Russian Chemical Bulletin, International Edition, Vol. 53, No. 9, pp. 2041—2044, September, 2004

Synthesis of poly(arylene ether ketones) with terminal phenolic groups

D. S. Sharapov,*★ *V. V. Shaposhnikova, S. N. Salazkin, I. A. Mamedova,
L. V. Dubrovina, I. V. Blagodatskikh, and T. A. Babushkina

A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,
28 ul. Vavilova, Moscow, 119991, Russian Federation.
Fax: +7 (095) 135 5085. E-mail: dimash@ineos.ac.ru

Poly(arylene ether ketones) with preset molecular weights (reduced viscosity from 0.2 to 0.82 dL g^{-1}) containing terminal phenolic groups were synthesized by the reactions of 4,4´-difluorobenzophenone with bisphenol A or phenolphthalein in the presence of K_2CO_3 in *N*,*N*-dimethylacetamide. The influence of an excess of bisphenols on the molecular weights of the polymers obtained was studied. The structures of the polymers were confirmed by ^{1}H NMR spectroscopy. The molecular weight distributions of the polymers were determined.

Key words: 4,4´-difluorobenzophenone, bisphenol A, phenolphthalein, polycondensation, nucleophilic substitution of activated aryl halide, poly(arylene ether ketones).

The possibility of controlling the chemical structure of block copolymers opens prospects for the synthesis of polymers exhibiting a variety of valuable properties. Poly(arylene ether ketones) (PAEK) are well known to possess high thermal and physico-mechanical properties.[1—3] Nevertheless, the perfection of synthetic routes to, and improvement of the properties of, these compounds remains topical. No synthesis of block poly(arylene ether ketones) by nucleophilic substitution of activated aryl halide has been reported so far. Therefore, the aim of the present study was to synthesize poly(arylene ether ketones) containing terminal phenolic groups and having preset molecular weights keeping in mind the possibility of using them as precursors for the synthesis of block copolymers following the reaction mentioned above. Here we present the results of a study on the influence of an excess of bisphenols on the molecular weigths of poly(arylene ether ketones), structure assessment using NMR spectroscopy, and molecular weight distributions of the polymers obtained.

Experimental

2,2-Bis(4-hydroxyphenyl)propane (bisphenol A) (1a) (A label, "pure" grade, "Khimprom" Ufa Production Association) was additionally purified following a known procedure;[4] m.p. 158.0—159.0 °C.

3,3-Bis(4-hydroxyphenyl)phthalide (phenolphthalein) (1b) ("pharmacopeia" grade, the Moscow Alkaloid Plant), m.p. 260.5—261.0 °C was dried at 120 °C for 4 h.

4,4´-Difluorobenzophenone (2), m.p. 107.5—108.0 °C was synthesized following a known procedure.[5]

Synthesis of poly(arylene ether ketones) containing terminal phenolic groups (general procedure). Synthesis was carried out in *N*,*N*-imethylacetamide (DMAA) at a monomer (**2**) concentration of 0.5 mol L^{-1}.

A mixture of compound **1** (0.0155—0.0164 mol), compound **2** (0.015 mol), thoroughly ground and calcined K_2CO_3 (0.0195—0.0214 mol), DMAA (30 mL) and freshly distilled chlorobenzene (15 mL) was stirred under argon with gradual (~0.5 h) heating to 185 °C (oil bath). After azeotropic distillation of water, the reaction mixture was heated for an additional 6 h, cooled (0.5—1.0 h), and dissolved in chloroform. The solution was filtered and washed with water (×10) with 5% HCl added to the initial washings to remove KF and non-consumed K_2CO_3. The polymer was isolated as a film by evaporating its solution in chloroform (3.0—4.0 g of the polymer per 100 mL of chloroform) and dried on gradual heating from 60 to 140 °C for 16 h and then at 150 °C for 25 h for poly(arylene ether ketones) based on **1a** and from 60 to 190 °C for 18 h and than at 200 °C for 22 h for poly(arylene ether ketones) based on **1b**.

