General features of the reaction of 4,4'-difluorobenzophenone with potassium diphenoxide of 2,2-bis(4-hydroxyphenyl)propane

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The major factors determining molecular weights of polyarylene-ether ketones formed by the reaction of 4,4'-difluorobenzophenone with 2,2-bis(4-hydroxyphenyl)propane in the presence of K_2CO_3 were revealed. The optimum conditions for the preparation of high-molecular-weight polymers were found, and it was demonstrated that it is possible to control their molecular weights ($\bar{M}_w$ from 10 000 to 200 000).

Key words: 4,4'-difluorobenzophenone, dipotassium diphenoxide of 2,2-bis(4-hydroxyphenyl)propane, nucleophilic substitution of activated aryl halides; polycondensation, polyarylene-ether ketones.

Nucleophilic substitution of aryl halides activated with electronegative groups (NO_2, SO_2, CO, N=N, SO, oxadiazole ring, *etc.*) in dipolar aprotic solvents is widely used in the synthesis of high-molecular-weight polycondensation polymers[1—7] including polyarylene-ether ketones. However, only scattered data are available in the literature,[8] whereas systematic data on the general features of the synthesis of polyarylene-ether ketones by nucleophilic substitution are absent. The aim of this work is to study these general features.

Experimental

4,4'-Difluorobenzophenone (1a) was synthesized analogously to **1b** (see below), m.p. 107.5—108.0 °C. The isomeric purity was analyzed by HPLC (the content of the *o,p'*-isomer was << 0.3%).

4,4'-Dichlorobenzophenone (1b), m.p. 147.5—148.0 °C, was synthesized according to the known procedure[9] modified by us.[10]

2,2-Bis(4-hydroxyphenyl)propane (2) ("A" grade, the "Khimprom" Ufa Research and Production Association) was additionally purified according to the procedure reported previously.[11]

4-Fluorobenzophenone (3), m.p. 46.0—47.0 °C, was synthesized according to the known procedure[12] modified by us.[10]

Synthesis of polyarylene-ether ketones. Below is described a general procedure for polycondensation at the concentration of each monomer (*C*) of 0.5 mol per 1 L of *N,N*-dimethylacetamide (the **1a** : **2** : K_2CO_3 molar ratio was 1 : 1 : 1.3). In some cases, polycondensation was carried out under other conditions (the quantity of components, their concentrations, *etc.* were changed).

A four-neck flask equipped with a stirrer, a thermometer, a gas-inlet tube, and an adapter for azeotropic distillation of water was placed in an oil bath and purged with argon. Then **1a** (21.8 g, 0.1 mol), **2** (22.8 g, 0.1 mol), K_2CO_3 (18 g, 0.13 mol), which had previously been ground and calcined, *N,N*-dimethylacetamide (200 mL), and chlorobenzene (100 mL) were placed into the flask. The temperature of an oil bath was gradually increased (~0.5 h) to 185 °C. After completion of azeotropic distillation of water, the mixture was heated for 6—10 h (when **1b** was used, the mixture was heated for 30 h). After completion of the synthesis, the reaction mixture was cooled. Then chloroform was added, the solution was filtered, and the polymer was precipitated with ethanol. The precipitate was washed with ethanol, water, and once again with ethanol and dried at a gradually increasing temperature (from 60 to 140 °C) for 18 h and then at 150 °C for 22 h. The yield was 40.0 g (98.5%).

The effect of the reaction time on the reduced viscosity (η_{red}) and the average molecular weight ($\bar{M}_w$) were studied by withdrawing samples (10—15 mL) from the reaction mixture at certain intervals after the beginning of polycondensation. The samples were separated from salts and washed with water, and then the $\bar{M}_w$ values were determined by gel permeation chromatography (GPC) in chloroform. The values of η_{red} were measured for films prepared by casting from solutions in chloroform.

2,2-Bis[4-(*p*-benzoylphenoxy)phenyl]propane (4). Synthesis was carried out according to the procedure described above. Compounds **2** (9.70 g, 0.043 mol), **3** (17.85 g, 0.089 mol), K_2CO_3 (7.62 g, 0.055 mol), which has previously been ground and calcined, *N,N*-dimethylacetamide (97 mL), and toluene (36 mL) were placed under a stream of argon in a four-neck flask equipped with a stirrer, a thermometer, a gas-inlet tube, and an adapter for azeotropic distillation of water. The temperature of the reaction mixture was gradually increased (~0.5 h) to 185 °C, and the mixture was kept at this temperature for 4 h. Then the reaction mixture was cooled, the upper layer was separated, and the product was precipitated with water. The precipitate was washed repeatedly with water, twice recrystallized from ethanol, and dried *in vacuo* at 105 °C for 6 h and at

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†Deceased.

