

CLOUD POINT CURVES OF AQUEOUS SOLUTIONS OF POLY(*N*-ETHYLMETHACRYLAMIDE)

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Received April 6, 1993

Accepted June 15, 1993

Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Aqueous solutions of poly(*N*-ethylmethacrylamide) have a lower critical solution temperature (LCST). Cloud point curves of five polydisperse samples ($M_w \cdot 10^{-6} = 0.06$ to 2.04) in aqueous solutions at concentrations from 0.002 to 0.1 g/ml were obtained. The threshold concentration was found to be almost independent of the molecular weight. The threshold temperature decreases moderately with increasing M and the limiting value for infinite M obtained by the Shultz-Flory method is $\Theta_L^{PE} = 340.5$ K. This value is lower by 2.5 K than the temperature Θ_L^{η} at which the intrinsic viscosity is proportional to the square root of the molecular weight. The difference cannot be assigned to experimental errors. The entropy-of-dilution parameter is negative ($\psi = -2$) and much higher than the value obtained from dilute solution properties. The differences in Θ and ψ values are discussed in terms of the theory of polymer solutions where a higher-order interaction parameter is included.

Taylor and Cerankowski¹ and Ito² found that dilute aqueous solutions of poly(*N*-ethylmethacrylamide), PEMA, become cloudy on heating at temperatures above 50 °C but reported no information on the effects of polymer concentrations and molecular weight on the cloud point curves. These effects are dealt with in the present paper. Hydrodynamic properties of this system at temperatures from 5 to 70 °C are discussed in another paper³.

EXPERIMENTAL

Materials

Methacryloyl chloride, p.a., ethylamine, p.a., and dimethyl sulfoxide (DMSO, dried over a molecular sieve and rectified under nitrogen on a column packed with Helifpack at 55 °C/533 Pa) and 2,2'-azobisisobutyronitrile (AIBN, recrystallized from methanol) were from Fluka A.G. All solvents were dried and purified by usual procedures.

N-Ethylmethacrylamide (EMA) was prepared⁴ by reaction of 2.2 mol of ethylamine with 1 mol of freshly distilled methacryloyl chloride in benzene solution at -5 °C.

Poly(*N*-ethylmethacrylamide) was prepared by radical polymerization of EMA in DMSO or methanol using AIBN as initiator. Polymerization mixtures were dosed into ampoules, and bubbled through with catalytically purified nitrogen. Ampoules were sealed and placed into a bath thermostatted to 50, 55 or 60 °C. Polymers were isolated by precipitation in the mixture of petroleum ether and diethyl ether (1 : 3 v/v) and purified by reprecipitation from methanol into the same mixture. Conditions for polymerization (see Table I) were chosen so as to obtain polymers with molecular weight between 5 · 10⁴ and 2 · 10⁶. Weight-average (M_w) and number-average (M_n) molecular weights estimated by light scattering and osmometry are listed in Table II.

TABLE I
Polymerization of *N*-ethylmethacrylamide

Sample	Solvent	[M] ^a mmol/l	[AIBN] ₀ mol/l	Temperature °C	Time h
1	DMSO	5.65	1.02	50	18
2	DMSO	4.06	2.98	55	16
3	DMSO	2.84	8.06	60	17
4	CH ₃ OH	2.44	15.27	60	17
5	CH ₃ OH	2.12	26.74	60	17

^a Monomer.

TABLE II
Characteristics of polymer samples

Sample	$M_w^a \cdot 10^{-3}$	$M_n^b \cdot 10^{-3}$	M_w/M_n	$A_2^a \cdot 10^4$ mol ml g ⁻²	M_w/M_n^c	T_t K
1	2 040	—	—	2.3	—	341.1
2	790	175	4.5	1.9	3.2	341.2
3	200	115	1.7	4.4	1.8	342.7
4	100	59	1.7	11.4	1.5	343.3
5	61	—	—	20.3	1.4	343.5

^a By light scattering in DMF at 25 °C; ^b by osmometry in methanol at 25 °C; ^c by size exclusion chromatography.

