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Influence of isomerism of difluorobenzophenone on the synthesis and properties of poly(arylene ether ketones)

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The influence of isomerism of difluorobenzophenone on the efficiency of polycondensation and the properties of homo- and copoly(arylene ether ketones) was studied. The latter were prepared by the reaction of 2,4′- and 4,4′-difluorobenzophenone with potassium diphenolates of bisphenol A and phenolphthalein in *N,N*-dimethylacetamide. A high content of an admixture of the 2,4′-isomer in 4,4′-difluorobenzophenone decreases the molecular weight of related poly(arylene ether ketones) and has no substantial effect on their glass transition temperature.

Key words: 2,4′-difluorobenzophenone, 4,4′-difluorobenzophenone, isomers, potassium diphenolate, nucleophilic substitution, polycondensation, poly(arylene ether ketones), molecular weight, glass transition temperature.

The problem of optimization of conditions for synthesis and the ways of controlling the molecular weight (MW) and properties of polymers is urgent in chemistry of poly(arylene ether ketones) (PAEK).[1—3] It is known that the presence of admixtures in monomers used for polycondensation can substantially affect the results of polycondensation and properties of the polymer obtained.

This work is aimed at studying the influence of isomerism of difluorobenzophenone on polycondensation *via* the mechanism of nucleophilic substitution of aryl halide and the properties of PAEK. The problem of isomerism of difluorobenzophenone is general regardless of the method of its synthesis. For example, the 2,4′-isomer can be formed not only in the synthesis of difluorobenzene by the method described below but also by other known methods, *viz.*, by the reaction of fluorobenzene with phosgene.

Results and Discussion

Compound **1a**, prepared according to Scheme 1, was used in the synthesis of PAEK.

The formation of **1b** along with **1a** was found by HPLC. A mixture of the 4,4′- (67%) and 2,4′-isomers (33%) was isolated from the reaction mixture. Treatment by hydrolysis, filtration, washing, and crystallization enriches the mixture in the 4,4′-isomer. Data in Table 1 indicate a change in the ratio of two isomers after each crystallization and also show the influence of the isomeric composition on the melting point of **1a**. Crystallization from EtOH decreases the concentration of the 2,4′-isomer from 12.7 to 0.3% (*cf.* fractions *1* and *13*) after three crystallizations, and no 2,4′-isomer was detected after final crystallization from hexane. This can clearly be illustrated by a comparison of Figs. 1 and 2. A high content of the 2,4′-isomer in sample **1a** decreases

Scheme 1

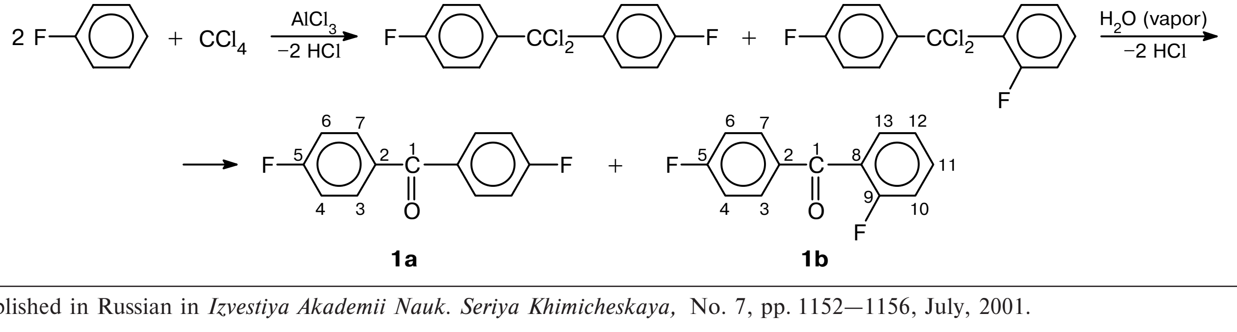

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Table 1. Influence of crystallization on the isomeric composition and melting point of difluorobenzophenone