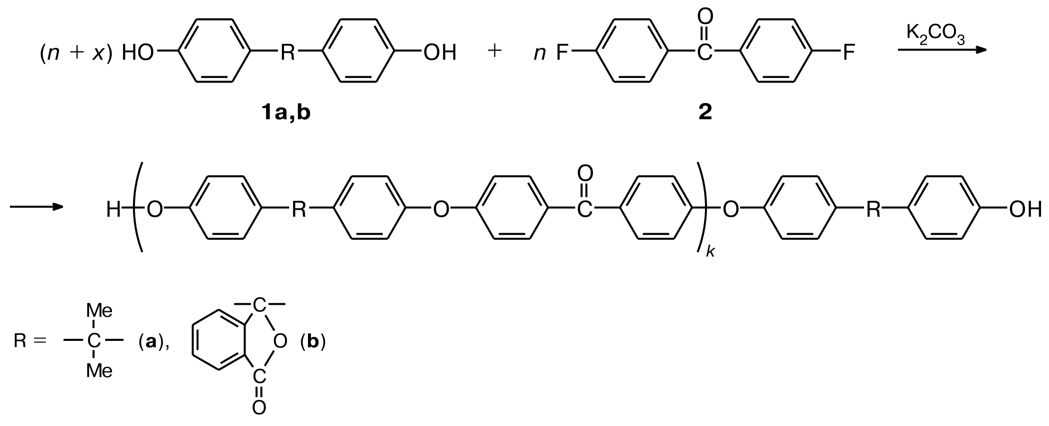
The reduced viscosities (η_{red}) of the polymers were determined using an Ostvald viscometer at 25 °C (0.5 g of the polymer in 100 mL of chloroform).

The molecular weight distribution and the average molecular weights of the polymers were determined by GPC on a Waters instrument comprising an H-600 pump, an M-410 refractometric detector, a Millenium data processing system, and two U-Styragel Linear columns. THF was used as the eluent at a rate of 1 mL min^{-1}. A universal calibration was carried out against PS standards using the following Mark-Houwink relations: $[\eta]_{PS} = 1.5 \cdot 10^{-4} \cdot M^{0.7}$ and $[\eta]_{PAEK} = 6.4 \cdot 10^{-4} \cdot M^{0.65}$ (*M* is the molecular weight of PAEK) following a known procedure.[5—7] The mass-average molecular weights ($\bar{M}_w$) were measured by light scattering on a Fica photogoniodiffusometer at $\lambda = 546$ nm in a vertically polarized light at 25 °C for a solition in chloroform using double extrapolation according to Zimm. The instrument was calibrated against benzene. The d*n*/d*c* = 0.248 was obtained using a Pulfrich refractometer with a differential cell.

^{1}H NMR spectra of the polymers containing terminal phenolic groups were recorded on a Bruker WX-250 spectrometer in $CDCl_3$ (the signal of the residual proton in $CDCl_3$ at δ 7.25 was used as the internal standard). Signals in the ^{1}H NMR spectra

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1958—1961, September, 2004.

Scheme 1



x = 0.5—9.5 mol.%

were assigned in accord with the results of calculations using the additivity scheme.

Results and Discussion

Poly(arylene ether ketones) containing terminal phenolic groups were synthesized by reactions of bisphenols **1a,b** with 4,4´-difluorobenzophenone **2** in DMAA (Scheme 1).

To obtain PAEK samples with preset molecular weights, we preliminarily calculated[8] the $\overline{M}_n$ values at different excesses of bisphenols (Table 1). The calculation for a 1 mol.% excess of **1a** with respect to **2** is presented below as an example.

The stoichiometric disbalance is given by:

$$r = N_F/N_{OH} = 2/2.02 = 0.99,$$

where N_F is the number of functional groups in molecule **2** and N_{OH} is the number of functional groups in molecule **1a**.

The number-average degree of polymerization is

$$\overline{X}_n = (1 + r)/(1 + r - 2pr) =$$
$$= (1 + 0.99)/(1 + 0.99 - 2 \cdot 0.996 \cdot 0.99) = 111,$$

where p = 0.996 is the degree of completion of the reaction (calculated from GPC data).

$$\overline{M}_n = M_0 \cdot \overline{X}_n,$$

where M_0 is the average of the molecular weights of compounds **1a** and **2**.

