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Viscosity of Dilute Solutions of Styrene Copolymers in the Course of Polymer-Analogous Transformations

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Abstract—The properties of dilute solutions of styrene copolymers and their porphyrin derivatives prepared via the functional group transformations have been studied in DMF at 20–35ºC. The effect of the copolymer composition, on the intrinsic viscosity, the Huggins constant, the macromolecule dimensions, and thus on the interaction with solvent has been elucidated. The nature and content of functional groups in the polymer influence the behavior of macromolecule coil in the solution. Introduction of the porphyrin fragment loosens the macromolecular coil, but does not qualitatively change the solution behavior.

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Development of the functional materials (including nanomaterials) with the desired properties is a topical issue in many engineering, technology, and medicine areas. Materials with outstanding catalytic, optical, and sensory properties can be created on the basis on porphyrins and their metal complexes. Therefore, development of efficient methods to prepare porphyrin-polymer materials is important. Most often such processes are performed in the solutions. Obviously, the efficiency of porphyrin reaction with the (co) polymer functional groups depends on many factors, including the accessibility of these groups which in turn is governed by the solution structure, thermodynamic quality of the solvent, and polymer–solvent interaction. The study of solution behavior of porphyrin-containing polymers in the course of modification will allow adjusting the mechanical, complexing, catalytic, and other properties of the modified materials.

The methods of porphyrin-polymers preparation have been intensively developed recently [1–5]. Much attention has been paid to synthesis of styrene copolymers containing functional groups available for modification with macroheterocyclic compounds [1, 2, 6, 7]. The modification under mild conditions is crucial to retain the porphyrins properties; this is possible, for instance, with epoxy-containing polymers: high reactivity without additional activation is typical of the epoxy groups [4, 5, 8].

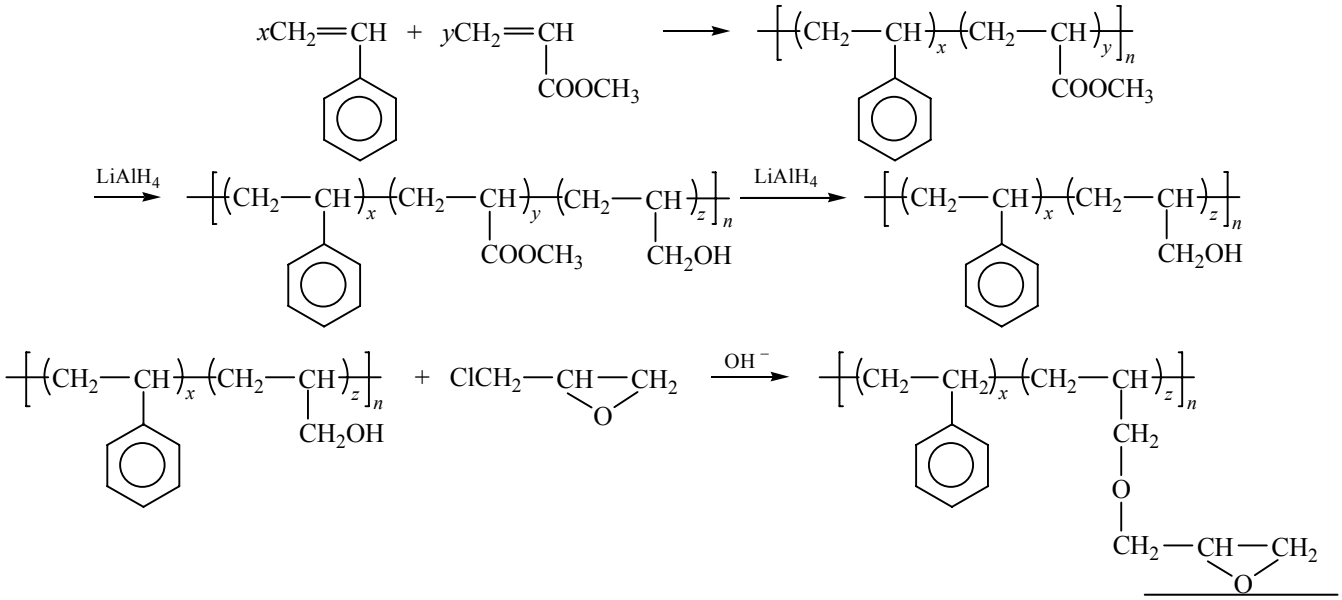
There two main approaches have been used to obtain porphyrin-containing polymers: immobilization of porphyrins and their analogs on the polymer with a complex of desired physical and mechanical properties, and porphyrin-containing monomer copolymerization with a suitable comonomer. The first approach has been most widely used so far [1, 4].