Crystallization	Solvent	Analyzed fraction[a]	Content by HPLC data (wt. %)			M.p. /°C
			1b	**1a**	X[b]	
I	EtOH	*1*	12.7	93.3	—	95.0—101.0
		2	70.0	21.7	8.3	60.0—76.0
		3	6.5	94.5	—	99.0—103.0
		4	66.0	26.1	7.9	69.0—82.0
II	EtOH	*5*	1.6	98.4	—	105.5—107.0
		6	53.0	40.8	6.2	80.0—95.5
		7	1.1	98.9	—	105.5—106.5
		8	37.0	63.0	—	90.0—100.0
III	EtOH	*9*	0.4	99.6	—	106.0—107.5
		10	30.0	70.0	—	95.0—97.0
		11	0.3	99.7	—	106.0—107.5
		12	9.5	90.5	—	102.0—103.0
IV	Гексан	*13*	0.3	99.7	—	106.5—107.0
		14	4.0	96.0	—	105.0—106.5
		15	—[c]	99.7	—	107.0—107.5
		16	—[c]	99.7	—	106.0—107.0

[a] *1, 5, 9,* and *13* are the product after the first, second, third, and fourth crystallization, respectively; *2, 6, 10,* and *14* are the mother liquor after the first, second, third, and fourth crystallization, respectively; *3, 7, 11,* and *15* are the product after the first, second, third, and fourth crystallization, respectively, and washing with a solvent; *4, 8, 12,* and *16* are the solvent used for washing of the product after the first, second, third, and fourth crystallization, respectively.

[b] It can be assumed that 2,2′-difluorobenzophenone is the nonidentified component (X).

[c] The admixture of **1b** is << 0.3 wt.%, found qualitatively.

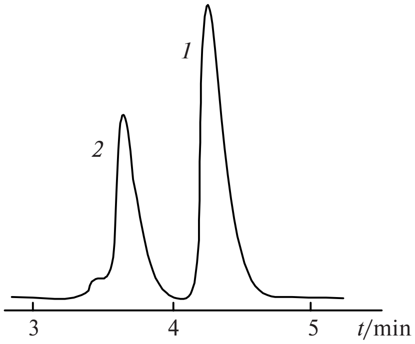


Fig. 1. Chromatogram of nonpurified compound **1a**. Eluent methylene chloride—hexane, 3 : 1. Peak *1* corresponds to **1a**, *2* corresponds to **1b**.

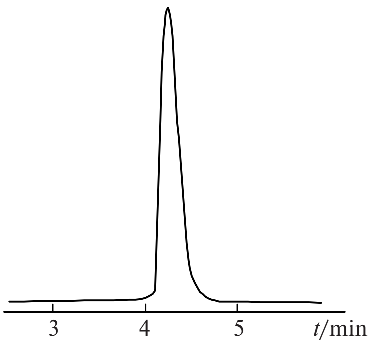


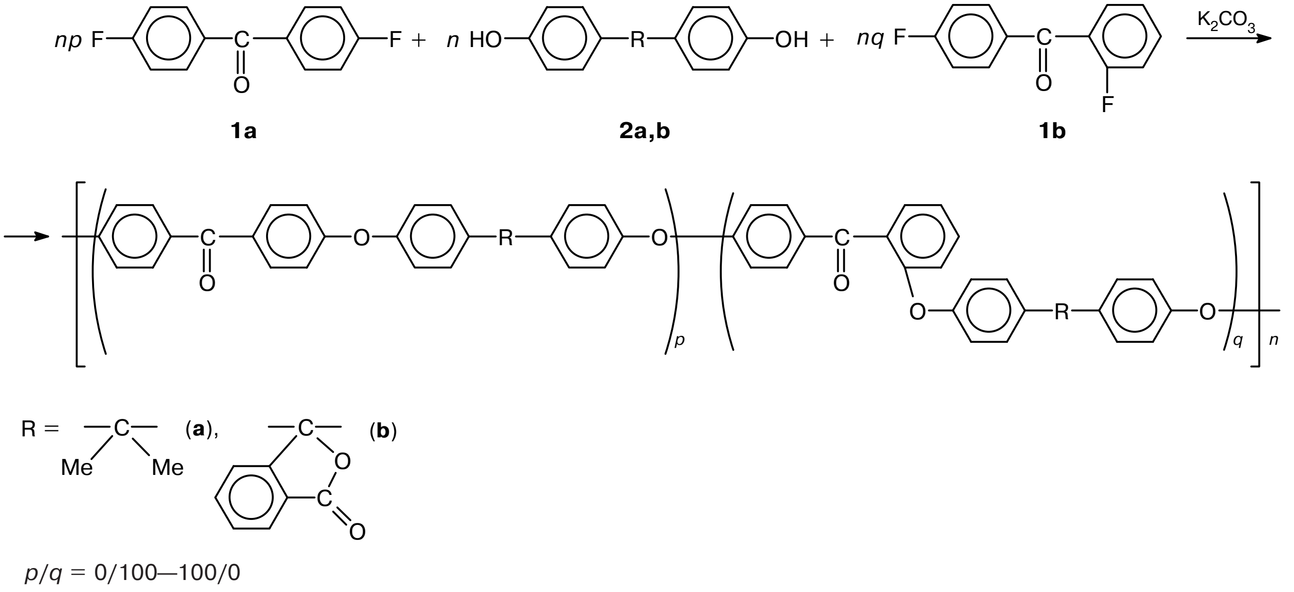
Fig. 2. Chromatogram of purified compound **1a**. Eluent methylene chloride—hexane, 2 : 1.

