit.[9] mp 154–155 °C).

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(10) Measured at 30 °C on a 0.3 g/dL solution in 96% sulfuric acid.

(11) The amorphism of the polyketones was ascertained by the absence of melting peaks in the DSC curves of the polymer sample prepared by gradual cooling from 350 °C.

(12) T_g's were determined by DSC measurements.

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