In this paper we studied the solution behavior of the series of copolymers, the initial ones and the products of modification with porphyrin. The following hydrodynamic parameters were investigated: intrinsic viscosity [η], the Huggins constant (K_H), and the average distance between the ends of a macromolecule in solution $<h^2>^{1/2}$. Those three interrelated parameters characterized the hydrodynamic resistance of the macromolecule to flow, the efficiency of polymer–solvent interactions, and the macromolecule coil size.

The first approach used to prepare the polymer to be modified was copolymerization of styrene and methyl acrylate, followed by reduction of methyl acrylate ester group to hydroxyl and the reaction with epichlorohydrin [9] (Scheme 1).

Poly(styrene-*co*-methyl acrylate) was prepared by emulsion copolymerization [10]. We previously studied the rheological properties of such copolymers of varied composition in dilute toluene solutions by viscometry method [11].

Scheme 1.



Stepwise reduction of the copolymer with lithium aluminum hydride gave terpolymers of styrene, methyl acrylate, and allyl alcohol or the styrene–allyl alcohol copolymer.

The results of viscometry of the so prepared copolymers in dimethylformamide (DMF) solutions are compiled in Table 1. The [η] and K_H values were average results of at least three measurements; the experimental error was below 3%.

Molecular weights of the copolymers were determined by gel permeation chromatography with Shimadzu LC-20 Prominence liquid chromatograph (Japan) equipped with two columns (GMHHR-L 30 cm×7.8 mm and G2500-HHR 30 cm×7.8 mm) at 40°C. Chloroform was applied to the column at 0.75 mL/min. The system was calibrated according to polystyrene references with $M_w/M_n \le 1.05$.

The size of macromolecular coil $\langle h^2 \rangle^{1/2}$ was evaluated from the Flory-Fox equation [12].

The data in Table 1 show that the unmodified copolymers with 8 and 12 mol% of methyl acrylate units formed DMF solutions with UCST, [η] increased with temperature (**I** and **II** in Table 1). Increase of the methyl acrylate units fraction to 23 mol% and above led to the LCST behavior, [η] decreased with temperature (**III**–**V**, Table 1). In general, behavior of the reduced copolymers, containing the alcohol units, was similar to that of the respective starting copolymer; however, the difference of numerical values of the intrinsic viscosity and the Huggins constant revealed the changes in the polymer–solvent interaction efficiency upon the copolymer modification.

The reduction reaction leading to increasing fraction of allyl alcohol units in the 80 : 20 and 70 : 30 styrene–methyl acrylate copolymer resulted in substantial increase in the intrinsic viscosity (**I** and **II** in Table 1, Fig. 1). As the degree of polymerization did not change in the reduction reaction, the observed effect was definitely due to expansion of the macromolecular coil due to increasing the efficiency of polymer–solvent interaction. Thus, thermodynamic quality of DMF as a solvent was increasing with more of the polar groups in the copolymer, efficiently interacting with polar DMF.

For the copolymers with 23 mol % of methyl acrylate or more, the reduction with $LiAlH_4$ resulted in decreasing [η], thus, it seemed that thermodynamically DMF became poorer solution with introduction of polar alcohol groups. As temperature behavior of the initial copolymer also changed at this point from HCST to LCST, this could mark some mutual influence of the functional groups on the solution behavior of the macromolecular coil, possibly including inter- or intramolecular association.

The epoxy-containing copolymers could be alternatively directly prepared by radical copolymerization. As an example, we performed emulsion copolymerization of styrene with glycidyl methacrylate (Scheme 2).

