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CHEMISTRY

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ON THE INFLUENCE OF THE STERIC FACTOR ON THE VISCOMETRIC PROPERTIES AND POLYDISPERSITY OF POLYARYLATES

The influence of the steric factor on the viscometric properties and polydispersity of high-molecular-weight compounds has still been very little studied. We investigated these relationships using as an example polyarylates based on isophthalic acid and such dihydric phenols as 4,4′-dioxydiphenylpropane (equilibrium polyarylate D-1), phenolphthalein (equilibrium polyarylate F-1) (^1) and 9,9-bis-(4-hydroxyphenyl)-fluorene (equilibrium polyarylate D-10), which differ from one another in the size of the side substituent.

Fig. 1. Dependences $\lg[\eta] = f(\lg M)$ for polyarylates in tetrachloroethane: 1 —D-1 interfacial, 2 —D-1 equilibrium, 3 —D-10 equilibrium.

Fig. 2. Dependence of the exponent a on the weight of the side substituent. a —data corresponding to the polyarylates studied; b —data of the authors (^5). 1 —straight line corresponding to equation (I) for equilibrium polymers; 2 —corresponding to equation (II) for interfacial polymers.

The polyarylates studied were synthesized by the method of equilibrium polycondensation (^2), and, for comparison of properties, the polyarylate based on isophthalic acid and 4,4′-dioxydiphenylpropane was also synthesized by the method of interfacial polycondensation (^3) (interfacial polyarylate D-1). Fractionation, measurement of the molecular weights of the fractions by the light-scattering method, measurement of viscosities, and determination of the characteristic viscosity of the fractions were carried out according to the methods indicated by us earlier (^1). Equilibrium polyarylate D-1 (2 samples) was refractionated into 26 and 18 fractions; equilibrium F-1 (2 samples) into 28 and 17 fractions; equilibrium D-10 into 19 fractions; and interfacial D-1 into 28 fractions. Processing of the fractionation results was carried out by the usual method of constructing integral and differential distribution curves (^4). The number-average $\overline{M}n$ and weight-average $\overline{M}w$ molecular weights of the unfractionated samples studied were measured by independent methods and also calculated from the molecular-weight distribution curves.

On the basis of the data obtained, relationships were derived between the molecular weight and the intrinsic viscosity of the fractions in tetrachloroethane (TCE) (Table 1 and Fig. 1).

From the data in Table 1 it is evident that, with an increase in the side substituent, the value of the exponent a decreases. Figure 2 shows the dependence of the exponent a on the weight of the side substituent (ΔM). As can be seen from the figure, for polyaryltes synthesized by the methods of equilibrium and interfacial polycondensation, the dependences between the exponent a and the weight of the side substituent do not coincide and are expressed by approximately parallel straight lines.

Table 1

Values of the constants K and a of the Mark–Houwink equation $[\eta] = K \cdot M^a$

Polyarylate based on	Weight of side substituent	Solvent	$K \cdot 10^4$	a	Source
Isophthalic acid and 4,4′-dioxydiphenylpropane (polyarylate D-1, equil.)	30	TKhE	7.87	0.61	
Isophthalic acid and phenolphthalein (polyarylate F-1, equil.)	120	TKhE	16.0	0.53	(1)
Isophthalic acid and 9,9-bis-(4-oxyphenyl)-fluorene (polyarylate D-10, equil.)	152	TKhE	23.0	0.49	

Polyarylate based on	Weight of side substituent	Solvent	$K \cdot 10^4$	a	Source
Isophthalic acid and 4,4′-dioxydiphenylpropane (polyarylate D-1, interfacial)	30	TKhE	2.04	0.75	
Isophthalic acid and phenolphthalein (polyarylate F-1, interfacial)	120	TKhE	3.35	0.67	(1)

Although it is premature to extend this result to other polymers, it may nevertheless be thought that the analytical dependences we have found,

$$a = 0.64 - \Delta M \cdot 10^{-3} \tag{I}$$

for polyaryltes obtained by the method of equilibrium polycondensation, and

$$a = 0.77 - \Delta M \cdot 10^{-3} \tag{II}$$

for polyaryltes obtained by the method of interfacial polycondensation, may have a more general character; this is confirmed by the data of other authors, given by us in the same figure, for benzene solutions of carbocyclic polymers with various substituents (5), and also by good agreement with the theoretical premises of Zimm and Stockmayer (10).

Fig. 3. Dependence of K on a for aliphatic polyesters, corresponding to equation (III)

Apparently, an increase in the volume of the substituent increases the density of the macromolecular coil in such a way that, with a large substituent, such as, for example, the biphenylene group in polyarylate D-10 or the octadecyloxy group in polyvinyl octadecyl ether (5), the value of the exponent a becomes less than 0.5, i.e., the polymer in solution behaves as, according to Flory’ s theory, a branched polymer should behave. The same effect of increased interaction between side radicals with an increase in their size was observed by Tsvetkov and Bychkova in studying the anisotropy of double refraction in a solution of polymethacrylates with different substituents (6).