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110 °C for 20 h. M.p. 120 °C. The yield was 22.0 g (88%). Found (%): C, 83.60; H, 5.52. $C_{41}H_{32}O_4$. Calculated (%): C, 83.67; H, 5.44.

Fractionation of polyarylene-ether ketones was carried out by fractional extraction.[13] A 3 : 1 tetrachloroethane—phenol mixture was used as the solvent, and *n*-heptane was used as the precipitating agent. The concentration of the initial solution was 1.0—1.5%.

Determination of the molecular-weight characteristics. The $\overline{M}_w$ values of fractions were measured in chloroform on a Fica photogoniodiffusometer (vertically polarized light, $\lambda = 546$ nm) by light scattering with the use of the Zimm double extrapolation. The $dn/dc = 0.248$ was determined on a Pulfrich refractometer equipped with a differential cell.

The values of the inherent viscosity ($[\eta]$/dL g^{-1}) of the fractions were measured on a Ubbelohde viscosimeter with a hanging level in chloroform at 25 °C. The following Mark—Houwink relation was obtained:

$$[\eta] = 3.9 \cdot 10^{-4} \cdot \overline{M}_w^{0.72}. \qquad (1)$$

The reduced viscosity was measured in chloroform at 25 °C (the concentration of the polymer was 0.5 g per 100 mL of the solvent).

The GPC analysis of polymers was carried out on a Waters instrument consisting of an M-600 or M-501 pump, a U-Styragel Linear column ($N = 14000$ t.p.), and an M484 UV detector (280 nm) or an M410 IR detector. Chloroform was used as the eluent. The flow rate was 1 mL min^{-1}*. The data were processed with the use of the MAXIMA program. Calibration was carried out by the direct method using $\overline{M}_w$ of the fractions and the model compound **4** and by the universal Benoit calibration method with the use of the Mark—Houwink equation for polystyrene.[15]

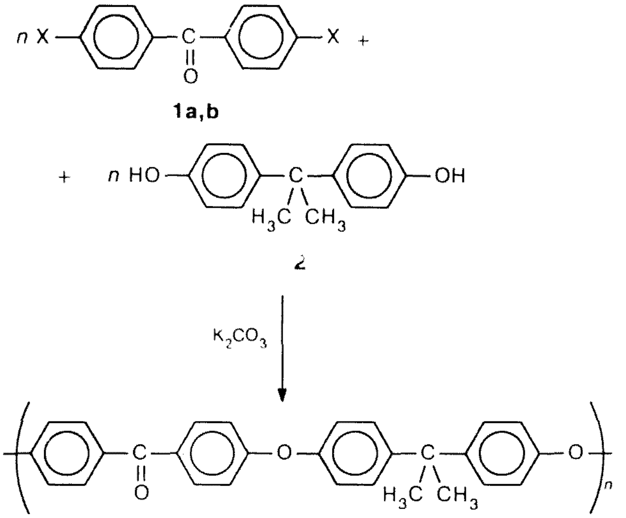
$$[\eta] = 7.169 \cdot 10^{-5} \cdot \overline{M}_w^{0.76} \qquad (2)$$

In the region of $M > 1 \cdot 10^4$, a rather good agreement between both calibration curves is observed. At $M < 1 \cdot 10^4$, the relationships differ from each other. The calibration equation obtained with the use of the universal equation was corrected taking into account the retention time of the model compound **4**.

Results and Discussion

Studies were carried out using the model reaction of potassium phenoxide **2** with **1a** or **1b** in *N,N*-dimethylacetamide (Scheme 1).

Scheme 1



X = F(**a**), Cl(**b**)

The curves of the molecular weight distribution of all the polyarylene-ether ketones synthesized have two maxima (Fig. 1). The major maximum shifts with time to a higher-molecular-weight region, whereas the minor maximum in the oligomeric region remains virtually unchanged. Apparently, the low-molecular-weight maximum is determined by the presence of cyclic oligomers.** Because the presence of low-molecular-weight fractions has a pronounced effect on the number-average molecular weight ($\overline{M}_n$), whereas the value of $\overline{M}_w$ approximately corresponds to the molecular weight distribution of linear chains, the $\overline{M}_w$ parameter is more convenient to use for the analysis of the growth rate of polymer chains.