Table 1. Rheological properties of solutions of styrene copolymers **I–V** with methyl acrylate and/or allyl alcohol in DMF

Comp. no.	Styrene : methyl acrylate in the initial copolymer, wt %	M_r	Styrene : methyl acrylate : allyl alcohol after reduction, mol %	T, °C	[η], dL g^{-1}	K_H, **g^2 dL^{-2}**	$\langle h^2\rangle^{1/2}\times10^6$, dm
I	80:20	35000	92:8:0	20	0.08	34.94	0.99
				25	0.15	8.01	1.22
				30	0.17	2.08	1.28
				35	0.18	0.59	1.30
			92:6:2	20	0.50	3.21	1.82
				25	0.68	1.48	2.01
				30	0.99	1.03	2.28
				35	1.17	0.65	2.41
			92:3.5:4.5	20	0.88	4.42	2.19
				25	1.09	2.95	2.35
				30	1.10	0.28	2.36
				35	1.46	0.15	2.59
			92:0:8	20	0.90	18.11	2.21
				25	0.99	11.41	2.30
				30	1.49	1.61	2.64
				35	1.55	1.44	2.67
II	70:30	32000	88:12:0	20	0.09	23.65	1.00
				25	0.12	13.17	1.11
				30	0.18	1.95	1.27
				35	0.20	0.76	1.31
			88:10:2	20	0.23	1.47	1.37
				25	0.30	0.63	1.50
				30	0.35	0.46	1.58
				35	0.38	0.32	1.62
			88:4:8	20	0.26	1.22	1.43
				25	0.31	0.83	1.52
				30	0.45	0.67	1.72
				35	0.46	0.51	1.73
			88:0:12	20–35	–	–	–
III	50:50	30000	77:23:0	20	0.16	6.20	1.19
				25	0.15	12.49	1.17
				30	0.11	14.68	1.05
				35	0.10	21.92	1.02
			77:21:2	20	0.35	2.41	1.55
				25	0.29	6.19	1.45
				30	0.18	11.16	1.24
				35	0.15	12.07	1.17

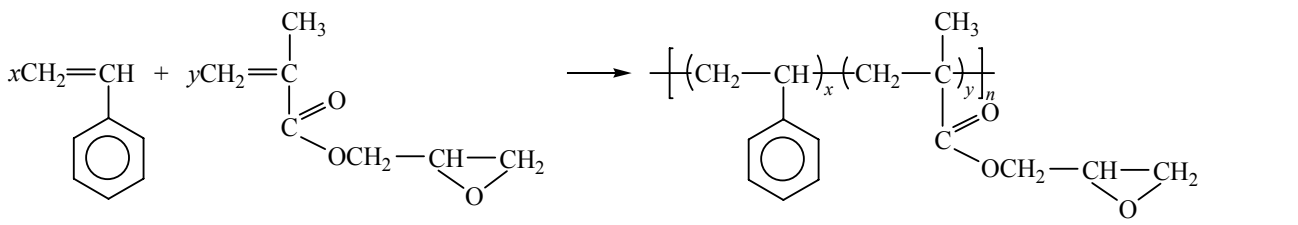
Table 1. (Contd.)

Comp. no.	Styrene : methyl acrylate in the initial copolymer, wt %	M_r	Styrene : methyl acrylate : allyl alcohol after reduction, mol %	T, °C	[η], dL g^{-1}	K_H, g^2 dL^{-2}	$\langle h^2\rangle^{1/2}\times10^6$, dm
IV	30:70	26000	36:64	20	0.64	1.34	1.80
				25	0.24	2.11	1.30
				30	0.21	3.05	1.24
				35	0.10	3.84	1.02
V	20:80	23000	34:66	20	0.39	1.30	1.47
				25	0.27	4.45	1.30
				30	0.20	7.38	1.17
				35	0.13	21.73	1.02

Table 2. Rheological properties of solutions of styrene copolymers **VI–VIII** with glycidyl methacrylate in DMF

Comp. no.	Styrene : glycidyl methacrylate in the copolymer (monomers mixture), wt %	M_r	T, °C	[η], dL g^{-1}	K_H, g^2 dL^{-2}	$\langle h^2\rangle^{1/2}\times10^6$, dm
VI	100:0	25770	20	0.187	0.91	1.19
			25	0.181	1.05	1.18
			30	0.176	1.19	1.17
			35	0.170	1.29	1.16
VII	97:3	43000	20	0.071	7.08	1.02
	(95:5)		25	0.098	2.57	1.14
			30	0.099	1.08	1.15
			35	0.105	0.84	1.17
VIII	90:10	72000	20	0.188	7.38	1.68
	(90:10)		25	0.194	7.34	1.70
			30	0.217	3.71	1.77
			35	0.237	1.67	1.82

Scheme 2.



