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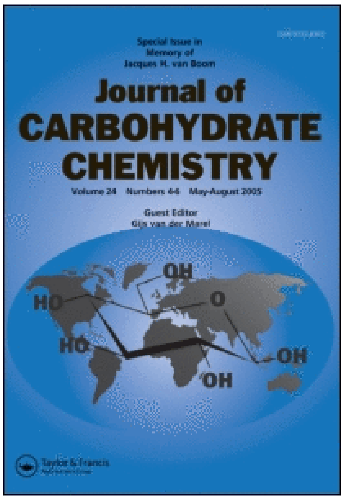

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Molecular Characteristics of Poly(methacrylamido d-Glucose)[1]

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MOLECULAR CHARACTERISTICS OF POLY(METHACRYLAMIDO D-GLUCOSE)[1]

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ABSTRACT

The fractions of poly(methacrylamido D-glucose) with molecular weights $7 < M \cdot 10^{-4} < 550$ have been studied in water by the methods of molecular hydrodynamics. Kuhn-Mark-Houwink equations were obtained. The hydrodynamic invariant and the sedimentation parameter were also calculated. The equilibrium rigidity and the hydrodynamic diameter of molecules modeling macromolecules in solution were evaluated on the basis of the theory of the wormlike necklace model with the effects of excluded volume taken into account at different values of the excluded-volume parameter. The effect of fraction polydispersity on the quantitative values of exponents in the equations of the Kuhn-Mark-Houwink type and the Kuhn segment length is discussed.

INTRODUCTION

Poly(vinyl saccharides) are a relatively new polymer class synthesized from carbohydrate-containing vinyl monomers.[2,3] They broaden the range of hydrophilic polymers which might serve in the preparation of synthetic vaccines and in the

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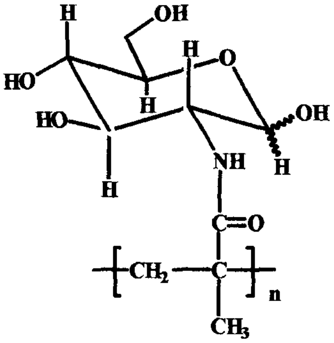
modification of polymers that are carriers of biologically active groups. Poly(vinyl saccharides) are closer in structure to natural metabolites of the organism than such widely used synthetic hydrophilic polymers as polyacrylamide, poly(*N*-vinylpyrrolidone), and some others. The information about their molecular characteristics is scarce.[2,3] Some poly(vinyl saccharides), in spite of the aliphatic structure of their main chain, exhibit some properties typical of rigid-chain polymers.[3]

In the present work the methods of molecular hydrodynamics were used to study the fractions of poly(methacrylamido D-glucose) (PMGA) samples with the following structural formula of the monomer unit:



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The velocity sedimentation, translational diffusion, viscous properties of aqueous solutions of PMGA fractions were studied. Molecular weights were obtained according to Svedberg, and the M_w/M_n ratios characterizing the polydispersity of fractions were determined by GPC. Scaling ratios (of the Kuhn-Mark-Houwink type) relating hydrodynamic characteristics to M were obtained. The prevailing influence of volume effects is shown. These effects are taken into account in evaluating the equilibrium chain rigidity determined by different procedures.

RESULTS AND DISCUSSION

The main experimental characteristics being discussed are as follows: velocity, sedimentation coefficient S_0, translational diffusion coefficient D_0 and intrinsic viscosity $[\eta]$. All these values are related to the size of molecular coil in solution and its molecular weight M.[4,5] The experimental data are listed in Table 1.

Table 1. Hydrodynamic and molecular characteristics of poly(methacrylamido D-glucose) fractions in water at 25°C.