$$M_0 = M_{ru}/2 = 406/2 = 203,$$

where M_{ru} is the molecular weight of the repeating unit of the polymer based on compounds **1a** and **2**,

$$\overline{M}_n = 203 \cdot 111 = 22533.$$

The number of repeating units in the polymer chain is given by

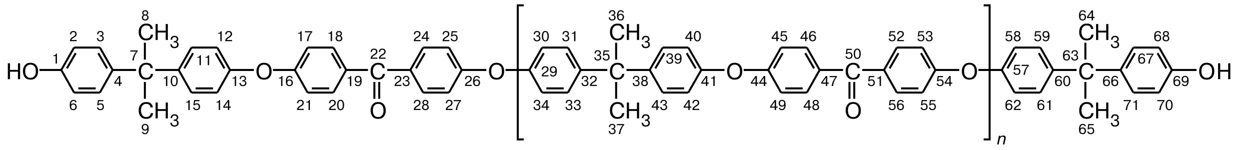
$$n = \overline{M}_n/M_{ru} = 22533/406 \approx 56.$$

Table 1. The effect of an excess of bisphenols on the molecular weight and reduced viscosity of poly(arylene ether ketones) based on compounds **1a,b** and **2**

Bisphenol	Excess of bisphenol (mol.%)	Molecular weights determined by different methods										η_{red} /dL g^{-1}
		Calculated		^{1}H NMR		Light scattering			GPC			
		$\overline{M}_n \cdot 10^{-3}$	n	$\overline{M}_n \cdot 10^{-3}$	n	$\overline{M}_w \cdot 10^{-3}$	$\overline{M}_n \cdot 10^{-3}$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_w \cdot 10^{-3}$	$\overline{M}_n \cdot 10^{-3}$	$\overline{M}_w/\overline{M}_n$	
1a	0*	50.75	125	—	—	—	—	—	—	—	—	2.3
	1	22.533	56	25.8	63	—	—	—	—	—	—	0.82
	3	10.597	26	12	29	25.1	11.7	2.14	22.5	12.1	1.86	0.42
	5	6.872	17	10.4	25	—	—	—	—	—	—	0.28
	9.5	3.979	10	4.3	10	7.01	—	—	8.7	4.9	1.77	0.2
1b	0*	62	125	—	—	270.0	—	—	—	—	—	2.26
	3	12.946	26	—	—	28.2	12.4	2.27	—	—	—	0.46
	9.5	4.861	10	—	—	8.8	—	—	—	—	—	0.20

* Data given for comparison.

Table 2. Chemical shifts and multiplicities of signals in the ^{1}H NMR spectra of poly(arylene ether ketones) based on compounds **2** and **1a** containing terminal phenolic groups (η_{red} = 0.42 dL g^{-1}) and containing no terminal phenolic groups (η_{red} = 0.75 dL g^{-1})[9]



δ (*J*/Hz)	
η_{red} = 0.42 dL g^{-1}	η_{red} = 0.75 dL g^{-1} *
1.66 (s, H(8), H(9), H(64), H(65));	
1.72 (s, H(36), H(37));	1.72 (s, H(36), H(37));
7.00 (d, H(2), H(6), H(12), H(14), H(30), H(34), H(40), H(42), H(58), H(62), H(68), H(70), $^3J_{H,H}$ = 8.3);	7.00 (d, H(30), H(34), H(40), H(42), $^3J_{H,H}$ = 8.3);
7.03 (d, H(17), H(21), H(25), H(27), H(45), H(49), H(53), H(55), $^3J_{H,H}$ = 8.3);	7.03 (d, H(45), H(49), H(53), H(55), $^3J_{H,H}$ = 8.3);
7.28 (d, H(3), H(5), H(11), H(15), H(31), H(33), H(39), H(43), H(59), H(61), H(67), H(71), $^3J_{H,H}$ = 8.3);	7.28 (d, H(31), H(33), H(39), H(43), $^3J_{H,H}$ = 8.3);
7.78 (d, H(18), H(20), H(24), H(28), H(46), H(48), H(52), H(56), $^3J_{H,H}$ = 8.3)	7.79 (d, H(46), H(48), H(52), H(56), $^3J_{H,H}$ = 8.3)

* Published data[9] are given for comparison.

Taking into account the results reported earlier[6] and the results of calculations of $\overline{M}_n$ and *n*, we synthesized samples of poly(arylene ether ketones) based on compounds **2** and **1a,b** at different excesses of bisphenols (see Table 1). Studies of the effect of the excess of a bisphenol on the reduced viscosity of polymers showed that polycondensation in the presence of an excess of compound **1a** (1 mol.%) results in dramatic decrease in η_{red} from 2.3 to 0.82 dL g^{-1}. An increase in the excess of compound **1a** from 1 to 3 mol.% favors a substantial decrease in η_{red} from 0.82 to 0.42 dL g^{-1}. Further increase in the excess of **1a** from 5 to 9.5 mol.% has a little effect on the molecular weights of the polymers. A similar trend was observed for the poly(arylene ether ketones) based on compound **1b**.