Rheological properties of the so prepared copolymers in solution are collected in Table 2. As the copolymerization constants in this pair were close (r = 0.55 for glycidyl methacrylate and 0.45 for styrene), the copolymer composition was close to that of the initial monomers mixture (Table 2) [13].

Introduction of glycidyl units to polystyrene resulted in significant changes in the solution behavior: whereas polystyrene in DMF revealed LCST, in the case of poly(styrene-*co*-glycidyl methacrylate), [η] in DMF increased with temperature, and K_H decreased (Figs. 2, 3). Thus, the poly(styrene-*co*-glycidyl methacrylate) in DMF revealed the UCST behavior. With increasing the glycidyl units fraction, the polymer coil in DMF expanded, meaning the improvement of DMF thermodynamic quality (Table 2).

In order to modify the prepared copolymers with porphyrin groups, 5-(4'-aminophenyl)triphenylporphyrin was used (Scheme 3).

The choice of that porphyrin derivative was due to high reactivity of meso-aminophenylporfirins amino group. 5-(4'-aminophenyl)(triphenyl) porphyrin was prepared by reduction of the corresponding nitroporphyrin with tin(II) chloride in methanol and in the presence of concentrated hydrochloric acid [14].

Immobilization of 5-(4'-aminophenyl)triphenylporphyrin on the copolymers was performed in DMF solution at 50°C during 8–10 h.

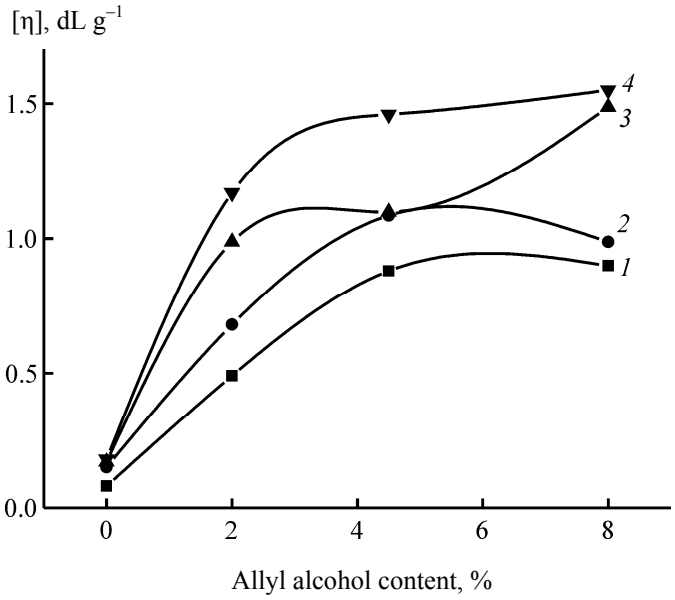
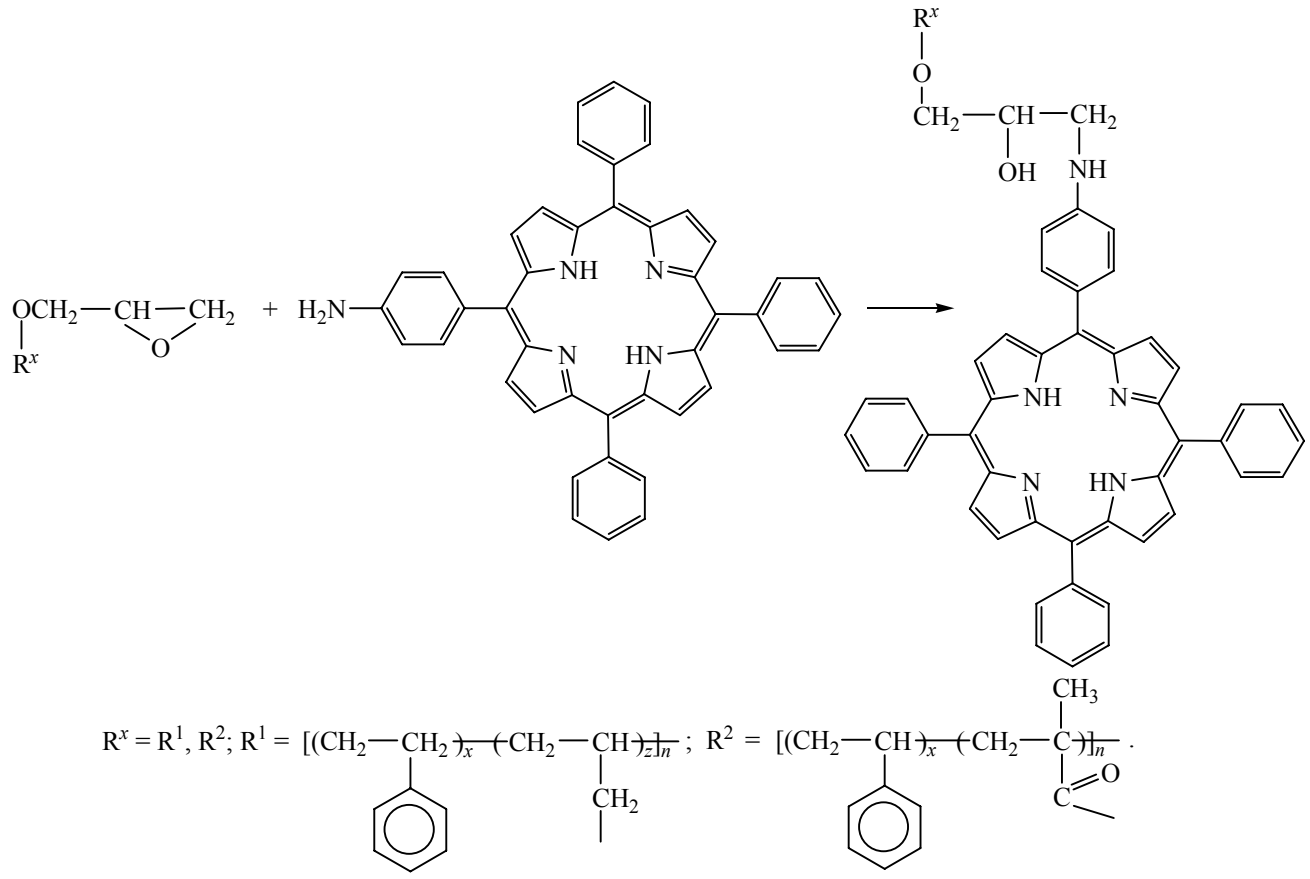