N	[η] cm^3/g	$D_0 \cdot 10^7$ cm^2/s	$S_0 \cdot 10^{13}$ s	$M_{SD} \cdot 10^{-3}$	M_w/M_n	$A_0 \cdot 10^{10}$
1	340	0.44	32.6	5520	-	3.51
2	175	0.68	21.7	2380	1.66	3.28
3	136	0.83	21.2	.1900	1.53	3.42
4	110	0.98	15.2	1155	1.50	3.18
5	82	1.08	16.6	1140	1.35	3.17
6	90	1.08	14.3	990	1.97	3.11
7	75	1.37	-	660	-	-
8	47	1.76	13.3	560	-	3.39
9	52	1.76	12.6	530	1.40	3.44
10	40	2.64	10.8	305	1.19	3.92
11	25	2.74	8.6	230	1.17	3.19
12	29	2.45	6.2	190	2.56	2.79
13	11	4.82	4.7	73	1.50	2.89

Figure 1 shows the dependences of the Kuhn-Mark-Houwink type (KMH) in which M were calculated from Svedberg's equation (M= R•[S]/[D]). Table 2 gives the equation parameters obtained by the least-squares method (LSM). The last column in Table 2 gives the linear correlation coefficients r for the equation $\log B_i = \log K_i + b_i \cdot \log M$ where B_i = [η], S_0 or D_0. The mean-square errors which symbolized by the Greek letter Δ in Table 2 and in other tables were calculated from the values of the linear correlation coefficients.[6]

Table 2 gives for comparison the ratios of exponents b_i/b_j calculated from M and obtained from pair logarithmic dependences of experimental values of [η], D_0, and S_0. A satisfactory (within the mean-square error) agreement between the values of b_i calculated

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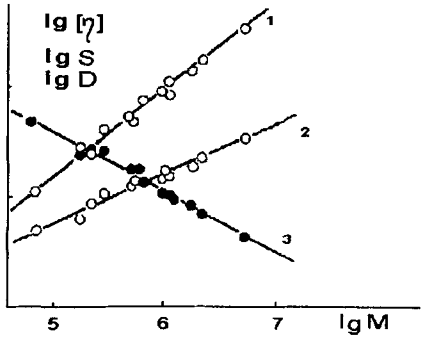

Figure 1. Dependences of (1) [η], (2) S_0 and (3) D_0 on M_{SD} on a double logarithmic scale. S_0 is expressed in Svedberg units and D_0 in units of $10^{-7} cm^2/s$.

Table 2. Parameters of equations of the Kuhn-Mark-Houwink type for poly(methacrylamido D-glucose) fractions in water at 25°C in the range $70 < M \cdot 10^{-3} < 5500$.

N	Correlate values	b_i	Δb_i	$\log K_i$	$\Delta \log K_i$	K_i	r_i
1	D_0 - [η]	-0.719	0.032	2.458	0.059	$2.87 \cdot 10^{-7}$	0.9902
2	S_0 - [η]	0.556	0.045	0.110	0.083	$1.29 \cdot 10^{-13}$	0.9682
3	k_s - S_0	2.0	0.30	-0.47	0.36	0.34	0.9549
4	[η]- M	0.772	0.031	-2.69	0.18	$2.03 \cdot 10^{-3}$	0.9922
5	D_0 - M	-0.560	0.024	4.42	0.14	$2.64 \cdot 10^{-4}$	0.9907
6	S_0 - M	0.440	0.024	-1.45	0.14	$3.55 \cdot 10^{-15}$	0.9855

from the dependences obtained by using M and their ratios b_i/b_j is observed: $b_1= b_5/b_4$; $b_2= b_6/b_4$. The subscripts are the numbers of lines of Table 2.

Moreover, within the error of the determination we have $b_5= (b_4+1)/3$[5] and $b_6= 2/(b_3+3)$.[7] This fact indicates that the experimental values of $[\eta]$, D_0, S_0, and k_s correlate with each other, which is characteristic of linear polymer homologues.

The values of the hydrodynamic invariant[5] $A_0= (R\cdot[D]^2\cdot[S]\cdot[\eta])^{1/3}$ and the sedimentation parameter[7] $\beta_S= N_A(R^{-2}\cdot[D]^2\cdot[S]\cdot k_S)^{1/3}$ were calculated from the experimental values of D_0, $[\eta]$, S_0, and k_S. The mean value of the hydrodynamic parameter is $A_0= (3.25\pm0.3)\cdot10^{-10}$ erg mol$^{1/3}$ K^{-1} and that of the sedimentation parameter $\beta_S= (1.1\pm0.2)\cdot10^7$ mol$^{1/3}$ where N_A is Avogadro's number, R is the gas constant, $[D]= D_0\cdot\eta_0\cdot T^{-1}$, $[S]= S_0\eta_0(1-v\rho_0)$, and η_0 is the solvent viscosity, ρ_0 is its density, v being the partial specific volume of the polymer in solution.