sharply the melting point and extends the melting interval.

For using compound **1a** obtained by Scheme 1 in polymer synthesis, it was important to study the influence of **1b** (this monomer was synthesized by the condensation of 2-fluorobenzoyl chloride with fluorobenzene) on the MW and properties of the obtained PAEK. With the purpose for studying the influence of the isomeric composition of difluorobenzophenone on polycondensation, we obtained homopolymers based on monomers **1a**,**b** and **2a**,**b** and copolymers at different ratios of the starting monomers (Scheme 2).

A comparison of the IR spectra of the homopolymers based on **1a**,**b** and **2a** in the region of 600—900 cm^{-1} does not allow us to pick out a sufficiently intense and isolated absorption band for the identification of the *ortho*-substituted derivative. The type of substitution is more pronounced in other spectral regions. For example, the type of substitution noticeably affects the position of the band of stretching vibrations of C=O. For the homo-PAEK based on **1a**, the maximum of the band of stretching vibrations of C=O is observed at 1651 cm^{-1}, and in the spectrum of the **1b**-based homopolymer it is observed at 1662 cm^{-1}. The most significant differences are observed in the region of 1400—1500 cm^{-1}. The spectrum of the homopolymer based on **1b** exhibits two rather intense bands, which do not overlap with other bands, with maxima at 1480 and 1446 cm^{-1}. These two bands can serve as a good indicator for determining the *ortho*-substituted fragments in copolymers. However, a comparison of the IR spec-

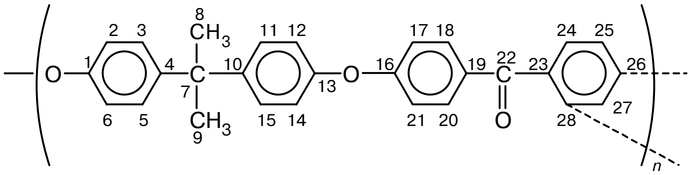
Scheme 2



tra of copolymers with different compositions with each other and homopolymers shows the identity of the spectra of all copolymers (when the content of fragments **1b** ≤ 10 mol.%) with the homopolymer containing fragment **1a**. Additional studies are necessary to reveal reasons for this fact.

The structure of the synthesized homo-PAEK based on **1a**,**b** and **2a** was also confirmed by the data of ^{1}H and ^{13}C NMR spectroscopy (Table 2). The ^{1}H NMR spectrum of the homopolymer based on **1b** and **2a** has a specific feature: the presence of a triplet of protons of methyl groups at C(8) and C(9) with δ 1.61, 1.66, and

Table 2. Chemical shifts and multiplicities of signals in ^{1}H and ^{13}C NMR spectra of homo-PAEK based on **1a** or **1b** and **2a**



