Measurements of molecular characteristics of the extremely high molecular mass polystyrene in solution

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Extremely high molecular mass polystyrene samples with $\bar{M}_w$ of the order of 10^7 have been characterized by light scattering in toluene, by viscometry in toluene and decaline, and by gel permeation chromatography in methyl ethyl ketone and methanol mixture. From the obtained data, the K and a constants of the Kuhn—Mark—Houwink equation, and the dependence of the second virial coefficient A_2 on $\bar{M}_w$ have been calculated.

Образцы полистирола с высоким молекулярным весом $\bar{M}_w$, порядка 10^7, были характеризованы рассеянием света в толуоле, вискозиметрией в толуоле и декалине, гель-проникающей хроматографией в смеси метил-этилкетона и метилового спирта. Из полученных данных были рассчитаны K и а константы уравнения Куна—Марка—Гаувинка и зависимость второго вириального коэффициента A_2 от $\bar{M}_w$.

In 1972 and 1974 American [1] and Japanese [2] authors reported on the synthesis (anionic polymerization) and the characterization of extremely (E) high molecular mass (HMM) polystyrene (PS) samples. At that time an original emulsion polymerization method yielding similar HMM—EHMM polymer was patented in Czechoslovakia [3, 4]. This method, termed emulsion polymerization with initiator forming a heterogeneous phase, was applied for the preparation of the investigated EHMM PS 8a, 4a, 1a, and Ot samples [5, 6].

Experimental

Light scattering (LS) measurements were performed with a Brice—Phoenix Series 2000 photometer. Solutions of EHMM PS samples in toluene were filtered at elevated pressure through a fine porosity sintered-glass (G-4). Superfine sintered-glass (G-5) was used for

solvent purification. Solutions of the initial concentrations were diluted directly in the measuring cuvette and their concentrations were determined by weighing. In view of a relatively low sensitivity of the photometer detector, the scattered beam ($\lambda = 546.1$ nm) was measured at room temperature in the angle and concentration range of $\Theta = 45$—$135°$ and $c \leqslant 0.9 \times 10^{-3}$ g cm^{-3}. A series of scattering data was evaluated graphically as a plot of $Kc/R_\Theta = f(\sin^2(\Theta/2), c)$. A typical example of such an evaluation is shown in Fig. 1. For the calculations of K and R_Θ, the data from photometer manual and the tabulated parameters at
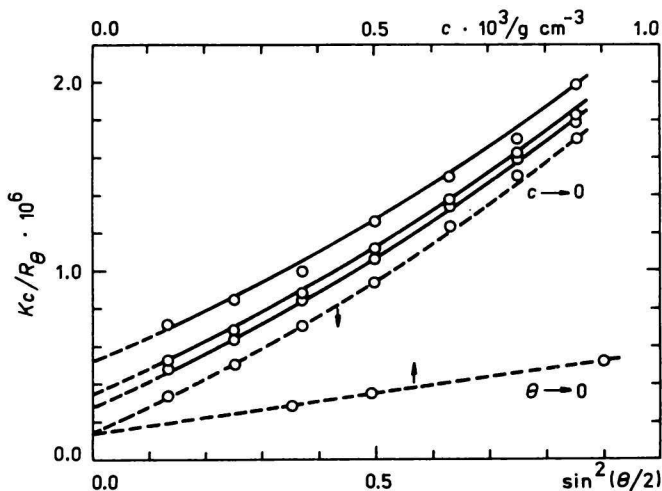

Fig. 1. Plots of Kc/R_Θ *vs.* $\sin^2(\Theta/2)$ and c for PS 8a sample.