Methods

Light scattering. Measurements were performed with commercial Sofica 40000 apparatus in vertically polarized light at 546 nm in the angular range from 30 to 150° at 25 °C. The refractive index increment in DMF ($dn/dc = 0.095 \text{ ml/g}$) was measured with a Brice-Phoenix differential refractometer. Experimental data for five polymer concentrations were treated by the Zimm extrapolation method (Fig. 1). The Zimm diagrams were smooth with all samples.

Osmometry. An automatic osmometer Knauer was used with methanol as solvent at 30 °C. The number average molecular weight M_n was calculated from the reduced osmotic pressure extrapolated to zero polymer concentration (Table II).

Viscometry. Viscosity was measured in Ubbelohde capillary viscometers adapted for subsequent dilution. The correction for the loss of kinetic energy was negligible. The concentration of solutions was chosen so that the specific viscosity was $0.1 < \eta_{sp} < 0.8$. The intrinsic viscosity $[\eta]$ was determined by extrapolating to zero concentration the values of η_{sp}/c measured at four to five polymer concentrations. The intrinsic viscosity was determined by the Heller extrapolation method⁵ (Table III). Concentrations of solutions were calculated from those at 25 °C employing the temperature coefficients of density of water.

TABLE III
Intrinsic viscosity (ml/g) of PEMA in water at various temperatures

Sample	343 K	340.5 K	338 K
1	67.2	93.5	119
2	38.0	—	56.6
3	19.3	22.0	24.8
4	13.3	14.8	16.3
5	10.9	11.5	12.0

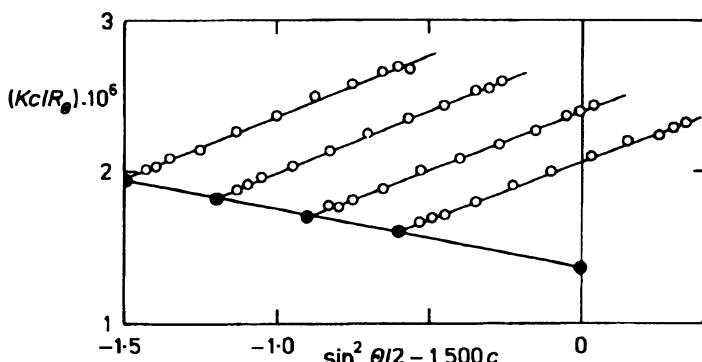


FIG. 1
Zimm diagram for PEMA, sample 2, in DMF at 25 °C

Size exclusion chromatography. The SEC diagrams were obtained using a column (1.5 × 100 cm) packed with Sephadryl S 500 (flow rate 11 ml/h, injection 1 ml, detection by differential refractometer Knauer) and a FPLC column Pharmacia Superose 6TM (flow rate 0.25 ml/h; injection 0.1 ml, detection by RI Knauer). 0.5% polymer solutions were injected and a buffer containing tris(hydroxymethyl)aminomethane (0.05 mol/l) and NaCl (0.5 mol/l) was used as eluent. Its pH value was adjusted to 8.0 by HCl. The former column was calibrated with polysaccharides (Polymerlab, U.K.) and was used for sample 2. The latter column was calibrated with poly[*N*-(2-hydroxypropyl)methacrylamide] fractions characterized by light scattering and was used for samples 3 and 5.

Preparation of solutions. In view of strong hygroscopicity, polymer samples were kept over Mg(ClO₄)₂ or P₂O₅. A small amount of polymer was put in a weighed volumetric flask, the system was evacuated and heated to 50 °C for two days. After this time, the weight was constant. Then the solvent was quickly added and the flask was shaken overnight at laboratory temperature. Dissolution was very quick and perfect.

Cloud point curves. For each polymer sample, stock solutions of the highest concentration used were prepared by dissolving a proper amount of dried polymer in a known amount of distilled water. Solutions of lower concentrations were obtained by mixing known amounts of the stock solutions with water in ampoules (4 ml) which were then sealed after adding a few glass beads.