Homo-PAEK	δ	
	^{1}H	^{13}C
1a + **2a**	1.72 (s, 6 H, H(8), H(9)); 7.00 (d, 4 H, H(2), H(6), H(12), H(14))[a]; 7.03 (d, 4 H, H(17), H(21), H(25), H(27))[a]; 7.28 (d, 4 H, H(3), H(5), H(11), H(15))[a]; 7.79 (d, 4 H, H(18), H(20), H(24), H(28))[a]	30.68 (C(8), C(9)); 41.98 (C(7)); 114.68 (C(17), C(21), C(25), C(27)); 118.37 (C(2), C(6), C(12), C(14)); 127.39 (C(18), C(20), C(24), C(28)); 131.65 (C(3), C(5), C(11), C(15)); 131.77 (C(19), C(23)); 146.36 (C(4), C(10)); 153.07 (C(16), C(26)); 161.04 (C(1), C(13)); 193.69 (C(22))
1b + **2a**	1.61, 1.66, 1.71 (t, 6 H, H(8), H(9)); 7.82 (d, 2 H, H(18), H(20))[b]; 6.79—7.60 (м)	30.63 (C(8), C(9)); 41.70, 41.81, 41.95 (C(7)); 116.78 (C(17), C(21)); 118.00 (C(27)); 118.51 (C(2), C(6), C(12), C(14)); 119.28 (C(18), C(20)); 123.00 (C(25));127.71 (C(23)); 128.05 (C(3), C(5), C(11), C(15)); 129.60 (C(24)); 133.00 (C(26)); 152.91 (C(4), C(10)); 154.36 (C(28)); 154.60 (C(16)); 154.60 (C(16)); 194.03 (C(22))

[a] $^3J_{\mathrm{H,H}}$ = 8.3 Hz.
[b] $^3J_{\mathrm{H,H}}$ = 7.6 Hz.

1.71 and relative integral intensities of 1.2, 2.1, and 1.0, respectively. In the ^{13}C NMR spectrum of the homopolymer based on **1b** and **2a**, the C(8) and C(9) atoms of the methyl groups appear as a singlet signal at δ 30.63 ($\Delta\nu = 0.09$ ppm). By contrast, the signal from C(7) is observed as a triplet with δ 41.70, 41.81, and 41.95 and relative integral intensities of 1.4, 2.3, and 1.0. The presence of this triplet splitting of the corresponding signals in the ^{1}H and ^{13}C NMR spectra is due to the presence in the macromolecule of fragments **2a** with different types of substitution (*o,o′*, *o,p′*, *p,o′*, and *p,p′*) in two adjacent phenoxy groups with ratios close to the statistical one.

A study of the dynamics of changing MW of the homo-PAEK based on **1b** and **2a**,**b** showed that a lower activity of **1b** compared to **1a**, which is illustrated by a much slower increase in the reduced viscosity (η_{red}) of polymers in time compared to the homo-PAEK based on **1a** and **2a**,**b**.[1–3] The η_{red} values of the homo-PAEK based on **1b** and **2a** were 0.06, 0.18, and 0.20 dL g^{-1} after 3, 7, and 50 h, respectively, and those for the homo-PAEK based on **1b** and **2b** were 0.10, 0.18, and 0.13 dL g^{-1}. This indicates that a sharp increase (to 50 h) in the polycondensation duration is not efficient. The decrease in η_{red} of the homo-PAEK based on **2b** after 50-h synthesis is due, most likely, to destructive processes, which is indirectly indicated by strong darkening of the reaction mixture.

A comparison of the MW of **2a**-based PAEK and difluorobenzophenone isomers **1a** and **1b**, obtained under similar conditions and presented in Table 3, indicates a more than tenfold decrease in $\bar{M}_w$ when the 4,4′-isomer is replaced by the 2,4′-isomer (*cf.*, the data for the **1a**-based homo-PAEK obtained without MW regulation and for the **1b**-based homo-PAEK). Similarly, the PAEK based on **2b** and **1a**,**b** differ strongly by η_{red}.