25°C [7] were used. The individual $\bar{M}_w$ and A_2 values are given in Table 1. Double logarithmic plot of A_2 against $\bar{M}_w$ for EHMM PS samples in toluene, shown in Fig. 2, is described by the following regression equation

$$A_2 = 4.17 \times 10^{-4} \bar{M}_w^{-0.042} \qquad r^2 = 0.9991 \tag{1}$$

Viscosity measurements of solutions of EHMM PS samples in toluene and decaline (*cis/trans* = 50 : 50 v/v, determined by g.l.c.) were done at 25°C using Seide—Deckert viscometers with the capillary diameter of 0.4 and 0.6 mm. The viscosity data were evaluated according to plots of $(\eta - \eta_0)/\eta_0 c = f(c)$ and $(\ln(\eta/\eta_0)/c = f(c))$. The $[\eta]$ and k_H values are given in Table 1. Double logarithmic plots of $[\eta]$ against $\bar{M}_w$ for EHMM PS samples in toluene and decaline at 25°C, shown in Fig. 3, are described by the following regression equations

$$\text{(PS, toluene, 25°C) } [\eta] = 2.69 \times 10^{-2} \bar{M}_w^{0.66} \qquad r^2 = 0.9987 \tag{2}$$

$$\text{(PS, decaline, 25°C) } [\eta] = 6.66 \times 10^{-2} \bar{M}_w^{0.53} \tag{3}$$

Characterization of EHMM PS samples by gel permeation chromatography (g.p.c.) has been described previously [6]. The $\bar{M}_w/\bar{M}_n$ and $\bar{M}_w$ values are given in Table 1.

Table 1

Molecular characteristics of EHMM PS samples

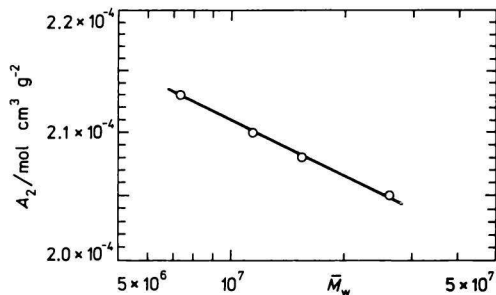| Sample	LS		Capillary viscometry				G.p.c.	
			Toluene, 25°C		Decaline, 25°C			
	$\bar{M}_w \cdot 10^{-7}$	$A_2 \cdot 10^4$ mol cm³ g⁻²	$[\eta]$ cm³ g⁻¹	k_H	$[\eta]$ cm³ g⁻¹	k_H	$\bar{M}_w / \bar{M}_n$	$\bar{M}_w \cdot 10^{-7}$
PS 8a	0.735	2.13	936	0.39 (0.37)	290	0.54 (0.54)	1.81	1.07
PS 4a	1.16	2.10	1230	0.36 (0.36)	370	0.57 (0.51)	2.32	1.49
PS 1a	1.56	2.08	1470	0.30 (0.32)	476	0.59 (0.50)	1.94	2.29
PS Ot	2.63	2.05	2110	0.38 (0.37)	—	—		

Fig. 2. Double logarithmic plot of A_2 against $\bar{M}_w$ for EHMM PS samples in toluene at room temperature.
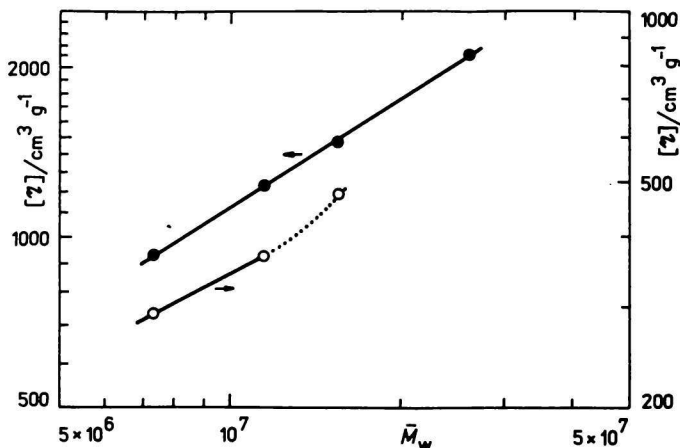

Fig. 3. Double logarithmic plots of $[\eta]$ against $\bar{M}_w$ for EHMM PS samples at 25°C in toluene (●) and in decaline (○).

Correction [7] of the calculated K_w and a values (eqns (2) and (3)) by means of postulating the type (log normal) and the mean width of the molecular mass distribution of the studied EHMM PS samples ($\bar{M}_w/\bar{M}_n = 2$), led to the individual K and a constants of the Kuhn—Mark—Houwink equation (Table 2).

