3,3-Bis[4-(4′-fluorobenzoyl)phenyl]phthalide as a new monomer for the synthesis of cardo polyarylene-ether ketones

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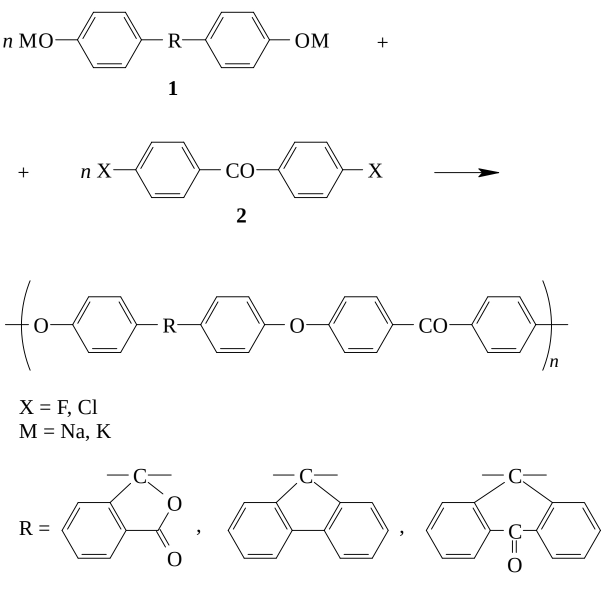
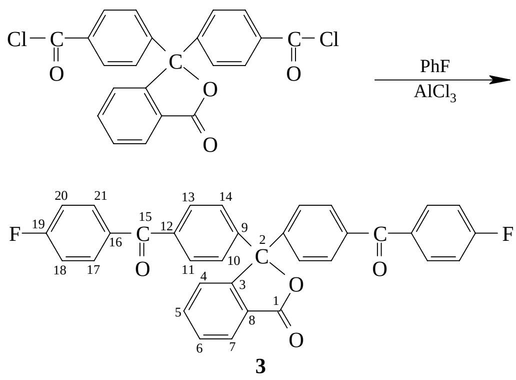
3,3-Bis[4-(4′-fluorobenzoyl)phenyl]phthalide has been synthesised for the first time; this compound can be used for the preparation of polyarylene-ether ketones by nucleophilic substitution.

Cardo aromatic polyketones occupy a prominent place among aromatic polyketones owing to their high glass transition temperature.[1–3] In the synthesis of cardo polyarylene-ether ketones by nucleophilic substitution, only one method for introducing cardo groups into a polymeric chain is known. This method is based on polycondensation involving bisphenols containing cardo groups (phthalide, fluorene, anthrone *etc.*), Scheme 1.



Scheme 1

Up to now, dihalo-derivatives incorporating cardo groups have not been employed in this polycondensation. This has limited the possibilities of synthesising cardo polyarylene-ether ketones possessing new valuable properties. We were the first to synthesise 3,3-bis[4-(4′-fluorobenzoyl)phenyl]phthalide **3**, which can be used in the synthesis of cardo polyarylene-ether ketones by nucleophilic substitution.[†] In this case, a cardo group can be introduced for the first time into a macromolecule from an activated dihalo(difluoro)derivative containing a cardo (namely, phthalide) group. This monomer was synthesised according to Scheme 2.[‡]



3

Scheme 2

The structure of **3** was confirmed by ^{13}C, ^{19}F and ^{1}H NMR spectral data.[§] The IR spectrum of the compound **3** shows absorption bands at 1670 and 1780 cm^{-1} corresponding to a carbonyl group between aromatic rings and the carbonyl group of the phthalide ring, respectively.[¶]

The use of this monomer provides new opportunities for the synthesis of cardo polyarylene-ether ketones. This monomer is highly reactive under polycondensation conditions and ensures the preparation of polyarylene-ether ketones with high molecular weights. The procedure was used to synthesise the first amorphous cardo homopolyarylene-ether ketone based on bisphenol A with η_{red} = 0.97 cm^3 g^{-1} in chloroform (Scheme 3).

The resulting polymer is characterised by a glass transition temparature of 215 °C; it is readily soluble in many organic solvents, for example, in chloroform, *N,N*-dimethylacetamide, *N,N*-dimethylformamide, tetrahydrofuran, 1,4-dioxane, *m*-cresol, cyclohexanone. Strong transparent films can be prepared by casting solutions of the polymer into the above solvents.

[†] Polyarylene-ether ketones were synthesised according to the procedure reported previously.[4]

[‡] The dichloride of 4,4′-diphenylphthalidedicarboxylic acid (7.5 g, 0.018 mol), fluorobenzene (25 ml, 0.27 mol) and finely divided AlCl$_3$ (9.5 g, 0.071 mol) were placed in a three-necked flask equipped with a stirrer and reflux condenser. The mixture was heated at reflux for 16 h, poured into ice–water, filtered and washed with water up to a neutral pH. The remaining fluorobenzene was then removed by steam distillation. Yield 9.6 g (99%). Extraction of impurities with boiling EtOH followed by crystallization from a mixture of EtOH and toluene (1:1 v/v) gave a white crystalline product with mp 184.5–185.5 °C. Found (%): C 77.29; H 3.66; F 7.28. Calc. for $C_{34}H_{20}F_2O_4$ (%): C 76.98; H 3.77; F 7.17.