The set of ampoules was immersed into a water bath. Temperature was gradually increased until the cloud points were achieved for all concentrations. Cloud points were determined by visual inspection. The procedure was repeated at least twice with the heating rate of 0.1 °C/min. The cloud points T_p could be estimated within 0.2 °C (Fig. 2). No significant difference was established between the T_p values obtained on heating and on cooling.

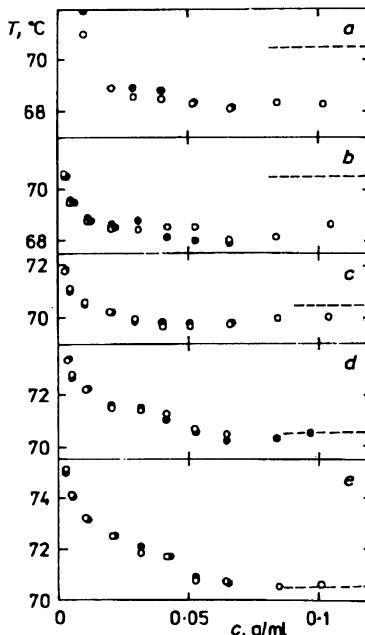


FIG. 2

Cloud point curves for PEMA in water. $M_w \cdot 10^{-6}$:
 a 2.0, b 0.77, c 0.20, d 0.10, e 0.061. ○, ●, ⊕ repeated experiments with fresh solutions. Broken horizontal lines denote the temperature Θ_L^n at which $[\eta]/M_w^{1/2}$ is invariant with respect to M_w

RESULTS AND DISCUSSION

Polymer Characteristics

Poly(*N*-ethylmethacrylamide) is readily soluble in water, DMF, and aliphatic alcohols but insoluble in hydrocarbons, ketones, ethers, esters, dioxan, tetrahydrofuran and γ -butyrolactone. In spite of the wide set of non-solvents, we could not find any suitable and convenient solvent–nonsolvent system for preparative fractionation. Therefore, non-fractionated samples were used in the present and subsequent studies.

The samples cover a broad range of molecular weights ($60 < M_w \cdot 10^{-3} < 2040$). The values of M_w/M_n (Table II) of three samples are in the range which is usual with products of a radical initiated polymerization. The values obtained for samples 3 and 4 from SEC are in fair agreement with those calculated from the M_w and M_n values measured by absolute methods. With sample 1, the polydispersity index could not be estimated by either method because the size of the macromolecules was partly above the exclusion limit of the SEC columns and the number-average molecular weight was too high to be measured by osmometry. The polydispersity index of sample 2 is unusually high.

Cloud Point Curves

The present study confirms the finding^{1,2} that the system PEMA–water has a lower critical solution temperature (LCST). However, for reasons unknown to us, the cloud point temperatures T_p are higher than the reported ones. The cloud point curves (Fig. 2) have shallow minima (threshold cloud points). They are characterized by the threshold polymer volume fraction $\phi_{2,t}$ and the threshold temperature T_t . In view of the shape of the curves, the $\phi_{2,t}$ values can be assessed only roughly (0.07–0.1). They are not markedly dependent on the molecular weight although the range of molecular weights is broad. The threshold temperatures can be estimated with better accuracy. They moderately decrease with increasing M (Fig. 3, Table II).

With polydisperse samples such as those used here, the threshold cloud points are not identical with the critical points^{6–8}. For the case where the polymer has a molecular weight distribution of the Schulz–Zimm type and where the Flory–Huggins polymer–solvent interaction parameter χ is assumed to be independent of concentration and to depend on the temperature according to Eq. (1)

$$\chi = \frac{1}{2} - \psi (1 - \Theta/T) \quad (1)$$

Shultz⁸ has derived a relation between T_t and the weight-average number of segments per chain m_w

$$1/T_t = 1/\Theta + (1/\psi\Theta) [Qm_w^{-1/2} + \left(\frac{1}{2}\right)m_w^{-1}], \quad (2)$$

where

$$Q = 1 - [1/4(h+1)^2] [1 - 0.184(h+1)^{-7/6}] \quad (3)$$

and

$$1/h = m_w/m_n. \quad (4)$$

Here, m_n is the number-average number of segments per chain and ψ is the entropy-of-dilution parameter. For large m_w , Eq. (2) simplifies to

$$1/T_t = 1/\Theta + (1/\psi\Theta)QM_w^{-1/2}. \quad (5)$$

Since m_w is proportional to M_w , the plot of $1/T_t$ vs $QM_w^{-1/2}$ is expected to be linear and to yield $1/\Theta$ as intercept.