To verify the derived relations, we made an attempt, using relation (II) for interfacial polyarylates, as well as the analogous equation published earlier (^{7}) for the dependence between the parameters K and a for aliphatic polymers (Fig. 3),

$$K = 0{,}289(6{,}8 \cdot 10^{-5})^a, \tag{III}$$

to calculate the parameters K and a of the Mark—Houwink equation for polyarylate D-10, synthesized by the method of interfacial polycondensation, for which no dependence between viscosity and molecular weight had previously been derived, and then from them to calculate the molecular weights of several fractions. The values of K and a calculated by the indicated method are: $K = 6{,}22 \cdot 10^{-4}$, $a = 0{,}64$.

As is seen from the data of Table 2, the agreement with the molecular weights of these same fractions measured by the light-scattering method proved, within experimental error, to be quite satisfactory.

Table 2

Comparison of measured and calculated molecular weights of fractions of polyarylate based on isophthalic acid and 9,9-bis-(4-oxyphenyl)-fluorene, synthesized by the method of interfacial polycondensation (polyarylate D-10 interfac.)

Fraction	$[\eta]$ in THF	Molecular weight of fractions, measured by light scattering	Molecular weight of fractions, calculated from the equation $[\eta] = 6{,}22 \cdot 10^{-4} M^{0{,}64}$
1	0,148	6 100	5 200
4	0,326	21 000	17 750
5	0,424	25 000	26 800
8	0,633	54 300	50 100

In addition, we established that, with an increase in the side substituent, the polydispersity coefficient of polyarylates synthesized by the method of equilibrium polycondensation increases (Table 3). The increase in polydispersity may be explained by the fact that, in the presence of large side substituents, chain-exchange reactions,

Table 3

Value of the polydispersity coefficient of some polyarylates

Polymer	Weight of substituent	Data for unfractionated sample: [η] THF	Data for unfractionated sample: $\overline{M}_w^*$	Data for unfractionated sample: $\overline{M}_n^{**}$	Data for unfractionated sample: $K = \frac{\overline{M}_w}{\overline{M}_n}$	Data calculated from curves: [η] THF	Data calculated from curves: $\overline{M}_w$	Data calculated from curves: $\overline{M}_n$	Data calculated from curves: $K = \frac{\overline{M}_w}{\overline{M}_n}$	Source
D-1 equil. 1st sample	30	0,485	36 000	20 800	1,73	0,477	38 800	23 100	1,68	
2nd sample	30	0,458	35 000	22 200	1,57	0,453	34 600	23 200	1,49	
3rd sample	30						31 400	19 650	1,60	(9)
F-1 equil. 1st sample	120	0,464	33 300	15 300	2,18	0,466	36 900	17 700	2,09	(1)
2nd sample	120	0,382	30 300	14 100	2,15	0,38	32 600	15 800	2,06	
D-10 equil.	152	0,440	42 200			0,432	47 000	21 500	2,19	
D-1 interfac. 1st sample	30	0,522	39 800	19 300	2,06	0,518	38 700	18 800	2,06	

Polymer	Weight of substituent	Data for unfractionated sample: [η] THF	Data for unfractionated sample: $\overline{M}_w^*$	Data for unfractionated sample: $\overline{M}_n^{**}$	Data for unfractionated sample: $K = \frac{\overline{M}_w}{\overline{M}_n}$	Data calculated from curves: [η] THF	Data calculated from curves: $\overline{M}_w$	Data calculated from curves: $\overline{M}_n$	Data calculated from curves: $K = \frac{\overline{M}_w}{\overline{M}_n}$	Source
2nd sample	30						49 200	24 300	2,02	(9)
3rd sample	30						49 980	24 650	2,07	(9)

* Measured by the light-scattering method (1).

** Measured by the isopiestic method (8).

leading to equalization of the length of polymer chains, are more hindered in the course of synthesis because of a purely steric factor. This conclusion is also confirmed by the data of our studies on destruc-

…of polyarylates synthesized by the equilibrium polycondensation method under the action of sebacic acid (Table 4).

As is evident from the data in Table 4, degradation of polyarylates with a small substituent proceeds more deeply than in polyarylates with large side substituents, which also indicates that, in the case of degradation as well, an increase in the volume of the side substituents creates steric hindrances to the occurrence of exchange and destructive processes.

Table 4

Dependence of the intrinsic viscosity on the concentration of the degrading agent for the polyarylates studied

Concentration of sebacic acid, mol/polymer unit	Intrinsic viscosity in tetrachloroethane of the polyarylate solution after degradation, $[\eta]$ TCE	Intrinsic viscosity in tetrachloroethane of the polyarylate solution after degradation, $[\eta]$ TCE	Intrinsic viscosity in tetrachloroethane of the polyarylate solution after degradation, $[\eta]$ TCE
	polyarylate D-1 equil.	polyarylate F-1 equil.	polyarylate D-10 equil.
0.0	0.485	0.464	0.440
0.2	0.470	0.410	0.422
0.4	0.393	0.372	0.410
0.6	0.290	0.328	0.395
0.8	0.275	0.320	0.368
1.5	0.285	0.320	0.362

Note. Degradation was carried out for 12 h at 200° in a Savol medium.

Apparently, precisely this explains the fact that, with increasing substituent size, the polydispersity coefficient approaches the value found for the products of interfacial polycondensation (see Table 3). In the process of interfacial polycondensation, as is known, interchain exchange reactions are practically absent.

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Note: Figure translations are in progress. See original paper for figures.

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