Fig. 1. Intrinsic viscosity in DMF as function of allyl alcohol units content in the styrene-*co*-methyl acrylate-*co*-allyl alcohol polymer with 92 mol% of styrene. (*1*) 20°C, (*2*) 25°C, (*3*) 30°C, and (*4*) 35°C.

Scheme 3.



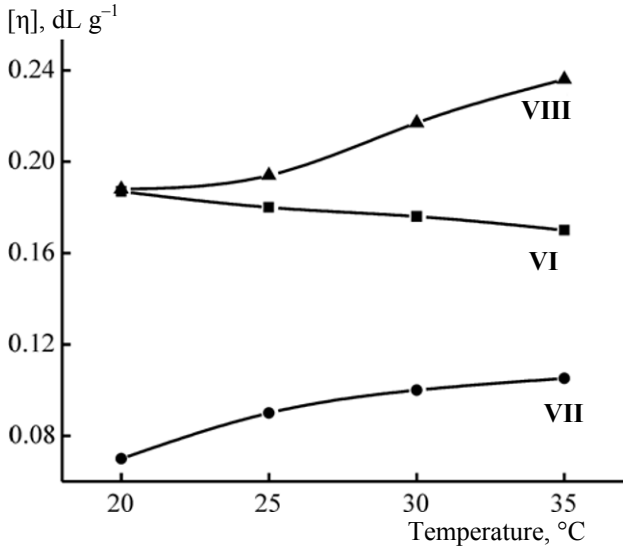


Fig. 2. Intrinsic viscosity in DMF as function of temperature for polystyrene **VI** and styrene copolymers with glycidyl methacrylate **VII** and **VIII**.