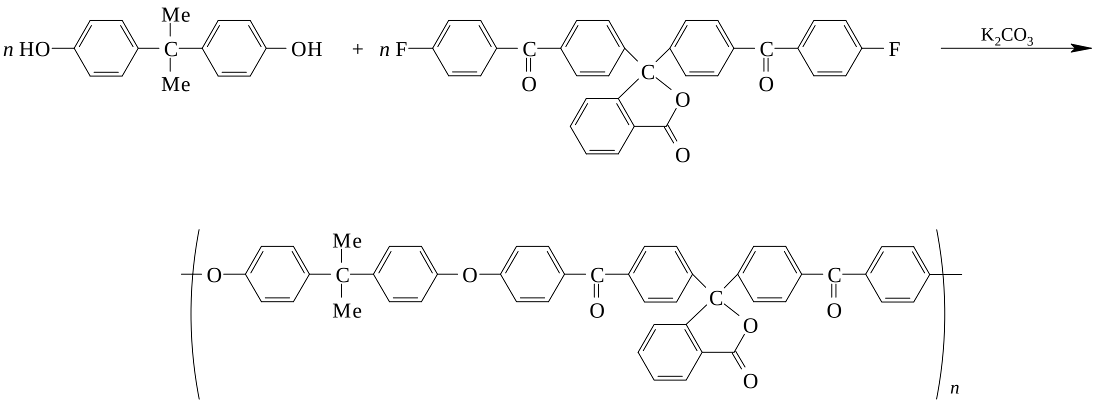
[§] The ^{13}C and ^{1}H NMR spectra were recorded on a ‘Bruker AMX-400’ spectrometer (100.61 and 400.13 MHz respectively) in $CDCl_3$, using TMS as internal standard. The ^{19}F NMR spectrum was measured on a ‘Bruker WP-2000-SY’ spectrometer (168.31 MHz) in $CDCl_3$, using CF_3CO_2H as internal standard.

Spectral data for **3**. ^{1}H NMR δ: 7.983 (d, 1H, H$_7$, $^3J_{H_6-H_7}$ 7.5 Hz), 7.766 (t, 1H, H$_5$, $^3J_{H_4-H_5}$ 7.5 Hz, $^3J_{H_5-H_6}$ 7.5 Hz), 7.654 (d, 1H, H$_4$, $^3J_{H_4-H_5}$ 7.5 Hz), 7.621 (t, 1H, H$_6$, $^3J_{H_5-H_6}$ 7.5 Hz, $^3J_{H_6-H_7}$ 7.5 Hz); 7.804 (dd, 4H, H$_{17}$ and H$_{21}$, $^3J_{H_{17}-H_{18}}$ 8.6 Hz, $^4J_{F-H_{17}}$ 5.4 Hz), 7.122 (t, 4H, H$_{18}$ and H$_{20}$, $^3J_{H_{17}-H_{18}}$ 8.6 Hz, $^3J_{F-H_{18}}$ 8.6 Hz); 7.740 (d, 4H, H$_{11}$ and H$_{13}$, $^3J_{H_{10}-H_{11}}$ 8.2 Hz), 7.492 (d, 4H, H$_{10}$ and H$_{14}$, $^3J_{H_{10}-H_{11}}$ 8.2 Hz).

^{13}C NMR δ: 168.86 (s, C-1), 90.37 (s, C-2), 150.43 (s, C-3), 123.98, 126.34, 129.90, 134.48 (s, C-4, C-5, C-6, C-7), 125.22 (s, C-8), 144.27 (s, C-9), 126.88 (s, C-10), 129.96 (s, C-11), 137.71 (s, C-12), 129.96 (s, C-13), 126.88 (s, C-14), 194.16 (s, C-15), 133.09 (d, C-16, $^4J_{C-F}$ 3.0 Hz), 132.53 (d, C-17, $^3J_{C-F}$ 9.1 Hz), 115.44 (d, C-18, $^2J_{C-F}$ 22.1 Hz), 165.38 (d, C-19, $^1J_{C-F}$ 254.5 Hz), 115.44 (d, C-20, $^2J_{C-F}$ 22.1 Hz), 132.53 (d, C-21, $^3J_{C-F}$ 9.1 Hz).

^{19}F NMR δ: –27.373 (s).

[¶] The IR absorption spectrum was recorded using a ‘Perkin-Elmer-457’ spectrophotometer.



Scheme 3

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