The effect of fractions polydispersity on the numerical values of the coefficients in the KMH equation was analyzed in agreement with the results of calculations.[8] In this case, for instance, for $[\eta]$ the corresponding KMH equation is written in the form $[\eta]= K\cdot M^b\cdot q$, where q is the dimensionless coefficient depending on M_w/M_n, the MWD type, the method of determination of the corresponding hydrodynamic characteristics, and MW. In our case the results given in Tables 1.7 and 1.8[8] were used and the parameters of the KMH equations were calculated for two distribution types: the Schulz-Flory-Zimm ($[\eta]=2.07\cdot10^{-3}\cdot M^{0.766\pm0.034}$; r = 0.9923) and normal logarithmic distributions ($[\eta]= 2.18\cdot10^{-3}\cdot M^{0.762\pm0.030}$; r =0.9938). The comparison with the results given in Table 2 ($b_4= 0.772\pm0.031$) shows that in our case the parameters of KMH equation remain virtually unchanged when fraction polydispersity is taken into account. The correction coefficients q for equations relating S_0 and D_0 to M have not yet been published but the analysis[9] shows that the correction coefficients q_S and q_D do not exceed q. Therefore, it may be expected that the evaluation of polydispersity of fractions in the case of D and S will not lead to changes in the coefficients of the corresponding KMH equations. Hence, in further discussion the coefficients listed in Table 2 are considered.

The values of b_4 and $|b_5|$ are greater than 0.5 characteristic for Gaussian chains. This deviation of the values of b_4 and b_5 may be due either to the effects of swelling of

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the macromolecules (excluded volume effect) or to those of their intramolecular draining.

As we have pointed out previously[6,10] the plot of M/[η] vs $M^{1/2}$ can serve over a wide MW range as a test plot for assigning a polymer-homologous series either to a class of flexible-chain polymers with dimensions perturbed by volume effects (in this case an increase in the slope of this dependence is observed on passing to the range of low M) or to that of rigid-chain polymers (the sign of the slope of this dependence changes on passing to the range of low M). This fact is illustrated in Figure 2 in which the data for PMGA and a representative of rigid-chain polymers (a cellulose nitrate with a high degree of substitution[11]) are plotted in a system of coordinates taking into account the difference between the MW and length of the repeat unit of the polymers being compared. When the dependences of $L/M_L \cdot [\eta]$ on $L^{1/2}$ are compared for these two systems, two points should by mentioned: (1) at high L the values of $L/M_L \cdot [\eta]$ differ by one order of magnitude, (2) the shape of this dependence is different for flexible- and rigid-chain polymers, where L is the contour length of the molecule.

In our opinion the plot in Figure 2 shows that volume effects prevail in PMGA chains. The effect of intramolecular draining of molecular coils will be neglected to a first approximation. In order to evaluate quantitatively the length of the Kuhn segment from viscometric data the Burchard-Stockmayer-Fixmann plot (BSF plot)[12,13] will be used first. It corresponds to the following equation:

$$[\eta]/M^{1/2} = K_\theta + 0.51\Phi_0 \cdot B \cdot M^{1/2} = \Phi_0[(A/M_L)^{3/2} + 0.51 \cdot B \cdot M^{1/2}] \qquad (1)$$

where Φ_0 is the Flory viscosity coefficient, B is the coefficient characterizing the thermodynamic quality of the solvent, A is the length of the Kuhn segment, and M_L is the unit mass of the polymer chain.