It can be seen from Fig. 2, which shows time dependences of $\overline{M}_w$, that in each specific case, different time is required for the attainment of the maximum molecular weight. In all cases, this time is more than 5 h.

The mode of phenoxide formation also substantially affects the M_w value. The value of the molecular weight of the polymer, which was obtained when the initial reagents were loaded simultaneously (curve *1*), and the rate of its change is much higher than the analogous characteristics of polyarylene-ether ketones synthesized stepwise by adding the solution of **1a** in *N,N*-dimethylacetamide after the formation of potassium diphenoxide of **2** (curve *3*). In both cases, the character of the change in $\overline{M}_w$ with time is identical. These results can be interpreted assuming that when the initial reagents are loaded simultaneously, the phenoxide group that forms enters into the reaction with aryl halide immediately thus decreasing the probability of side transformations under the reaction conditions.

Studies of the effect of the concentration of the initial monomers (0.05, 0.5, 1.0, and 2.0 mol of each monomer per 1 L of *N,N*-dimethylacetamide) on $\overline{M}_w$ of polyarylene-ether ketones demonstrated that the highest $\overline{M}_w$ value and the highest rate of its growth were achieved at $C = 0.5$ mol L^{-1} (see Fig. 2, curve *1*).

When C decreases to 0.05 mol L^{-1} (curve *7*), polyarylene-ether ketone with $\overline{M}_w = 11000$ forms, which is characterized by a high concentration of oligomeric products including cyclic oligomers (among them, cyclic oligomers with $n = 2$ and 3 amount to 13 and 6%, respectively, according to the high-resolution GPC data). The character of the change in $\overline{M}_w$ with time is identical

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* Chloroform was used as the eluent because solutions of this polyarylene-ether ketone in THF tend to structurize.[14]

** The studies of oligomers including cyclic compounds will be reported elsewhere.

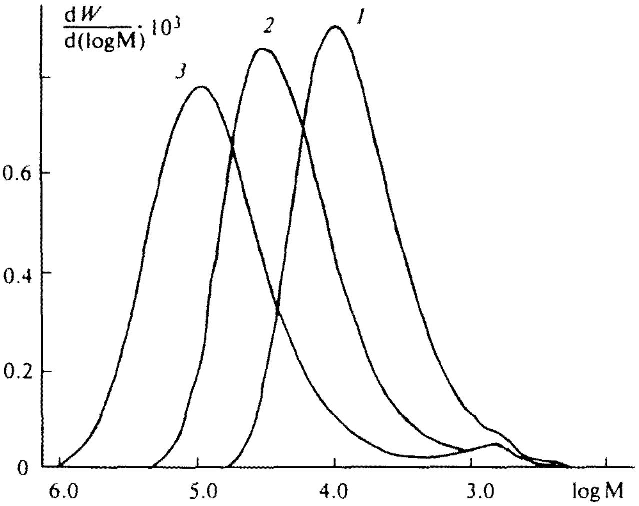

Fig. 1. Curves of the molecular weight distribution (*1—3*) of the samples of polyarylene-ether ketones taken after 3 h (*1*), 5 h (*2*), and 9 h (*3*), respectively. Conditions of polycondensation: the equimolar **1a** : **2** ratio, and $C = 2.0$ mol L^{-1}.

to that observed in the case of the synthesis of polyarylene-ether ketone at $C = 0.5$ mol L^{-1}.

When C increases to 1.0 mol L^{-1} (see Fig. 2, curve *4*), a regular change in $\bar{M}_w$ with time is observed only at the initial stage of the synthesis. When heated further, the reaction mixture became nonhomogeneous, which prevents the interpretation of the results. Apparently, the scatter in the results of measurements of the molecular-weight characteristics of the polymer samples are determined by an increase in nonhomogeneity of the reaction mixture.

Polyarylene-ether ketone synthesized at $C = 2.0$ mol L^{-1} (see Fig. 2, curve *6*) is characterized by a regular change in $\bar{M}_w$ with time, and a hardly noticeable phase separation in the reaction mixture occurred during the synthesis. However, in this case, the $\bar{M}_w$ value and the rate of its change are somewhat lesser than those observed at $C = 0.5$ mol L^{-1} (see Fig. 2, curve *1*), apparently due to the diffusion resistance, which exerts a substantial effect on the rate of polycondensation at high concentrations of monomers.

