

Synthesis of phthalide-containing dihalogeno derivatives and polyarylene ether ketones based on them

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New activated phthalide-containing dihalogeno derivatives were synthesized, and cardo polyarylene ether ketones based on them were prepared. The effect of the type of the halogen atom (fluorine, chlorine, or bromine) on the efficiency of polycondensation was estimated. It was demonstrated that high-molecular-weight cardo polyarylene ether ketones can be obtained only from the difluoro derivative. The synthesized polymers are amorphous compounds characterized by high glass transition temperatures (210–250 °C). These polymers are soluble in many organic solvents and form strong transparent films.

Key words: 3,3-bis[4-(4-fluorobenzoyl)phenyl]phthalide, 3,3-bis[4-(4-chlorobenzoyl)phenyl]phthalide, 3,3-bis[4-(4-bromobenzoyl)phenyl]phthalide, potassium bisphenoxide, nucleophilic substitution, polycondensation, polyarylene ether ketones.

Aromatic dihalides are widely used in the synthesis of organic compounds and polymers. Until recently,¹ the synthesis of phthalide-containing compounds was not reported in the literature in spite of the wide variety of available activated dihalogeno derivatives. These dihalides are of interest because they can be used in unconventional synthesis of cardo polyarylene ether ketones (PAEK), which are characterized by valuable properties, for example, by high glass transition temperature (T_g) and the ability to withstand large mechanical loads at high temperature. The conventional procedure for the preparation of cardo PAEK is based on polycondensation with the use of bisphenols containing a cardo group (phthalide, fluorene, anthrone, *etc.*).^{2–5}

The aim of the present work was to synthesize new activated phthalide-containing dihalides and new cardo PAEK. Polymers were synthesized by nucleophilic substitution of activated halogen atoms in the aromatic nuclei.

Results and Discussion

Dihalides containing the cardo (phthalide) group were synthesized according to Scheme 1.

The structures of compounds **2a–c** were confirmed by the data from ¹³C and ¹H NMR spectroscopy (Tables 1 and 2, respectively).

The IR spectra of these compounds have absorption bands at 1670 and 1780 cm⁻¹ corresponding to the carbonyl group between the aromatic rings and the carbonyl group of the phthalide ring, respectively.

Cardo dihalides, which were prepared by us for the first time, were used in the synthesis of cardo PAEK by nucleophilic substitution. In this case, it became possible to introduce the cardo group into a macromolecule by using activated dihalides containing the cardo (phthalide) group. Cardo polyarylene ether ketones were prepared by the reactions of compounds **2a–c** with potassium

Scheme 1

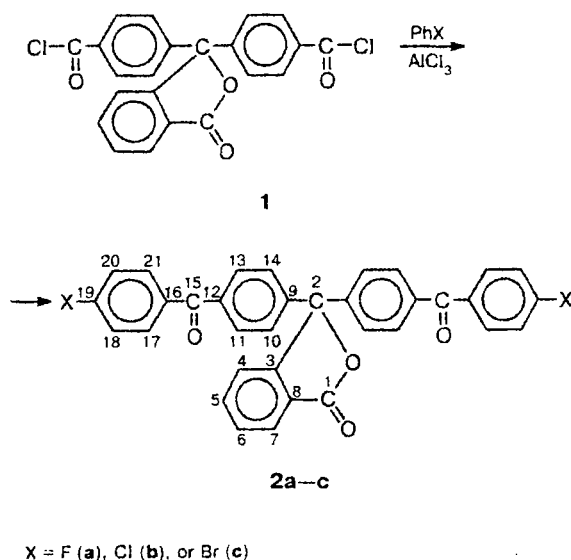


Table 1. Chemical shifts and multiplicities of the signals in the ^{13}C NMR spectra of dihalides **2a–c**

Atom ^a	δ		
	2a ^b (J/Hz)	2b	2c
C(1)	168.86	168.79	168.86
C(2)	90.37	90.34	90.42
C(3)	150.43	150.35	150.43
C(4)	123.98	123.99	124.05
C(5)	137.71	137.42	137.46
C(6)	129.90	128.59	128.31
C(7)	129.96	130.04	130.02
C(8)	126.88	126.92	126.89
C(9)	144.27	144.41	144.52
C(10)	125.22	125.21	125.33
C(11)	126.34	126.36	126.47
C(12)	134.48	134.51	134.56
C(13)	126.34	126.36	126.47
C(14)	125.22	125.21	125.33
C(15)	194.16	194.30	194.56
C(16)	133.09 (d, $^4J_{\text{C-F}} = 3.0$)	135.12	135.65
C(17)	132.53 (d, $^3J_{\text{C-F}} = 9.1$)	129.94	127.00
C(18)	115.44 (d, $^2J_{\text{C-F}} = 22.1$)	131.27	131.44
C(19)	165.38 (d, $^1J_{\text{C-F}} = 254.5$)	139.10	130.13
C(20)	115.44 (d, $^2J_{\text{C-F}} = 22.1$)	131.27	131.44
C(21)	132.53 (d, $^3J_{\text{C-F}} = 9.1$)	129.94	127.00

^a For the atomic numbering scheme, see Scheme 1. ^b $\delta_{\text{CF}} = -27.373$.

bisphenoxides **3a–e** in *N,N*-dimethylacetamide (DMAA) according to Scheme 2.