In Fig. 4 the reciprocals of T_t for PEMA in water are plotted against $M_w^{-1/2}$. The arrows associated with four points, where polydispersity is known, indicate the approximate change of their position if the $QM_w^{-1/2}$ values were used as abscissae. From the intercept we estimate Θ_L^{PE} to be 340.5 K. The subscript L and superscript PE are used to show that the Θ -temperature is a LCST and has been obtained from a study of phase equilibria. Assuming⁹ that

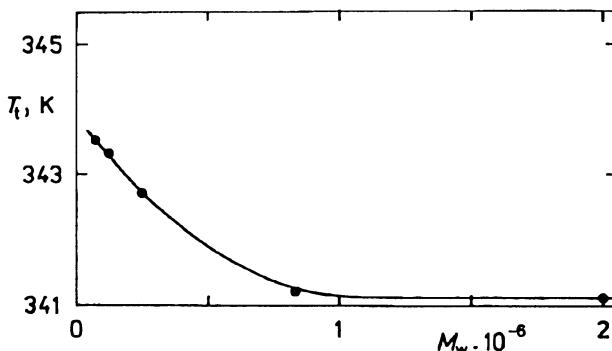


FIG. 3
Molecular-weight dependence of the threshold temperature T_t of PEMA in water

$$m_w = (\bar{v}/V_1) M_w, \quad (6)$$

where \bar{v} is the partial specific volume of the polymer and V_1 is the molar volume of the solvent, the slope of the plot of T_t^{-1} vs $M_w^{-1/2}$ is

$$S = (\Theta\psi)^{-1} (\bar{v}/V_1)^{-1/2}. \quad (7)$$

With $\bar{v} = 0.839$ ml/g, $V_1 = 18.4$ ml/mol (at $\Theta_L^{PE} = 340.5$ K) and $S = -6.8 \cdot 10^{-3}$, we obtain $\psi = -2.0$.

Θ_L^{PE} -Temperature

According to the theory of polymer solutions of flexible polymer chains^{6,7,9}, the Θ^{PE} temperature derived from phase equilibria should be equal to the temperature Θ^A at which the second virial coefficient vanishes. The Θ^n temperature at which, for random coils in the non-draining regime, the ratio of the intrinsic viscosity and square root of the molecular weight, $[\eta]/M_w^{1/2}$, is constant should also be⁹ equal to Θ^A .

In contradiction to this postulate, the values of $[\eta]/M_w^{1/2}$ for the present system are invariant with respect to the molecular weight at the temperature $\Theta_L^n = 343$ K which is higher than Θ_L^{PE} by 2.5 K (Fig. 5). This difference is comparable to the differences $\Theta^{PE} - \Theta^A$ found with polystyrene and polyethylene in several solvents, both at LCST

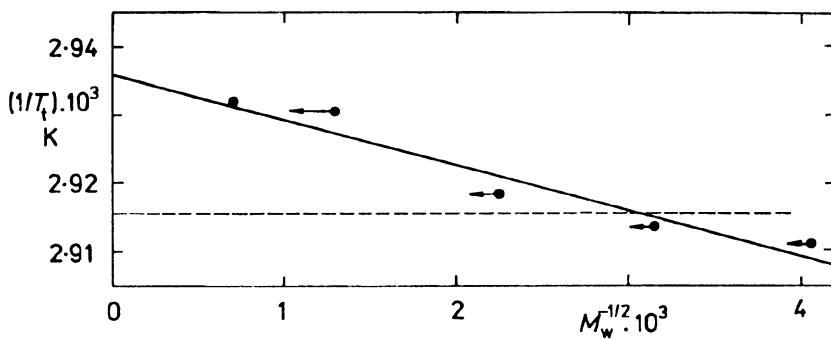


FIG. 4

Plot of the threshold temperature T_t of PEMA in water according to Eq. (5). Arrows indicate the effect of the correction for polydispersity. Broken line denotes the temperature at which the ratio $[\eta]/M_w^{1/2}$ is invariant with respect to M_w

and UCST (refs^{10–12}). As pointed out by Kamide et al.¹², the Θ_L^{PE} values depend somewhat on the method of estimation.