The structures of the polymers synthesized were confirmed by ^{1}H NMR spectroscopy (Tables 2 and 3).* According to ^{1}H NMR data for the polymers based on compounds **2** and **1a** containing terminal phenolic groups (see Table 2; data for the polymer with η_{red} = 0.42 dL g^{-1} are presented below as an example), signals of the terminal methyl protons H(8), H(9), H(64), and H(65) and the internal methyl protons (H(36) and H(37)) appear as singlets at δ 1.66 and 1.72 with the relative integrated intensities of 1 and 4.5—31 (depending on the excess of compound **1a**), respectively. For the polymer based on compounds **2** and **1a** containing no terminal phenolic groups (η_{red} = 0.75 dL g^{-1}, the molecular weight of the polymer was controlled by using a monofunctional reactant 4-fluorobenzophenone), signals of both the internal methyl protons, H(36) and H(37), and the terminal methyl groups appear as singlets at δ 1.72.[9] The ^{1}H NMR spectra of the polymers based on compounds **2** and **1b** (see Table 3) both with and without terminal phenolic groups[9] were identical.

The use of ^{1}H NMR spectroscopy was efficient not only for the proof of the structures of the polymers synthesized, determination of the terminal phenolic groups of the polymers based on compounds **2** and **1a** but also for the calculation of the $\overline{M}_n$ and *n* values of the polymers containing terminal phenolic groups. The method of calculations of $\overline{M}_n$ and *n* is based on the difference between the chemical shifts of the terminal and internal methyl protons. As an example, we present calculations of $\overline{M}_n$ for the polyarylene ether ketone based on compounds **2** and **1a** and characterized by η_{red} = 0.42 dL g^{-1} (the excess of **1a** was 3 mol.%).

$$\overline{M}_n = M_1 \cdot n + M_2,$$

where M_1 is the molecular weight of the repeating unit of the polymer without inclusion of terminal groups; M_2 is the molecular weight of the $OC_6H_4CMe_2C_6H_4OH$ terminal group; *n* is the number of repeating units in the polymer;

$$P_1(n - 1) = 0.5P_2; \qquad P_1/0.5P_2 = (n - 1),$$

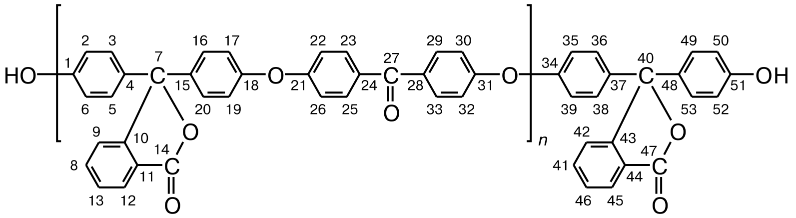
where P_1 is the integrated intensity of the peak corresponding to the internal methyl protons, and P_2 is the integrated intensity of the peak corresponding to twelve terminal methyl protons;

$$40.82/0.5 \cdot 2.97 = n - 1 = 27.5.$$

---

* The presence of terminal phenolic groups was supported by the results of allylation and benzoylation of the polymers obtained (D. S. Sharapov, V. V. Shaposhnikova, S. N. Salazkin, L. I. Komarova, and T. A. Babushkina; unpublished results).

Table 3. ^{1}H NMR spectra of poly(arylene ether ketones) based on compounds **2** and **1b** containing terminal phenolic groups (η_{red} = 0.46 dL g^{-1}) and containing no terminal phenolic groups (η_{red} = 0.50 dL g^{-1})[9]