Since the fractions exhibit marked polydispersity, the procedure[8] will be used to evaluate the difference between the M_w/M_n ratio and unity in using the BSF plot. In this case equation 1 is written in the following form:

$$[\eta]/M^{1/2} = K_\theta q + 0.51 \cdot \Phi_0 \cdot B \cdot M^{1/2} \qquad (2)$$

where q<1 and depends on both the M_w/M_n ratio and the type of MWD. The function $q(M_w/M_n)$ has been tabulated[8] for the distribution of the Schulz-Flory type and for normal logarithmic distribution. Figure 3 shows the dependences of $[\eta]/qM^{1/2}$ on $M^{1/2}/q$, which

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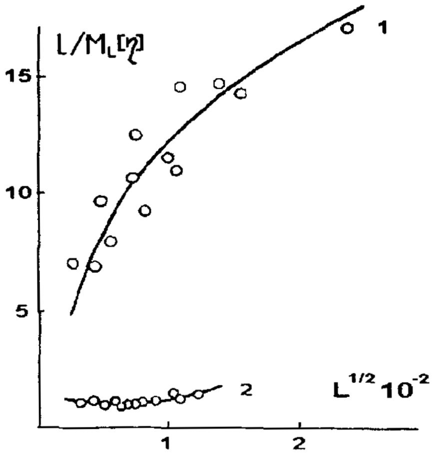

Figure 2. Dependences of $L/M_L \cdot [\eta]$ on $L^{1/2}$ for (1) PMGA according to data in Table 1 and (2) cellulose nitrate.[11]

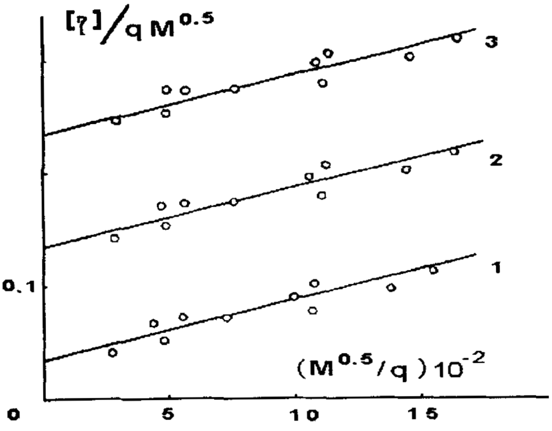

Figure 3. Burchard-Stockmayer-Fixman's plot for PMGA in water (1) without taking into account fraction polydispersity (parameter q=1) and (2,3) taking it into account. (2) for Schulz-Flory's distribution and (3) for normal logarithmic distribution. Each successive curve is displaced along the $[\eta]/qM^{0.5}$ axis by 0.1 with respect to the preceding curve.

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Table 3. Effect of fraction polydispersity on the plot of the BSF type for PMGA in water.

The parameter q	K_θ	ΔK_θ	$(0.51\cdot\Phi_0\cdot B)$ $\cdot 10^5$	$\Delta(0.51\cdot\Phi_0\cdot B)$ $\cdot 10^5$	r
1	0.033	0.009	5.5	1.2	0.8784
q_{SF}	0.034	0.010	5.5	1.2	0.8756
q_{LN}	0.035	0.010	5.6	1.3	0.8714

corresponds to equation 2 for three cases: 1) without taking into account the polydispersity of fractions (q=1), 2) for the Schulz-Flory distribution (q= q_{SF}, 0.941 <q< 0.983), 3) for the normal logarithmic distribution (q= q_{LN}, 0.917 <q< 0.980).

All dependences were processed by LSM, and the results are listed in Table 3. It follows from this table that in this case (at $M_w/M_n < 2$) the values of K_θ are virtually independent of fraction polydispersity. At the theoretical value $\Phi_0 = 2.87\cdot 10^{23}$ plots in Figure 3 lead to the value of the Kuhn segment length A= $(23\pm 4.5)\cdot 10^{-8}$ cm.

Further, to evaluate quantitatively the length of the Kuhn segment, we will use the Gray-Bloomfield-Hearst theory[14] which considers the molecular weight dependence of the translational friction coefficient of the wormlike necklace taking into account the influence of excluded volume effect on chain dimensions. This influence will be characterized by the parameter ε[15] calculated from the equation $\varepsilon = (2b_4 - 1)/3 = -(1+2b_5)$. This unique theory takes into account both the hydrodynamic draining and the excluded volume effects in polymer chains.