The differences in Θ_L^{PE} and Θ_L^{η} observed with the present system cannot be assigned to errors of experiments or extrapolation. As shown by Fig. 5 the plot of $[\eta]/M_w^{1/2}$ vs $M_w^{1/2}$ at 340.5 K clearly has a positive slope and the differences in $[\eta]/M_w^{1/2}$ at 343 and 340.5 K are such that an error of 2.5 K in Θ_L^{η} is excluded. Similarly, the extrapolation of the threshold temperatures (Fig. 4) is unambiguous. Moreover, the T_t values for high-molecular-weight samples are lower than Θ_L^{η} by 1.7 K.

Thus, dilute solution data suggest that, contrary to expectation, the χ parameter at Θ_L^{PE} is lower than 0.5 (which is currently assumed to be the critical value of χ for infinite chains¹⁹) and is equal to 0.5 at a temperature which is higher than Θ_L^{PE} . To the authors' knowledge, such unusual behaviour has not been observed so far.

Equations (2) and (5) underlying the estimation of Θ_L^{PE} follow from the classic theory of phase equilibria in polymer solutions advanced by Shultz and Flory^{8,9} where the chemical potential of solvent is expressed by Eq. (8)

$$\Delta\mu_1/RT = \ln \phi_1 + (1 - 1/m)\phi_2 + \chi \phi_2^2. \quad (8)$$

The symbols ϕ_1 and ϕ_2 stand for the volume fractions of solvent and polymer, respectively. The theory gives the chain length dependence of the critical interaction parameter χ_c in the form

$$\chi_c = (1/2)(1 + m^{-1/2})^2. \quad (9)$$

The limits for infinite chains of the critical values of χ_c and $\phi_{2,c}$ are

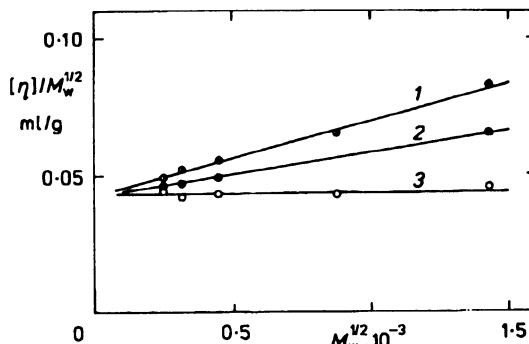


FIG. 5
Plot of $[\eta]/M_w^{1/2}$ vs $M_w^{1/2}$ for PEMA
in water. Temperature: 1 65, 2 67.5,
3 70.5 °C

$$\chi_c^\infty = 1/2 \quad \text{and} \quad \phi_{2,c}^\infty = 0. \quad (10)$$

Tompa¹³, and later on, Huggins and Okamoto¹⁴ have pointed out that inclusion of higher terms (e.g., $v\phi_2^3$ where v is another interaction parameter) into Eq. (8) significantly changes the coordinates of the critical point. Flory and Daoust¹⁵ have shown that, in this case, the critical concentration for infinite chains, $\phi_{2,c}^\infty$, need not be zero. By examining in more detail the consequences of the modification¹⁶ of Eq. (8), the results have been obtained which qualitatively correspond with the properties of the threshold points of the system PEMA–water. If $v > 1/3$, the threshold concentration $\phi_{2,t}$ do not markedly depend on the molecular weight. The dependence on M of the threshold temperature T_t is also moderate and, which is particularly interesting, the T_t values for high chain length and for $m \rightarrow \infty$ may be lower than the temperature where, according to dilute solution properties, the χ parameter is equal to 0.5.