The decrease in MW is a result of a considerable decrease in the reactivity of the F atom in the *ortho*-position to the activating group as compared to the *para*-position due to steric hindrances in the reaction with a sufficiently bulky nucleophile. The resulting MW is determined (at the rigidly equivalent ratio of monomers) by the ratio of the rates of the main chain growth reaction and side reactions, which restrict the chain growth. Probably, the MW restriction can be due to the fact that, in this case, the competing reaction with a stronger base, potassium hydroxide, and macrocyclization is most favorable. A comparison of the relative reactivities of the functional groups of molecules **1a**,**b** in the reaction with **2a** showed that in the symmetric monomer **1a** the reactivity of the second functional group decreases fourfold after the transformation of the first group into the ether bond. Meanwhile, in the case of the nonsymmetric monomer **1b**, the reactivity differs already by at least ten times (this problem will be considered in detail elsewhere). Thus, the halogen atom

Table 3. Influence of the chemical structure of homo- and co-PAEK based on **1a**,**b** and **2a**,**b** on η_{red}, $\bar{M}_w$, T_g, and mechanical properties of the films

Bisphenol	Molar ratio **1a** : **1b**	η_{red} /dL g^{-1}	$\bar{M}_w \cdot 10^{-3}$	T_g[a] /°C	$\bar{\sigma}_0$	$\bar{\sigma}$	$\bar{\sigma}_{int}$	$\bar{E} \cdot 10^{-3}$	$\bar{\varepsilon}_0$	$\bar{\varepsilon}$
					MPa				%	
2a	0 : 100	0.20	15.8[b] 9.6[d]	140	—[c]	—	—	—	—	—
	90 : 10	0.54	50[b] 45[d]	165	61	79	—	1.7	6.4	236
	97 : 3	0.68	—	145	71	70	—	1.9	5.5	110
	98 : 2	0.65	—	145	74	70	131	1.8	6.0	127
	99 : 1	0.95	—	150	69	66	109	2.0	6.5	79
	100 : 0	0.30[e]	10[d]	150	—[c]	—	—	—	—	—
		0.53[e]	22[d]	160	70	83	—	1.6	5.2	214
		0.75[e]	39[d]	165	62	95	—	1.6	4.6	240
		2.40	230[d]	160	70	95	195	1.9	5.3	240
2b	0 : 100	0.13	—	—	—[c]	—	—	—	—	—
	90 : 10	1.00	—	210	104	89	140	2.4	7.0	40
	97 : 3	1.02	—	210	101	84	135	2.0	8.0	57
	98 : 2	1.07	—	210	—	101	—	1.9	—	8
	99 : 1	1.28	—	225	101	87	143	3.0	7.0	15
	100 : 0	5.2	—	245	100	105	200	2.0	6.8	172

[a] The temperature corresponding to the interception point of tangents to the branches of the thermomechanical curve in the region of flow beginning was taken as T_g.

[b] $\bar{M}_w$ was determined using the light scattering method by T. P. Bragina at the Laboratory of Physical Chemistry of Polymers (Institute of Organoelement Compounds, RAS).

[c] The polymer forms brittle films, which are spilled on the support during molding and drying.

[d] $\bar{M}_w$ was determined by GPC using the calibration for PAEK based on **2a**.

[e] The samples of homo-PAEK were obtained using the monofunctional reagent 4-fluorobenzophenone as a regulator of MW.

in the *ortho*-position to the C=O group in molecule **1b** is more than 2.5-fold more active than the second halogen atom in the *para*-position in molecule **1a**. It follows from this that **1a** containing almost no 2,4′-isomer should be used for the synthesis of high-molecular PAEK.

A comparison of the glass transition temperatures (T_g) and some physicomechanical properties of the films (the forced elasticity limit ($\bar{\sigma}_0$), strength at the rupture moment calculated per initial cross section of the sample ($\bar{\sigma}$), deformation at which the forced elasticity limit appears ($\bar{\varepsilon}_0$), relative elongation upon rupture ($\bar{\varepsilon}$), strength at the rupture moment calculated per true cross-section of the sample ($\bar{\sigma}_t$), and high-elasticity modules ($\bar{E}$)) of the synthesized amorphous homo- and co-PAEK shows that the presence of fragments **1b** in them has no substantial effect on the studied properties of these polymers compared to the **1a**-based homopolymers.