Therefore, $C = 0.5$ mol L^{-1} is the optimum concentration for preparing polyarylene-ether ketones with high molecular weights, and hence, the relationships discussed below were studied at this concentration.

Replacement of **1a** by **1b** in the polycondensation results in a substantial decrease in both the $\bar{M}_w$ value and the rate of its change (see Fig. 2, curve *5*). The final values of $\bar{M}_w$ for polyarylene-ether ketones based on **1a** and **1b** were 130 000 and 44 000, respectively. This is associated with a lower reactivity of **1b** compared to that of **1a**. When **1b** is used, the curve of an increase in $\bar{M}_w$ also reflects the slow and rapid stages of the synthesis.

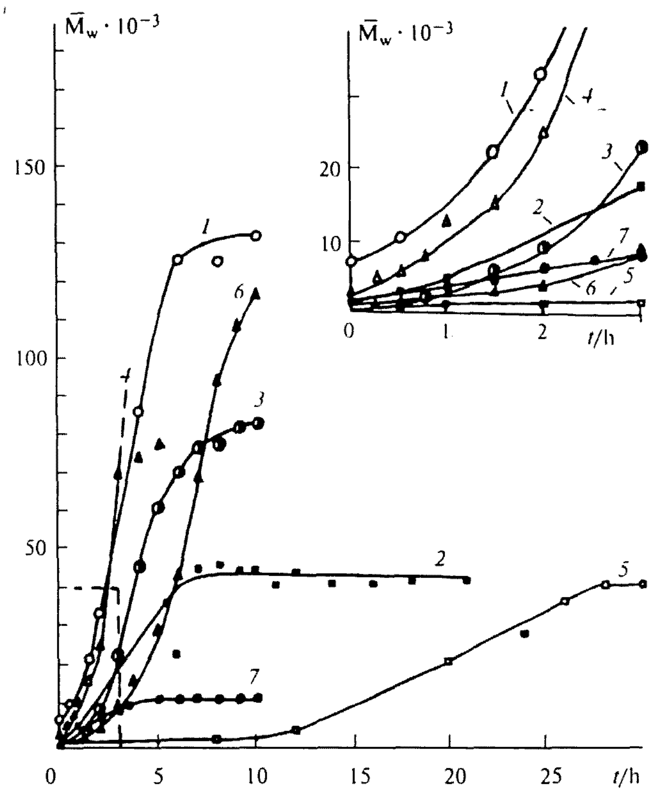

Fig. 2. Change in $\bar{M}_w$ with time during polycondensation of **2** with **1a** (curves *1—4*, *6*, and *7*) and **1b** (curve *5*). Conditions of polycondensation: a 30% excess of K_2CO_3; C/mol L^{-1}: 0.05 (*7*), 0.5 (*1—3*, *5*), 1.0 (*4*), and 2.0 (*6*); the equimolar ratio of **2** and dihalobenzophenones (curves *1*, and *3—7*); **2** : **1a** : **3** = 1 : 0.99 : 0.02 (curve *2*); simultaneous loading of all reagents (curves *1*, *2*, and *4—7*); addition of **1a** to the reaction mixture containing potassium diphenoxide **2** prepared previously (curve *3*).

When polyarylene-ether ketone is synthesized with the molecular-weight control by addition of **3**, the character of the change in $\bar{M}_w$ with time (see Fig. 2, curve *2*) is analogous to that occuring in the synthesis without an addition of a monofunctional compound and is observed at lower values of $\bar{M}_w$.

A characteristic feature of all the curves representing changes in $\bar{M}_w$ with time is that they are S-shaped with a pronounced initial region, which corresponds to a slow increase in $\bar{M}_w$. One of the causes of a slow increase in $\bar{M}_w$ is, apparently, heterogeneity of the reaction mixture, which is determined by low solubility of potassium diphenoxide **2** and of oligomers with terminal phenoxide groups in the reaction medium. The rate of formation of potassium diphenoxide **2**, which depends on heterogeneity of the reaction mixture, can also affect the course of the reaction. It can be assumed that the rate of polycondensation is controlled by the concentration of potassium diphenoxide **2** in the reaction zone, whose rate of formation depends on the degree of grinding of potassium carbonate. Apparently, the use of an excess of

Table 1. Effect of the amount of K_2CO_3 on the molecular weight of polyarylene-ether ketone

Excess of K_2CO_3 (mol.%)	$\bar{M}_w$	$\bar{M}_n$	η_{red} /dL g^{-1}
0	24300	9500	0.58
10	66600	23200	1.14
20	108200	18100	1.52
30	222000	21000	2.27
50	134000	20000	2.00

K_2CO_3 is necessary for a more efficient transformation of bisphenol to phenoxide, which proceeds under heterogeneous conditions. Actually, the maximum molecular weight of polyarylene-ether ketone is achieved in the presence of a 30% excess of potassium carbonate (Table 1).