In view of this finding the question emerges whether the inclusion of the v parameter into the two-parameter theory of dilute solution properties would also significantly affect the molecular-weight dependence of the ratio $[\eta]/M_w^{1/2}$ in the vicinity of the Θ temperature or, more specifically, whether, due to the contribution of the term with v , the dependence of $[\eta]/M_w^{1/2}$ vs $M_w^{1/2}$ could have a non-zero slope if $\chi = 0.5$. The calculations based on the three-parameter theory¹⁷ show (cf. Appendix) that the dependence on $M^{1/2}$ of the radius-of-gyration expansion factor α_S^2 is almost unaffected by the v term. Assuming that the same approach applies, at least semiquantitatively, to the intrinsic viscosity, we can conclude that the values of $[\eta]/M_w^{1/2}$ at $\chi = 0.5$ are independent of M_w irrespective of the value of v .

Thus, the difference of the values of Θ_L^{PE} and Θ_L^{η} for aqueous solutions of PEMA does not appear to be due to the effect of the v parameter on the dilute solution properties and on Θ_L^{η} but on the phase equilibria and Θ_L^{PE} .

ψ Parameter

The entropy-of-dilution parameter evaluated from the threshold temperatures, $\psi = -2.0$, is negative and surprisingly high. The value obtained from dilute solution properties³, $\psi = -0.2$, is ten times lower. Such a difference in values is not unusual^{10–12}.

The calculations in ref.¹⁶ offer an explanation. They show that the slope of the dependence of χ vs $(1 + m^{-1/2})^2$ (cf. Eq. (9)) is equal to unity only if $v = 0$. As the v value increases the dependences become non-linear and the slopes of linear approximations to the curves are significantly lower than unity. The same applies to the slope of the plot of $1/T_c$ vs $1/M_w^{1/2}$ because Eqs (2) and (5) result from a combination of Eqs (9) and (7). Hence, the values obtained by means of Eqs (2) or (5) are too high if $v > 0$.

Thermodynamic conditions for the LCST are such that the mixing process is exothermic and the entropy of mixing is negative¹⁸. With PEMA in water, the heat-of-dilution parameter κ defined⁹ by

$$\kappa = \psi \Theta / T \quad (11)$$

is obviously negative. According to Eq. (12)

$$\psi = 1/2 + \lim_{\phi_2 \rightarrow 0} (\bar{S}^R / R \phi_2^2), \quad (12)$$

where R is the universal gas constant, the ψ parameter consists of two parts, the combinatorial term (1/2) and the non-combinatorial contribution referred to as the reduced partial molar residual entropy¹³.

It is seen that with PEMA in water at $T < \Theta_L$, the residual entropy term is negative and acts against dissolution whereas the combinatorial entropy of mixing and the negative heat of mixing combine to promote dissolution. As the temperature increases the κ term decreases so that at $T > \Theta_L$ the residual entropy term prevails and induces phase separation.

Negative ψ implies negative values of $\lim_{\phi_2 \rightarrow 0} (\bar{S}^R / R \phi_2^2)$, i.e., a decrease in entropy on diluting the system (forming new polymer-solvent contacts). Such values have also been obtained from the measurements of swelling by water of crosslinked poly(*N,N*-diethylacrylamide) and poly(*N*-isopropylacrylamide)¹⁹ and appear to be typical of aqueous solutions of poly(*N*-alkylacrylamides).

The LCST and negative values of ψ for these polymers are to be distinguished from those found with nonpolar systems where the free-volume dissimilarity between the polymer and solvent is the determining factor^{19,20}. They are similar to those occurring with aqueous solutions of some low-molecular-weight solutes (amines, ethers) where they are associated with ordering of water molecules around the solute (cf. ref.¹⁸). Note that NMR studies of poly(*N*-isopropylacrylamide) in water have indicated a remarkable restriction of the molecular motion of water molecules at the phase transition temperature²¹.