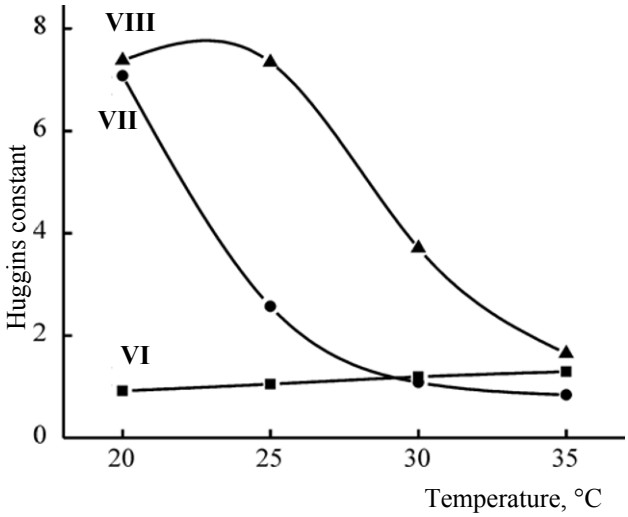


Fig. 3. The Huggins constant K_H in DMF as function of temperature for polystyrene **VI** and styrene copolymers with glycidyl methacrylate **VII** and **VIII**.

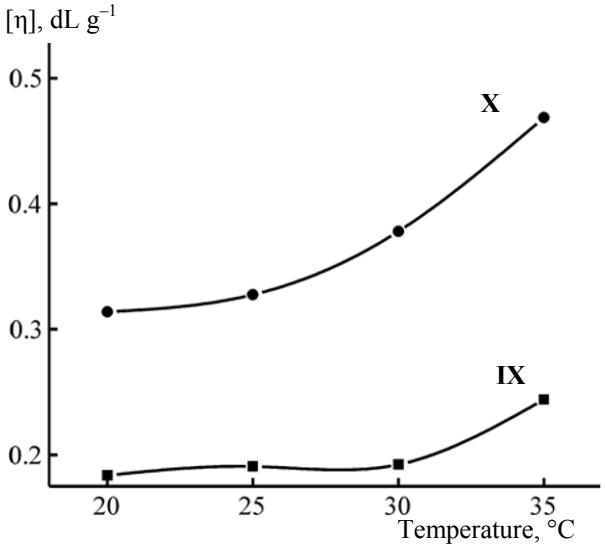


Fig. 4. Intrinsic viscosity in DMF as function of temperature for styrene copolymers with glycidyl methacrylate **IX** and **X** in DMF.

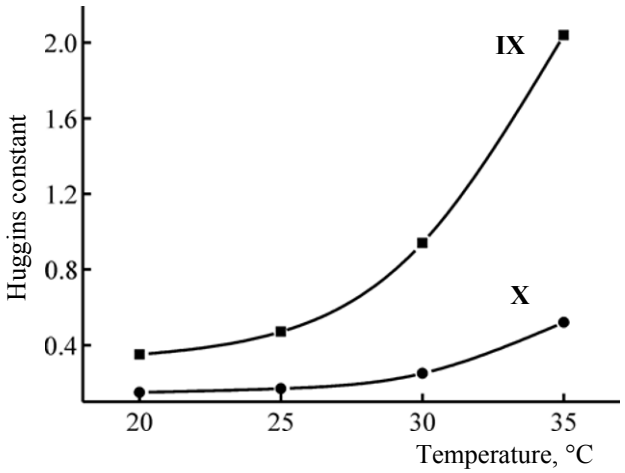


Fig. 5. The Huggins constant K_H in DMF as function of temperature for styrene copolymers with glycidyl methacrylate and porphyrin **IX** and **X**.

The rheological behavior of the prepared porphyrin-containing copolymers was similar to that of the above-described poly(styrene-*co*-glycidyl methacrylate): in DMF, with increasing temperature from 20 to 35°C, [η] increased and K_H decreased (Figs. 4 and 5). The obtained viscometry data is presented in Table 3.

Since the degree of polymerization upon modification with porphyrin did not change, comparison of the rheological parameters in the pairs **VII** and **IX**, **VIII** and **X** (Tables 2 and 3) should have revealed the effect on porphyrin-containing units on the interaction with the solvent. The corresponding data, replotted in Fig. 6, revealed that the copolymers bearing porphyrin-containing units had higher $\langle h^2 \rangle^{1/2}$ values. Thus, the copolymer coil expanded due to introduction of porphyrin groups; that was also supported by [η] values.

The rheological behavior of all polymers studied in this work is generalized in Table 4.