The high reactivity of difluoride **2a** under conditions of polycondensation allowed us to prepare high-molecular-weight PAEK. The properties of the resulting cardo PAEK are given in Table 3. Polycondensation with the use of chloride **2b** or bromide **2c** afforded low-molecular-weight polymers. It should be noted that dichloride **2b** is characterized by a substantially lower reactivity compared to 4,4'-dichlorobenzophenone. For example, a polymer with the reduced viscosity (η_{red}) of 0.3 dL g^{-1} was prepared from bisphenol **3a** and dichloride **2b** after

55 h, while a polymer with $\eta_{\text{red}} = 0.84 \text{ dL g}^{-1}$ was obtained from bisphenol **3a** and 4,4'-dichlorobenzophenone under analogous conditions after 30 h.⁶ The introduction of the cardo group (either as a component of cardo dihalide or cardo bisphenol) into the polymer chain leads to an increase in T_g of polymers compared to those of PAEK which do not contain the cardo group. For example, PAEK based on 4,4'-difluorobenzophenone and bisphenols **3a** and **3e** have T_g of 155 and 167 °C, respectively; T_g for PAEK based on 4,4'-bis-(4-fluorobenzoyl)biphenyl and **3a** and for cardo PAEK based on **2a** and **3a** are 180 and 215 °C, respectively.

The synthesized amorphous PAEK are soluble in DMAA, CHCl_3 , CH_2Cl_2 , THF, *m*-cresol, cyclohexanone, etc. and form strong transparent films.

Therefore, we synthesized for the first time activated di(fluoro, chloro, bromo) derivatives containing the cardo (phthalide) group and amorphous high-molecular-weight cardo homo-PAEK based on them. The resulting homo-PAEK are characterized by high T_g (up to 250 °C). High-molecular-weight PAEK were prepared only with the use of the difluoro derivative.

Conventional polymerization by nucleophilic substitution with the use of dichloro and dibromo derivatives, unlike dichloro- and dibromobenzophenone, did not allow us to prepare high-molecular-weight PAEK. Apparently, these derivatives can be used in polycondensation by nucleophilic substitution under more drastic conditions (at a temperature higher than 200–300 °C) or in the presence of catalysts (for example, copper compounds). In addition, these derivatives hold promise in a new procedure for the synthesis of polyarylene ketones including the formation of a C–C bond in the presence of nickel complexes.

Experimental

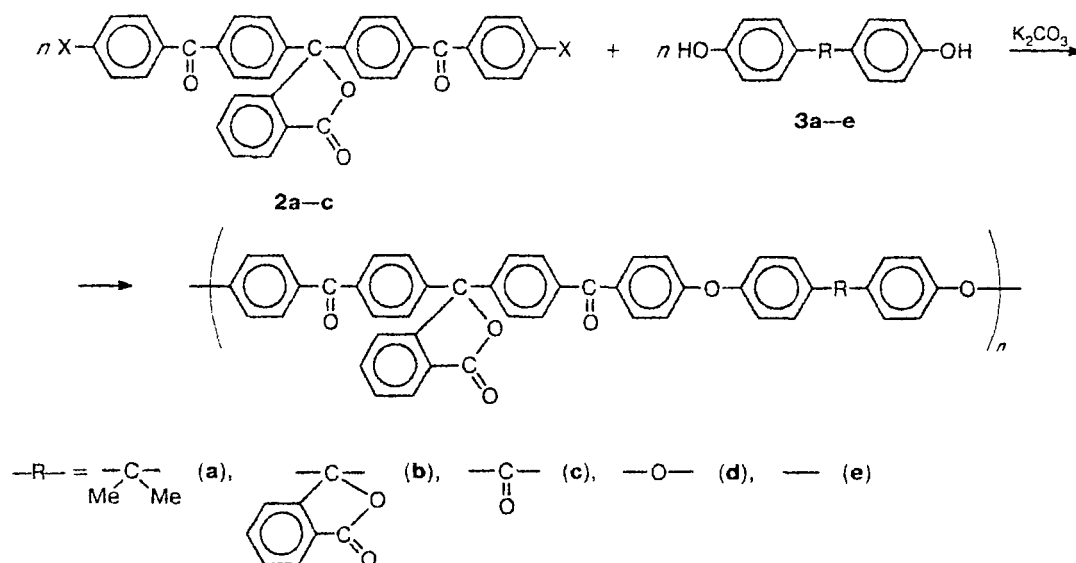
The viscosities of solutions of PAEK were measured in chloroform (0.5 g of the polymer per 100 mL of the solvent) at 25 °C.