A change in η_{red} with time in the polycondensation of **2** with **1a** or **1b** (Fig. 3) is indicative of the common character of the behavior of both η_{red} and $\bar{M}_w$.

In this work, we also studied the possibility of controlling the molecular weight of polyarylene-ether ketone.

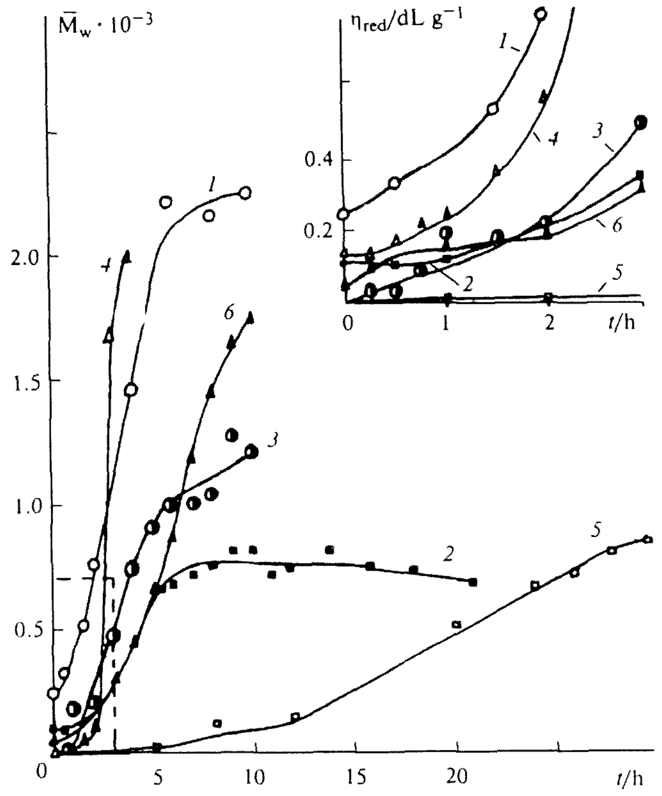

Fig. 3. Change in η_{red} with time during polycondensation of **2** with **1a** (curves *1—4*, and *6*) and **1b** (curve *5*). For conditions of polycondensation see Fig. 2 and the Experimental section.

The molecular weight of polyarylene-ether ketone decreases uniformly as the excess of **1a** or **2** increases (Fig. 4). The maximum values of $\bar{M}_w$ and η_{red} were attained in the presence of a 0.5% excess of **1a**, and the experimental curves are somewhat asymmetrical: the molecular weight decreases more substantially in the presence of an excess of **2** than in the presence of an excess of **1a**. In the presence of an excess of **1a**, the experimental $\bar{M}_w$ values agree (to within 10% of the experimental error) with the limiting values corresponding to the degree of completion of the reaction $p = 1$, which were calculated according to the Flory theory.[16]

$$\bar{M}_w = M_0(1 + r^{1/2}p)/(1 - r^{1/2}p), \tag{3}$$

where $r = AA/BB$ is the unbalance at $r \leq 0.98$ (at $r = 0.99\bar{M}_w$, the experimental $\bar{M}_w$ value is larger than the theoretical value).

In the presence of an excess of **2**, the experimental $\bar{M}_w$ values correspond to the theoretical values at $r \leq 0.97$. These results can be interpreted by assuming that in the course of polycondensation, the ratio of the functional groups is disturbed as a result of sublimation of **1a** from the reaction zone or as a result of a side reaction of hydrolysis of **1a**.