Table 2

Values of determined constants of the Kuhn—Mark—Houwink equation

K cm³ g⁻¹	a	System	$\bar{M}_w$
$(2.89 \times 10^{-2}$	0.66	EHMM PS, toluene, 25°C	0.735×10^7—$2.63 \times 10^7)$
7.26×10^{-2}	0.53	EHMM PS, decaline *cis/trans* $\cong 50 : 50$ v/v, 25°C	0.735×10^7; 1.16×10^7

Discussion

The molecular mass average $\bar{M}_w$ was determined by both the light scattering and gel permeation chromatography. Data in Table 1 show that $\bar{M}_w$ values resulting from LS and g.p.c. are not the same. Their relative difference is within 28 and 47%. According to the literature [8] similar, even larger differences are not unusual, when molecular mass of reference polymers in a common molecular mass range has been measured. The differences between $\bar{M}_w$ values recorded here are caused mainly by extrapolation of scattering data in a relatively wide interval of Θ (45°) and c (Fig. 1), and also by a relatively small number of commercial PS reference materials used for calibration of the g.p.c. instrument in EHMM region. Similar to other reports [7], for functional dependences between molecular characteristics and the corresponding regression eqns (1—3), only $\bar{M}_w$ values determined by LS have been used.

Since the expected course [2, 9] of the $A_2 = f(\bar{M}_w)$ dependence (Fig. 2) was confirmed, and excellent correlation coefficient ($r^2 = 0.9991$) was calculated for the experimental data described by eqn (1), the extrapolation to lower molecular mass is partly justified. For example, the value of $A_2 = 2.28 \times 10^{-4}$ mol cm³ g⁻² calculated from eqn (1) for reference HMM PS sample with $\bar{M}_w = 1.8 \times 10^6$ (Pressure Chem. Co.) is in a good agreement with the values of A_2 from 2.41×10^{-4} to 2.27×10^{-4} mol cm³ g⁻², published [10] for this sample in toluene at 25°C.

Viscosity measurements were carried out on all EHMM PS samples at 25°C in two thermodynamically different solvents, toluene and decaline (*cis/trans* ≅ 50 : 50 v/v; PS, decaline *cis/trans* = 50 : 50 v/v, $t_{theta} \cong 15.5°C$ [11]). In view of the used viscometer type and $\bar{M}_w$ values of the samples, the determined $[\eta]$ values (Table 1) and K and a constants calculated from them (Table 2) have to be evaluated as to various effects they depend upon.

Since $[\eta]/[\eta]_0 = 1 - A\beta^2 + ...$, where the generalized rate of shear, $\beta = G[\eta]_0\eta_0 M/RT$, with increasing molecular mass the determined values of $[\eta]$ become smaller than the values of $[\eta]_0$ with respect to a shear rate of $G = 0$ s⁻¹ [12]. This is sufficiently evident from graph [12] shown in Fig. 4, or especially from the results of measurements of the HMM PS with $\bar{M}_w = 7.14 \times 10^6$, determined in *trans* decaline at 23.8°C and benzene at 30°C with Ubbelohde-type viscometer of $G = 8.53 \times 10^2$ s⁻¹ and $G = 2.19 \times 10^3$ s⁻¹, respectively, where the subtraction $[\eta]_0 - [\eta]$ attains 6.9—17.5% [12]. Mainly because of the above given facts, the Japanese authors [2] limited their viscosity measurements of HMM—EHMM PS to those carried out with a Ubbelohde-type viscometer in *trans* decaline at 20.4°C or cyclohexane at 34.5°C up to $\bar{M}_w \leq 9.72 \times 10^6$ ($[\eta] \leq 240$ cm³ g⁻¹ or $[\eta] \leq 275$ cm³ g⁻¹), and in benzene at 25°C only up to $\bar{M}_w \leq 4.59 \times 10^6$ ($[\eta] \leq 798$ cm³ g⁻¹). On the other hand, the American authors [1] determined $[\eta]$ of their EHMM PS with $\bar{M}_w = 2.74 \times 10^7$ and $\bar{M}_w = 4.38 \times 10^7$ in cyclohexane at
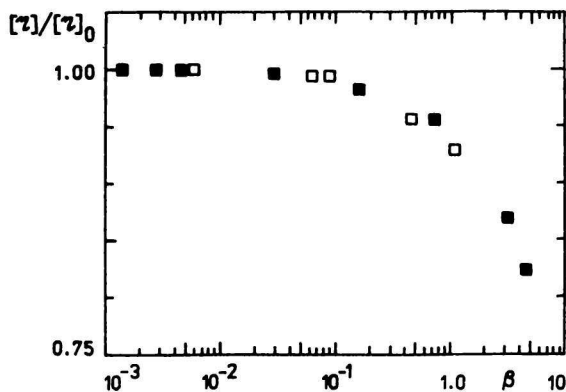
Fig. 4. Graph of $[\eta]/[\eta]_0$ *vs.* β for PS in benzene at 30°C (■) and in *trans* decaline at 23.8°C (□).