The main conclusions are as follows. In general, DMF was better solvent for alcohol-containing

Table 3. Rheological properties of solutions of porphyrin-containing styrene copolymers **IX** and **X** in DMF

Comp. no.	Styrene : glycidyl methacrylate : porphyrin in the copolymer, wt %	T, °C	[η], dL g^{-1}	K_H, **g^2 dL^{-2}**	$\langle h^2\rangle^{1/2}\times10^6$, dm
IX	97:2:1	20	0.186	2.04	1.41
		25	0.191	0.94	1.42
		30	0.192	0.47	1.43
		35	0.244	0.35	1.54
X	90:9:1	20	0.314	0.52	2.00
		25	0.327	0.25	2.02
		30	0.378	0.17	2.12
		35	0.469	0.15	2.28

Table 4. The influence of the functional groups on the solution behavior of the studied copolymers

Copolymer	Solvent	System type
Polystyrene	Toluene	LCST
	DMF	″
Poly(styrene-*co*-methyl acrylate), <20 wt% of methyl acrylate	Toluene	″
	DMF	UCST
Poly(styrene-*co*-methyl acrylate), >20 wt% of methyl acrylate	Toluene	″
	DMF	LCST
Poly(styrene-*co*-methyl acrylate-*co*-allyl alcohol)	Toluene	–
	DMF	UCST
Poly(styrene-*co*-allyl alcohol)	Toluene	–
	DMF	UCST
Poly(styrene-*co*-glycidyl methacrylate)	DMF	″
Poly(styrene-*co*-glycidyl methacrylate-*co*-porphyrin)	DMF	″

copolymers, and the polymer coil expanded upon transformation of methyl acrylate units into allyl alcohol ones. However, with higher fraction of methyl acrylate units the situation was complicated by the polymer–polymer interactions. Introduction of the porphyrin groups led to expansion of the polymer coil, but did not change the behavior of the system qualitatively.

EXPERIMENTAL

The intrinsic viscosity [η] of copolymer solutions was determined by the classical dilution method [15] with the Ubbelohde viscometer. 0.1000±0.0002 g of the copolymer was placed in a calibrated pycnometer (10 mL) and dissolved in DMF at room temperature. The resulting solution was poured into the Ubbelohde viscometer and incubated at the desired temperature (20, 25, 30, or 35°C) during 15 min, and the solution flow time τ_3 was measured. Then, a weighed portion of DMF was added, and after stirring and incubation

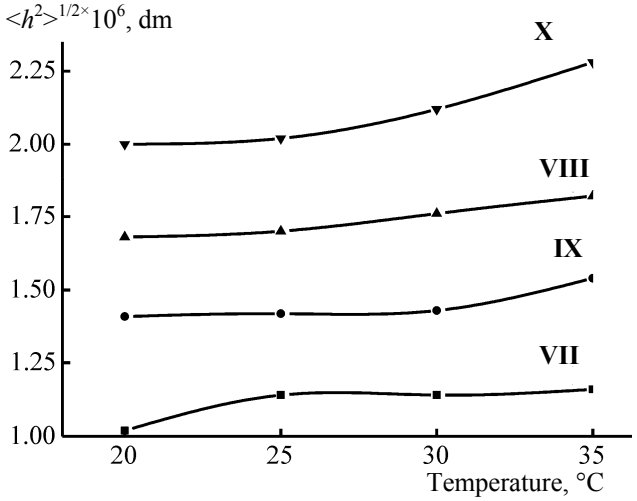


Fig. 6. Copolymer coil dimensions in DMF as function of temperature for styrene copolymers with glycidyl methacrylate **VII** and **VIII** and with glycidyl methacrylate and porphyrin **IX** and **X**.

during 15 min, the second flow time τ_2 was obtained; and so on. From the measured flow times, we determined the relative and specific viscosities:

$$\eta_{rel} = \tau_i/\tau_0,$$
$$\eta_{sp} = \eta_{rel} - 1$$

where τ_i, flow time of the respective polymer solution; τ_0, flow time of the pure solvent.

From the data $\eta_{sp}/c = f(c)$ fitted with straight line by least square method, we obtained the intrinsic viscosity [η] (the linear fit intercept) and the Huggins constant K_H:

$$K_x = \tan\alpha/[\eta]^2,$$

where tan α, the slope of the linear fit.

The copolymers composition was determined from titration of ether and hydroxyl [10, 16, 17], or of epoxy [16] groups.

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