The effect of the monofunctional reagent **3** was examined by adding it to an equimolar mixture of monomers and by using **3** so that the overall amount of functional groups remained equivalent. A comparison of the experimental $\bar{M}_w$ values and the limiting values corresponding to complete conversion of phenoxide groups, which were calculated according to the Flory theory, are shown in Fig. 5. In the case of the equivalent ratio of bifunctional monomers, we obtained the following equation:

$$\bar{M}_w \cong 2 \cdot M_0/X, \tag{4}$$

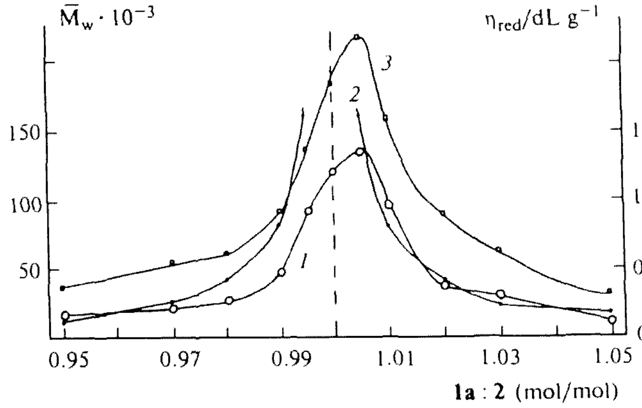

Fig. 4. Effect of the unbalance of monomers on $\bar{M}_w$ (curves *1* and *2*) and η_{red} (curve *3*). Curve *1* represents the experimental results, and curve *2* represents the calculated data.

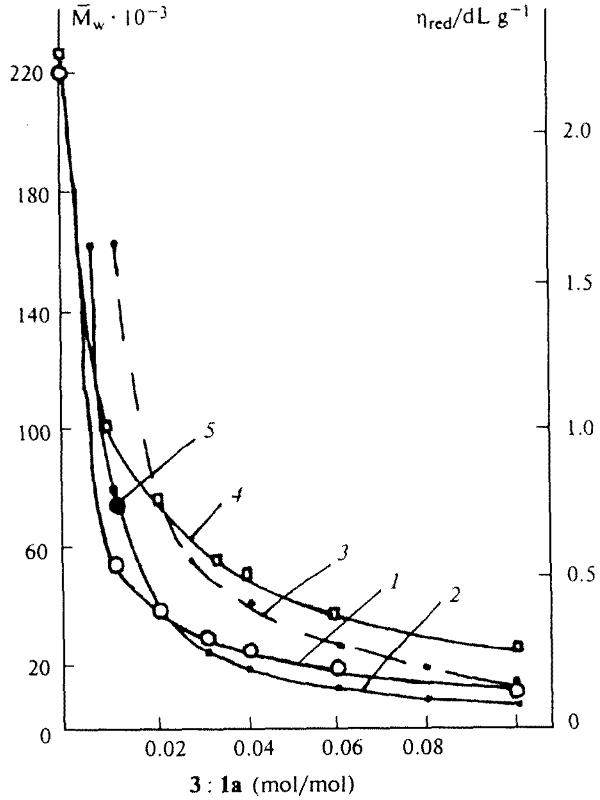

Fig. 5. Dependences of $\bar{M}_w$ (curves *1—3*) and η_{red} (curve *4*) of polyarylene-ether ketones on the amount of the monofunctional reagent: curve *2*, calculations according to Eq. (4); curve *3*, calculations according to Eq. (5); point *5* is the experimental results with the equivalent ratio of **1a** and **2**; curve *1*, the experimental results when **1a** and **2** were taken in a nonequivalent ratio (equivalent ratio of functional groups).

where M_0 is the molecular weight of the unit for $X = [\mathbf{3}]_0/[\mathbf{1a}]_0$. In the case of the equivalent amount of functional groups, we obtained:

$$\bar{M}_w \cong 4 \cdot M_0/X. \qquad (5)$$

It can be seen from Fig. 5 that when a nonequimolar mixture of monomers is used, the molecular weight of polymers is twice as low as the limiting calculated values (repeated syntheses gave reproducible results). Therefore, the degree of completion of the reaction $p < 1$.

In all the cases studied, the values of η_{red} changed simultaneously with $\bar{M}_w$, which is, apparently, indirect evidence that no branching processes occurred in the course of the synthesis or in the case when the conditions were varied.

Thus, we have found the optimum conditions for the reaction of **1a** with potassium diphenoxide **2** for preparing high-molecular-weight polyarylene-ether ketones. We have also demonstrated that it is possible to control $\bar{M}_w$ in the range from 10 000 to 200 000.

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