δ (*J*/Hz)	
η_{red} = 0.46 dL g^{-1}	η_{red} = 0.50 dL g^{-1} *
7.02 (d, H(2), H(6), H(17), H(19), H(35), H(39), H(50), H(52), $^3J_{H,H}$ = 8.8);	7.02 (d, H(2), H(6), H(17), H(19), H(35), H(39), H(50), H(52), $^3J_{H,H}$ = 8.8);
7.03 (d, H(22), H(26), H(30), H(32), $^3J_{H,H}$ = 8.5);	7.04 (d, H(22), H(26), H(30), H(32), $^3J_{H,H}$ = 8.8);
7.36 (d, H(3), H(5), H(16), H(20), H(36), H(38), H(49), H(53), $^3J_{H,H}$ = 8.8);	7.37 (d, H(3), H(5), H(16), H(20), H(36), H(38), H(49), H(53), $^3J_{H,H}$ = 8.8);
7.57 (t, H(13), H(46), $^3J_{H,H}$ = 7.6);	7.58 (t, H(13), H(46), $^3J_{H,H}$ = 7.6);
7.60 (d, H(9), H(42), $^3J_{H,H}$ = 7.6);	7.60 (d, H(9), H(42), $^3J_{H,H}$ = 7.6);
7.73 (t, H(8), H(41), $^3J_{H,H}$ = 7.6);	7.73 (t, H(8), H(41), $^3J_{H,H}$ = 7.6);
7.77 (d, H(23), H(25), H(29), H(33), $^3J_{H,H}$ = 8.8);	7.77 (d, H(23), H(25), H(29), H(33), $^3J_{H,H}$ = 8.8);
7.96 (d, H(12), H(45), $^3J_{H,H}$ = 7.6)	7.95 (d, H(12), H(45), $^3J_{H,H}$ = 7.6)

* Published data[9] are given for comparison.

Thus,

$$n = 28.5;\ \bar{M}_n = 406 \cdot 28.5 + 228 = 11799.$$

Analogously, the $\bar{M}_n$ and n values for the poly(arylene ether ketones) based on compounds **2** and **1a** synthesized in the presence of 1, 5, and 9.5 mol.% excess of compound **1a** (see Table 1) were determined from the corresponding NMR spectra.

It should be noted that the $\bar{M}_n$ values for the poly(arylene ether ketones) based on compounds **2** and **1a** (with a 3 mol.% excess of compound **1a**) calculated from ^{1}H NMR spectral data are nearly equal to the $\bar{M}_n$ values determined from the Zimm diagrams and to the results of calculations (see Table 1).

Thus, we studied the influence of an excess of bisphenols (1 to 9.5 mol.%) on the molecular weights of poly(arylene ether ketones), which permitted the synthesis of polymer samples with preset η_{red} values (from 0.2 to 0.82 dL g^{-1}) containing terminal phenolic groups and necessary for further use in the synthesis of block copolymers. The structures of these poly(arylene ether ketones) was confirmed by ^{1}H NMR spectroscopy and their molecular weight distributions were determined.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32104).

References

1. G.Yoshihisa, *Kogyo Zairyo, Eng. Mater.*, 1985, **33**, 80.
2. M. J. Mullins and E. P. Woo, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, 1987, **27**, 313.
3. H. J. Mair, *Kunststoffberater*, 1998, **43**, Iss. 6, 14.
4. S. N. Salazkin, A. I. Kalachev, V. V. Korshak, and S. V. Vinogradova, Deposited in and available from VINITI, No. 1064 (14.04.75), Moscow, 1975, 22 pp. (in Russian).
5. V. V. Shaposhnikova, Ph.D. (Chem.) Thesis, A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, 1993, 141 pp. (in Russian).
6. V. V. Shaposhnikova, S. N. Salazkin, V. A. Sergeev, I. V. Blagodatskikh, L. V. Dubrovina, A. A. Sakunts, and S.-S. A. Pavlova, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2526 [*Russ. Chem. Bull.*, 1996, **45**, 2397 (Engl. Transl.)].
7. I. V. Blagodatskikh, L. V. Dubrovina, S.-S. A. Pavlova, A. A. Sakunts, S. N. Salazkin, V. V. Shaposhnikova, and V. A. Sergeev, *Vysokomol. Soedin., Ser. A*, 1991, **33**, 580 [*Polym. Sci., Ser. A*, 1991, **33** (Engl. Transl.)].
8. G. Odian, *Principles of Polymerization*, McGraw-Hill Book Company, New York, 1970.
9. V. V. Shaposhnikova, S. N. Salazkin, K. I. Donetskii, G. V. Gorshkov, D. S. Sharapov, I. A. Mamedova, P. V. Petrovskii, A. A. Askadskii, K. A. Bychko, V. V. Kazantseva, A. P. Krasnov, O. V. Afonicheva, A. S. Tkachenko, and M. M. Genina, *Vysokomol. Soedin., Ser. A*, 2002, **44**, 925 [*Polym. Sci., Ser. A.* 2002, **44**, 563 (Engl. Transl.)].

Received June 24, 2004;
in revised form September 1, 2004