Thus, for S_0[14] the following equation is obeyed to the first approximation:

$$[S]P_0 N_A = \frac{3}{(1-\varepsilon)(3-\varepsilon)} \frac{M_L^{(1+\varepsilon)/2}}{A^{(1-\varepsilon)/2}} M^{(1-\varepsilon)/2} + \frac{M_L P_0}{3}\left[\ln\frac{A}{d} - \frac{1}{3}\left(\frac{A}{d}\right)^{-1} - \varphi(\varepsilon)\right] \qquad (3)$$

where d is the hydrodynamic diameter of the chain and φ(ε) is the tabulated function.[14]

The plot of [S] vs $M^{(1-\varepsilon)/2}$ is shown in Figure 4, and Table 5 lists the numerical values of A_f and d_f determined from data on translational friction and obtained by using

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Table 4. Lengths of the Kuhn segment (A) and hydrodynamic diameters (d) at different values of the parameter of poly(methacrylamido D-glucose) molecules in water.

Translational friction							Intrinsic viscosity	
ε	A_f nm	ΔA_f nm	$\varphi(\varepsilon)$	d_f nm	Δd_f nm	r	$\Phi(\varepsilon)\cdot 10^{-23}$	A_η nm
0.12	4.6	0.4	1.817	0.5	0.5	0.9918	2.075	2.9
0.16	3.7	0.4	1.970	0.9	0.8	0.9918	1.866	2.5
0.18	3.3	0.3	2.057	1.3	1.1	0.9918	1.771	2.3

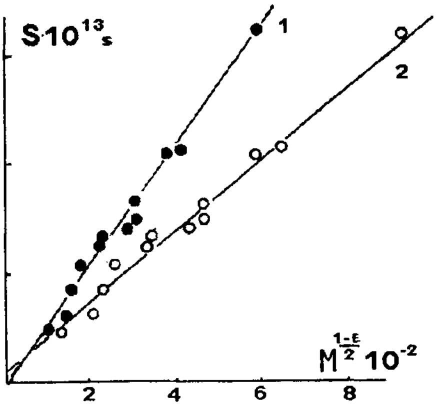

Figure 4. Dependences of S_0 on $M^{(1-\varepsilon)/2}$ at $\varepsilon = 0.18$ (1) and 0.12 (2) for PMGA molecules in water.

Table 5. Polymerization of methacrylamido D-glucose.

N	Type of initiator	Initiator concentration	Solvent	MAG conc. %	Time h	Conversion %	$[\eta]$ 0.1M Na_2SO_4 cm^3/g	$[\eta]$ H_2O cm^3/g	$M^a \cdot 10^{-4}$
I	1	1.0%	DMF	10.0	24	95.0	25	21	16
II	1	3.0%	DMF	10.0	24	96.5	18	17	12
III	1	0.5%	DMF	14.3	24	92.0	46	-	43
IV	2	$5.5 \cdot 10^{-2}M+$ $+3.4 \cdot 10^{-3}M$	H_2O	10.0	5.5	82.0	12	-	7.5
V	2	$4 \cdot 10^{-2}M+$ $+2.5 \cdot 10^{-2}M$	H_2O	10.0	5	70.0	9	8	4.5
VI	3	1.0%	H_2O	10.0	7	97.0	52	50	49
VII	3	1.0%	H_2O	20.0	0.5	50.0	122	137	180
VIII	3	0.1%	H_2O	15.0	3	67.0	-	20	15

a- calculated from the equation: $[\eta]= 2.03 \cdot 10^{-3} \cdot M^{0.77}$.