The conformational properties of the macromolecules containing fragments **1a** and **1b** differ most significantly. This is expressed, first, in a decrease in η_{red} of polymer solutions at the same MW (see Table 3); second, in underestimated $\bar{M}_w$ values of the **1b**-based polymers determined by GPC and calculated using the calibration for the **1a**-based polymers (see Table 3) compared to the absolute $\bar{M}_w$ values measured by the light scattering method; third, in an increase in the content of cyclic oligomers in reaction mixtures (cyclic dimer, from 2.6 to 3.8% and trimer, from 1.3 to 1.8%). The results of the detailed study of cycle formation in these PAEK will be published elsewhere. The data presented in this work indicate a more closed conformation of the chains of the **1a**-based PAEK macromolecules, which should be expected from a comparison of the chemical structure of PAEK based on **1a** and **1b**. It can be assumed that a higher affinity to cycle formation during the synthesis of the **1b**-based polymers and a more closed conformation of the chains of the PAEK macromolecule prevent, along with the low activity of the *o*-halogen atom in **1b**, the preparation of PAEK with higher MW.

Experimental

An admixture of **1b** in **1a** was analyzed by normal-phase HPLC using a Milikhrom-1 instrument with a spectrophotometric detector on a microcolumn (5 cm × 2 mm) packed with the Silasorb-600 sorbent in a mixture of methylene chloride—hexane (3 : 1 or 2 : 1). The sample volume was 5—10 μL, and the concentration was 1—2 mg mL^{-1}. The method allows the separation of the peaks of **1a** and **1b** to the basic line with the resolution coefficient $R > 1$ and the quantitative determination of the concentration of each component. The peaks were identified by the specially synthesized pure isomers, and the response coefficients were calibrated at different λ. The average reproducibility of the results of determination of the content of **1b** by two measurements in a mixture was 0.2%. The procedure allowed the measurement of the concentration of **1b** to 0.3% and detection of admixtures up to <0.3%.

The molecular weight distribution and mean molecular weight of polymers were determined by GPC using a previously described procedure.[1,3] The mean molecular weight was measured by the light scattering method on a Fica photogoniodiffusimeter at 25 °C and λ = 546 nm in the vertically polarized light using the double extrapolation according to Simm. The instrument was calibrated by benzene.

^{1}H and ^{13}C NMR spectra for compounds **1a,b** and PAEK were recorded on an Bruker AMX-400 instrument (400.13 and 100.61 MHz, respectively) for solutions in CDCl$_3$ using Me$_4$Si as the internal standard. Signals in the ^{1}H and ^{13}C NMR spectra were assigned according to calculated data obtained by the additive scheme. ^{19}F NMR spectra for **1a,b** were recorded on a Bruker WP-200-SY spectrometer (188.31 MHz) for solutions in CDCl$_3$ using CF$_3$COOH as the external standard.

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

The reduced viscosity (η_{red}) of PAEK solutions was measured in CHCl$_3$ (at a concentration of 0.5 g of the polymer per 100 mL of the solvent) at 25 °C.

Thermochemical tests of polymers were carried out according to a previously described procedure.[4]

4,4′-Difluorobenzophenone (1a) was synthesized by a procedure[5] modified by us,[3] its m.p. was 107.5—108.0 °C after sublimation (*cf.* Ref. 6: m.p. 107.5—108.0 °C). The isomeric purity was monitored by HPLC (content of **1b** ≪ 0.3 wt.%). IR, ν/cm^{-1}: 1646 (C=O). ^{1}H NMR (CDCl$_3$), δ: 7.10 (dd, 4 H, H(4), H(6), $^3J_{H,H}$ = 8.8 Hz, $^3J_{F,H}$ = 8.8 Hz); 7.76 (dd, 4 H, H(3), H(7), $^3J_{H,H}$ = 8.8 Hz, $^3J_{F,H}$ = 5.2 Hz). ^{13}C NMR (CDCl$_3$), δ: 115.26 (C(4), C(6), $^2J_{C,F}$ = 21.7 Hz); 132.24 (C(3), C(7), $^3J_{C,F}$ = 9.2 Hz); 133.41 (C(2), $^4J_{C,F}$ = 2.9 Hz); 166.35 (C(5), $^1J_{C,F}$ = 254.6 Hz); 193.43 (C(1)). ^{19}F NMR (CDCl$_3$), δ: −28.03 (s, 1 F, C(5)F) (for the numeration of atoms, see Scheme 1).