Table 2. Chemical shifts and multiplicities of the signals in the ^1H NMR spectra of dihalides **2a–c** *

δ (J/Hz)		
2a	2b	2c
7.98 (d, 1 H, H(7), $^3J_{\text{H(6)-H(7)}} = 7.5$); 7.77 (t, 1 H, H(5), $^3J_{\text{H(4)-H(5)}} =$ $^3J_{\text{H(5)-H(6)}} = 7.5$); 7.65 (d, 1 H, H(4), $^3J_{\text{H(4)-H(5)}} = 7.5$); 7.62 (t, 1 H, H(6), $^3J_{\text{H(5)-H(6)}} = ^3J_{\text{H(6)-H(7)}} = 7.5$); 7.80 (dd, 4 H, H(17, 21), $^3J_{\text{H(17)-H(18)}} = 8.6$, $^4J_{\text{F-H(17)}} = 5.4$); 7.12 (t, 4 H, H(18, 20), $^3J_{\text{H(17)-H(18)}} = 8.6$, $^3J_{\text{F-H(18)}} = 8.6$); 7.74 (d, 4 H, H(11, 13), $^3J_{\text{H(10)-H(11)}} =$ 8.2); 7.49 (d, 4 H, H(10, 14), $^3J_{\text{H(10)-H(11)}} = 8.2$)	8.00 (d, 1 H, H(7), $^3J_{\text{H(6)-H(7)}} = 8.0$); 7.78 (t, 1 H, H(5), $^3J_{\text{H(4)-H(5)}} =$ $^3J_{\text{H(5)-H(6)}} = 8.0$); 7.68 (d, 1 H, H(4), $^3J_{\text{H(4)-H(5)}} = 8.0$); 7.64 (t, 1 H, H(6), $^3J_{\text{H(5)-H(6)}} = ^3J_{\text{H(6)-H(7)}} = 8.0$) 7.77 (d, 4 H, H(17, 21), $^3J_{\text{H(17)-H(18)}} = 8.4$); 7.43 (d, 4 H, H(18, 20), $^3J_{\text{H(17)-H(18)}} = 8.4$) 7.72 (d, 4 H, H(11, 13), $^3J_{\text{H(10)-H(11)}} =$ 8.4); 7.50 (d, 4 H, H(10, 14), $^3J_{\text{H(10)-H(11)}} = 8.4$)	7.98 (d, 1 H, H(7), $^3J_{\text{H(6)-H(7)}} = 7.6$); 7.77 (t, 1 H, H(5), $^3J_{\text{H(4)-H(5)}} =$ $^3J_{\text{H(5)-H(6)}} = 7.6$); 7.65 (d, 1 H, H(4), $^3J_{\text{H(4)-H(5)}} = 7.6$); 7.62 (t, 1 H, H(6), $^3J_{\text{H(5)-H(6)}} = ^3J_{\text{H(6)-H(7)}} = 7.6$) 7.64 (d, 4 H, H(17, 21), $^3J_{\text{H(17)-H(18)}} = 8.4$); 7.59 (d, 4 H, H(18, 20), $^3J_{\text{H(17)-H(18)}} = 8.4$) 7.74 (d, 4 H, H(11, 13), $^3J_{\text{H(10)-H(11)}} = 8.4$); 7.49 (d, 4 H, H(10, 14), $^3J_{\text{H(10)-H(11)}} = 8.4$)

* For the atomic numbering scheme, see Scheme 1.

Scheme 2



The ^{13}C and ^1H NMR spectra were recorded on a Bruker AMX-400 spectrometer (100.61 and 400.13 MHz for ^{13}C and ^1H , respectively) in CDCl_3 with Me_4Si as the internal standard. The ^{19}F NMR spectrum was recorded on a Bruker WP-200 spectrometer (168.31 MHz) in CDCl_3 with CF_3COOH as the external standard. The assignment of the signals in the ^{13}C and ^1H NMR spectra was made based on the calculated data obtained according to the additive scheme.

The IR spectra were recorded on a Perkin-Elmer 457 spectrometer.

Thermomechanical testing of the polymers was carried out according to a procedure reported previously.¹⁰

The crystallinity of the polymers was estimated based on X-ray diffraction patterns obtained on a DRON-3 instrument.