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these plots for different values of ε. Viscometric data may be interpreted also in the framework of the theory[16] which describes the dependence of [η] on M, A, and ε for a wormlike necklace model. The results of this theory can be presented in the analytical form only for the limiting case of high MW and are the theoretical basis of the KMH equation for flexible chain polymers the size of which is perturbed by volume effects:

$$[\eta] = \frac{\Phi(\varepsilon) A^{(3-3\varepsilon)/2}}{M_L^{(3+3\varepsilon)/2}\left(1+5\varepsilon/6+\varepsilon^2/6\right)^{3/2}} M^{(1+3\varepsilon)/2} \qquad (4)$$

where

$$\Phi(\varepsilon)= 2.86 \cdot 10^{23}(1- 2.63 \cdot \varepsilon+ 2.86 \cdot \varepsilon^2)^{15} \qquad (5)$$

The corresponding values of the parameter Φ(ε) and the values of the equilibrium chain rigidity A, which are obtained from equation 3, are given in Table 4. The values of A estimated from the BSF plots and on the basis of the theory[16] are in satisfactory agreement with each other. It is usually assumed[17] that the difference in the values of A_f and A_η reflects the discrepancy between the theories describing the translational and rotational friction of polymer molecules in solutions. This discrepancy also leads to a lower theoretical mean experimental value of the hydrodynamic invariant A_0.

These values of A slightly exceed those of A determined for another water-soluble carbon chain poly(*N*-vinyl pyrrolidone) (PVP). The values of A_f= 2.5 nm and A_η= 1.9 nm were obtained for PVP.[6] This may be associated with a greater hindrance to rotation in the chain of the main valences of PMGA than that for PVP. The reason for this may be the interaction between the OH groups of glucosamine side chains with the formation of intrachain hydrogen bonds.

EXPERIMENTAL

Polymerization procedure. Methacrylamide D-glucose (MAG) was obtained by a method described in the literature.[18] 2,2'-Azobis(2-methylpropanediamine) dihydrochloride (ABPA) was prepared by a reported procedure .[19] $K_2S_2O_8$ and $K_2S_2O_5$ (analitical grade) and methanol (obtained commercially) were used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) and DMF (commercially obtained, were purified by standard methods. Polymers were prepared by solution polymerization in DMF or water with (AIBN) (**1**), $K_2S_2O_8$ - $K_2S_2O_5$ (**2**) or ABPA (**3**) as initiator. The required amounts of monomer, solvent and initiator were charged into a pure glass ampule, which was then degassed under vacuum by conventional freezing and thawing technique and sealed off under vacuum. The polymerization was carried out with continuous shaking in a thermostat at 60 °C for a given (Table 5). After polymerization the ampule was opened and its content was poured into a large amount of methanol to precipitate the polymer. The polymer was filtered and washed with methanol to remove the residual monomer. The resulting polymers were then purified by the reprecipitation from the DMF solution with excess methanol.

The highest intrinsic viscosity and, correspondingly, M were exhibited by PMGA samples synthesized in the presence of **3** (Table 5). Some samples were fractionated by fractional precipitation in a water-acetone system at initial concentrations $c = 1 \cdot 10^{-2} g/cm^3$.

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The ^1H NMR spectrum (recorded with a JEOL C60-HL spectrometer at an operating frequency of 60 MHz) of an MAG solution in D_2O confirms the structure: the proton signals of groups $=CH_2$ (5.65 and 5.45 ppm) and $-CH_3$ (2.3 ppm) show that the methacrylamide fragment is present. The glucopyranose ring exhibits peaks in the range from 3.5 to 4.2 ppm and the signals at 5.2 and 4.9 ppm assigned to ^1H in the α- and β-forms, respectively. The latter signal is concealed under the solvent signal (4.8 ppm).

Diffusion. Translational diffusion was studied by a classical method of forming a boundary between the solution and the solvent.[4,5] A diffusion boundary was formed in a glass cell of length **h** = 30 mm along the beam path at an average solution concentration $c= 2\cdot10^{-4}g/cm^3$. The average time of boundary formation was 20-30 min. The values of D obtained at these concentrations were assumed to be the values extrapolated to zero concentration (validity of this procedure was confirmed by numerous investigations of the concentrational dependence of D[5]). The optical system of recording the solution-solvent boundary in diffusion-sedimentation analyses was a Lebedev's polarizing interferometer.[5,20]