35.4°C ($[\eta] = 440$ and $550 \, cm^3 \, g^{-1}$) and benzene at 40°C ($[\eta] = 3650$ and $6770 \, cm^3 \, g^{-1}$) using a Zimm—Crothers viscometer ($G < 0.1 \, s^{-1}$). Since calculations using the latter data give a value of $a = 1.2$ (EHMM PS, benzene, 40°C), the determination of which at $[\eta]/[\eta]_0 = 1.0$ is not influenced by chain entanglement problems (measured solutions were below the critical concentration) [1], it can be assumed that with increasing molecular mass the solvated macromolecule coils become oriented and stretched, as a result of the flow field. For this reason, for measurements of EHMM samples under dynamic conditions the thermodynamically poor, or even theta conditions are preferred [1, 6].

Our viscosity measurements indicated ($a = 0.66$) that at the applied experimental conditions (EHMM PS, toluene, 25°C) the dominating effect is $[\eta]/[\eta]_0 < 1$. With increasing $\bar{M}_w$ of EHMM PS samples the values of $[\eta]$ become smaller than the $[\eta]_0$ values. After pertinent correction also a, in agreement with the literature [7], increases (Fig. 5). From the described measurements the contribution of other effects cannot be estimated.

In the system EHMM PS, decaline *cis/trans* $\cong 50 : 50$ v/v, 25°C the measurements of $[\eta]$ only for three samples were evaluated. Since the double logarithmic plot of $[\eta]$ against $\bar{M}_w$ could not be described by a first-order regression equation with $\alpha = 0.01$ in the whole range (Fig. 3), the results of measurements only of two samples with $\bar{M}_w = 0.735 \times 10^7$ and $\bar{M}_w = 1.16 \times 10^7$ were used for the K and a constant calculations. The resulting data (Table 2) are in good agreement with the expected values, as well as with the published data [2, 7]. Most probably, the viscosity measurements of the sample PS 1a (and maybe the PS 4a, too) were influenced by chain entanglements which, as can be deduced from the decreasing time of flow through the capillary of the viscometer observed in parallel measurements of the PS Ot sample, led to the degradation of macromolecules in solution [13]. It can be concluded, from a comparison of our results with studies on similar
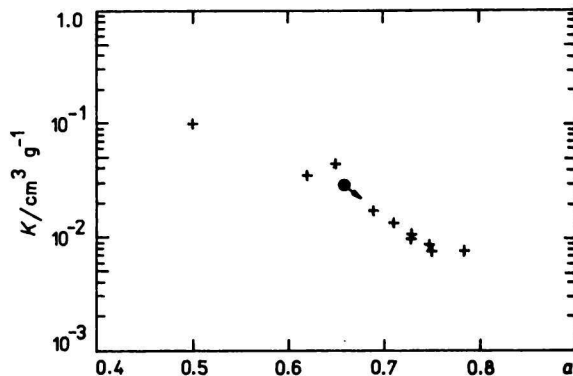
Fig. 5. Graph of the K and a constants of the Kuhn—Mark—Houwink equation for PS, toluene, 25°C. Data (+) from Ref. [7]; calculated (●) K and a constants.

HMM—EHMM samples, that the determination of molecular characteristics under static conditions (*e.g.* LS, ...) is not limited by the upper molecular mass of the samples. For dynamic measurements (*e.g.* viscometry, g.p.c., ...) theta conditions, "zero" shear rate ("zero" shear stress), and subcritical concentrations are preferred, which can be fulfilled in viscometry, but not fully in g.p.c. [6], at present.

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