2,4′-Difluorobenzophenone (1b) was synthesized by the reaction of 2-fluorobenzoyl chloride with fluorobenzene in the presence of AlCl$_3$ and FeCl$_3$ by a procedure modified by us,[3] m.p. 22.0—22.5 °C (*cf.* Ref. 7: m.p. 22.8—23.6 °C). IR, ν/cm^{-1}: 1664 (C=O). ^{1}H NMR (CDCl$_3$), δ: 7.13 (d, 2 H, H(4), H(6), $^3J_{H,H}$ = 8.8 Hz, $^3J_{F,H}$ = 8.8 Hz); 7.21 (t, 1 H, H(10), $^3J_{H,H}$ = 8.8 Hz, $^3J_{F,H}$ = 8.8 Hz); 7.26 (t, 1 H, H(12), $^3J_{H,H}$ = 8.8 Hz); 7.53 (m, 2 H, H(11), H(13)); 7.88 (dd, 2 H, H(3), H(7), $^3J_{H,H}$ = 8.8 Hz, $^3J_{F,H}$ = 5.6 Hz). ^{13}C NMR (CDCl$_3$), δ: 115.37 (C(4), C(6), $^2J_{C,F}$ = 22.1 Hz); 115.99 (C(10), $^2J_{C,F}$ = 21.3 Hz); 124.15 (C(12), $^4J_{C,F}$ = 3.6 Hz); 126.44 (C(8), $^2J_{C,F}$ = 14.9 Hz); 130.57 (C(13), $^3J_{C,F}$ = 2.8 Hz); 132.19 (C(3), C(7), $^3J_{C,F}$ = 9.2 Hz); 132.97 (C(11), $^3J_{C,F}$ = 8.0 Hz); 133.46 (C(2), $^4J_{C,F}$ = 2.4 Hz); 159.62 (C(9), $^1J_{C,F}$ = 252.2 Hz); 165.65 (C(5), $^1J_{C,F}$ = 255.8 Hz); 191.50 (C(1)). ^{19}F NMR (CDCl$_3$), δ: −33.34 (s, 1 F, C(9)F); −26.62 (s, 1 F, C(5)F) (for the numeration of atoms, see Scheme 1).

2,2-Bis(4′-hydroxyphenyl)propane (2a) (trade mark A, Ufa PO Khimprom, Russia) was additionally purified according to a previously described procedure.[8]

3,3-Bis(4′-hydroxyphenyl) phthalide (phenolphthalein) (2b) ("farmakopeinyi" trade mark, Moscow Alkaloid Plant) with m.p. 260.5—261.0 °C was dried for 4 h at 120 °C.

Synthesis of PAEK. Argon was passed through a four-necked flask with a stirrer, a pipe for argon supply, and a system for azeotropic water distillation. Then compound **1a** or **1b** (21.8 g, 0.1 mol), compound **2a** (22.8 g, 0.1 mol), preliminarily powdered and calcined K$_2$CO$_3$ (18 g, 0.13 mol), *N,N*-dimethylacetamide (200 mL), and PhCl (100 mL) were loaded into the flask. The temperature of the oil bath was gradually (within ~0.5 h) increased to 185 °C. The duration of the synthesis after the completion of the azeotropic water distillation off was 10 h (in the case of **1b**, 50 h). After the end of the synthesis, the reaction mixture was cooled, $CHCl_3$ was added, and the obtained solution was filtered to remove the salt and multiply washed with water. The polymer isolated as a film by the evaporation of the solvent was dried with a gradual increase in the temperature from 60 to 140 °C for 18 h and then at 150 °C for 25 h. The yield of PAEK was 40.0 g (98.5%).

When the dynamics of changing η_{red} was studied in time, the reaction mixture was sampled at time intervals.

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