Translational diffusion coefficients D were calculated from the equation:

$$\sigma^2 = \sigma_0^2 + 2Dt$$

where σ^2 is the dispersion of diffusion boundary calculated from the maximum ordinate and the area under the diffusion curve, σ_0^2 is the zero dispersion characterizing the quality of boundary formation, and t is the diffusion time. Experiments were carried out at 26°C, and diffusion coefficients reduced to 25°C according to a standard procedure.[4]

Sedimentation. Velocity sedimentation was investigated with an analytical MOM 3170 ultracentrifuge (Hungary) at a rotor speed $n= 40\cdot10^3$ rpm (cell height was 12 mm). Sedimentation coefficients S_0 were calculated from the displacement of the sedimentation curve maximum x during the time t (Figure 5).

For six samples the dependence of S_0 on c which corresponded to the equation $S^{-1}= S_0^{-1}\cdot(1+(k_S+v)c)$ was studied (k_s is the sedimentation-concentration coefficient). A correlation between S_0 and k_s was established: $k_s= 0.34\cdot S_0^{2.0\pm0.24}$ and was used to exclude concentration effects for other samples.

Density increment. The density increment of PMGA in water $\Delta\rho/\Delta c= (1- v\rho_0)= (0.333\pm0.006)$ was investigated by picnometry.

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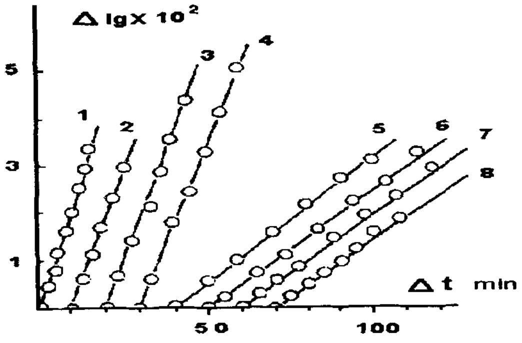

Figure 5. Dependences of Δlnx on Δt where x is the position of the sedimentation peak maximum at the time moment t_i; $\Delta t = t_i - t_1$, t_1 and t_i are sedimentation times at the moments of the first and the i-th sedimentograms for fractions 3 (1-4) and 13 (5-8) at concentrations $c \cdot 10^2 g/cm^3$:
1- 0.074; 2- 0.131; 3- 0.207; 4- 0.257;
5- 0.137; 6- 0.29; 7- 0.397; 8- 0.479.
Each successive curve is displaced to the right by 10 min along the t axis with respect to the preceding curve.

Figure 6. Chromatograms of PMGA fractions. Numbers under the curves are fraction numbers in Table 1.

Intrinsic viscosity. Viscosity measurements were conducted using an Ostwald viscometer. The flow times, t_0 and t, were measured at 25°C, for the solvent and polymer solutions, respectively with relative viscosities, $\eta_r = t/t_0$ in the range from 2.2 to 1.2. All flow times were sufficiently long to avoid kinetic energy correction. Shear dependence was also negligible. The intrinsic viscosity $[\eta]$ was determined as the value of $(\eta_r-1)/c$ at the limit of vanishing c. The Huggins parameter k' was calculated from the slope of this dependence according to the equation $(\eta_r-1)/c = [\eta] + k'[\eta]^2c + ...$ The average value of the Huggins parameter k' is 0.43±0.11.

GPC investigation. Chromatographic experiments were carried out on a "Millipore Waters" GPC II chromatograph with a refractometric detector, and the

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chromatograms were processed on a Data Module (M730). Columns of the "Toyo Soda TSK" company, G. 6000 PW and G. 3000 PW, were 600•7.5 mm each and were connected in series. The flow rate was 1 mL/min at room temperature and a pressure of (1-2)$\cdot 10^6$ Pa. The concentration of the sample was (0.5-1)$\cdot 10^{-3}$g/cm^3, and the injected volume was 0.15-0.25 mL. The chromatograms were unimodal (Figure 6).

The retention volume of fractions was established from the chromatogram maximum. A 0.1 M solution of sodium acetate was used as eluent. The columns were calibrated with poly(*N*-vinylpyrrolidone) fractions and poly(ethylene glycol) samples ("Serva" company).[6,21]

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