3,3-Diphenylphthalide-4',4''-dicarboxylic acid dichloride (1) was synthesized by the reaction of 3,3-diphenylphthalide-4',4''-dicarboxylic acid with SOCl_2 according to a known procedure.⁷

3,3-Bis[4-(4-fluorobenzoyl)phenyl]phthalide (2a). A mixture of 3,3-diphenylphthalide-4',4''-dicarboxylic acid dichloride (7.5 g, 0.018 mol), fluorobenzene (25 mL, 0.27 mol), and finely powdered AlCl_3 (9.5 g, 0.071 mol) was refluxed with stirring for 16 h. Then the reaction mixture was poured into ice water. The precipitate was filtered off and washed with water

until the reaction mixture became neutral. Then the remaining fluorobenzene was steam-distilled. The yield was 9.6 g (99%). After extraction of impurities with boiling EtOH and crystallization from a 1 : 1 (v/v) EtOH-PhMe mixture, the white crystalline difluoride was obtained, m.p. 184.5–185.5 °C. Found (%): C, 77.29; H, 3.66; F, 7.28. $\text{C}_{34}\text{H}_{20}\text{F}_2\text{O}_4$. Calculated (%): C, 76.98; H, 3.77; F, 7.17.

3,3-Bis[4-(4-chlorobenzoyl)phenyl]phthalide (2b) was synthesized analogously to 2a. The yield of the crude product was 96%. After extraction of impurities with boiling EtOH, crystallization from PhMe, PhCl, and glacial AcOH, washing with ether, and crystallization from PhMe, the white crystalline dichloride was obtained, m.p. 217.5–218.0 °C. Found (%): C, 72.61; H, 3.76; Cl, 12.33. $\text{C}_{34}\text{H}_{20}\text{Cl}_2\text{O}_4$. Calculated (%): C, 72.47; H, 3.55; Cl, 12.61.

3,3-Bis[4-(4-bromobenzoyl)phenyl]phthalide (2c) was synthesized analogously to 2a. The yield of the crude product was 85%. After extraction of impurities with boiling EtOH, crystallization from PhMe, the white crystalline dibromide was obtained, m.p. 212.5–213 °C. Found (%): C, 62.63; H, 3.27; Br, 24.10. $\text{C}_{34}\text{H}_{20}\text{Br}_2\text{O}_4$. Calculated (%): C, 62.58; H, 3.08; Br, 24.54.

2,2-Bis(4-hydroxyphenyl)propane (3a) ("A" grade, "Khimprom" Ufa Research and Production Association) was additionally purified according to a procedure reported previously.⁸

3,3-Bis(4-hydroxyphenyl)phthalide (phenolphthalein) (3b) ("Pharmacopoeia" grade, Moscow Alkaloid Plant), m.p. 260.5–261.0 °C, was dried at 120 °C for 4 h.

4,4'-Dihydroxybenzophenone (3c), m.p. 212.5–213.0 °C, was synthesized according to a procedure reported previously.⁹

4,4'-Dihydroxydiphenyl oxide (3d) was purified by crystallization from ethanol and sublimation at 175 °C (1×10^{-3} Torr), m.p. 167.0–168.0 °C.

4,4'-Dihydroxybiphenyl (3e). 4,4'-Dibromobiphenyl (20 g, 0.06 mol) and a solution of KOH (14.62 g, 0.26 mol) in water (250 mL) were placed into an autoclave. Hydrolysis was carried out at 250 °C for 6 h. After cooling, the reaction mixture was filtered. Then concentrated HCl (30 mL) was added to the filtrate and the mixture was filtered once again. The precipitates

Table 3. Reduced viscosities η_{red} and glass transition temperatures T_g of PAEK based on difluoride 2a

Bisphenol	$\eta_{\text{red}}/\text{dL g}^{-1}$	$T_g/^\circ\text{C}^*$
3a	1.30	215
3b	1.52	250
3c	0.74	220
3d	0.82	210
3e	1.00	>230

* T_g was determined from the thermomechanical curve.

were combined, washed with water until the mixture became neutral, and dried at 130 °C for 8 h. The resulting product was crystallized from EtOH three times, dried at 140 °C for 10 h, and sublimed at 180 °C (1×10^{-3} Torr). The yield was 5.7 g (48%), m.p. 286.0–286.5 °C (lit. data¹⁰: 284.0–284.5 °C).

Synthesis of PAEK (general procedure). A mixture of difluoride **2a** (21.8 g, 0.1 mol), bisphenol **3** (0.1 mol), and K_2CO_3 (18 g, 0.13 mol) that has preliminarily been ground and calcined in DMAA (200 mL) and PhCl (100 mL) was purged with argon and heated at 185 °C with azeotropic distillation of water. Heating was continued for 6–10 h (55 h when **2b** was used). Then the reaction mixture was cooled, chloroform was added, and the resulting solution was filtered. The polymer was precipitated with EtOH, successively washed with EtOH, water, and EtOH, and dried with a gradual increase in the temperature from 60 to 140 °C for 18 h and then at 150 °C for 22 h. The yield was 98.5 %.

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