CONCLUSION

It may be objected that interactions in aqueous systems are too specific to be treated in terms of a general theory of polymer solutions based on the mean-field approximation. In general, this approximation is expected to fail in the vicinity of the critical state because fluctuations in concentration of polymer segments correlate over a large distance. In view of the supramolecular structure of water, the correlation may be even

larger than with non-aqueous systems. Anyway, the χ and ν parameters can be taken as empirical functions which comprise all the deviations of the chemical potential from that given by the Flory-Huggins theory.

APPENDIX

The two-parameter theory of dilute polymer solutions is based on the assumption that the binary interaction of polymer segments is sufficient to account for the effect of solvent on the dimensions of polymer molecules and on the second virial coefficient. While this seems to be reasonable in good solvents, it need not be so if the temperature is close to the Θ -value where residual ternary interactions may be strong.

This problem was explored in several theories (cf. ref.⁷) based on the perturbation treatment or on the smooth-density sphere model. Since we are concerned with the situation in the vicinity of Θ temperature, the former theories would appear more adequate. However, the terms corresponding to ternary interactions in the final equations diverge under certain conditions. Unless this deficiency is removed, the latter theories must be employed for practical purposes.

Here we adopt the equations derived by Orofino and Flory¹⁷

$$\alpha^5 - \alpha^3 = 2 C_M [(1/2 - \chi) M^{1/2} + \pi^{-3/2} (\bar{v}/N_A) (\langle s^2 \rangle_o/M)^{-3/2} (1/3 - \nu) \alpha^{-3}] \quad (A1)$$

$$C_M = (3^{3/2}/2^4 \pi^{3/2}) (\bar{v}^2/N_A V_1) (\langle s^2 \rangle_o/M)^{-3/2} \quad (A2)$$

$$\alpha^2 = \langle s^2 \rangle / \langle s^2 \rangle_o, \quad (A3)$$

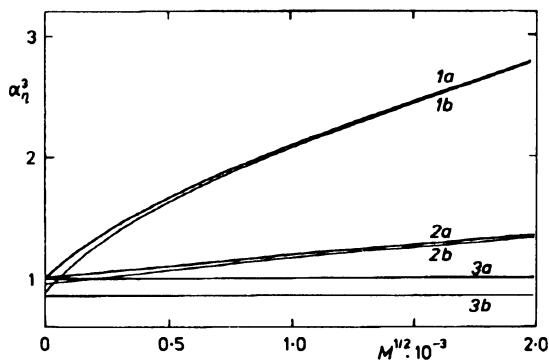


FIG. 6

The molecular-weight dependence of the viscosity expansion factor α_n^3 . The curves were calculated by means of Eq. (A7) using $\bar{v} = 1 \text{ ml/g}$, $V_1 = 100 \text{ ml/mol}$, $K_o = 0.1 \text{ ml/g}$ and the values of χ and ν , respectively: 1a 0.464, 0.333; 1b 0.464, 0.400; 2a 0.496, 0.333; 2b 0.496, 0.400; 3a 0.500, 0.333; 3b 0.500, 0.500

where α^2 is the radius-of-gyration expansion factor, $\langle s^2 \rangle_o$ and $\langle s^2 \rangle$ are, respectively, the mean-square radii of gyration "unperturbed" and "perturbed" by the excluded-volume effect, \bar{v} is the partial specific polymer volume, V_1 is the molar volume of the solvent, and N_A is the Avogadro constant.

Assuming that Eq. (A1) is, at least approximately, valid also for the viscosity expansion factor α_η^3 given⁹ by Eqs (A4) and (A6)

$$\alpha_\eta^3 = [\eta]/K_o M^{1/2} \quad (A4)$$

$$K_o = 6^{3/2} \phi_o (\langle s^2 \rangle_o/M)^{3/2}, \quad (A5)$$

where $\phi_o = 2.6 \cdot 10^{23}$ (if $[\eta]$ is expressed in cm^3/g), Eq. (A1) is transformed into

$$\alpha_\eta^5 - \alpha_\eta^3 = 3.70 (\bar{v}^2/V_1 K_o) [(1/2 - \chi)M^{1/2} + 1.14 \cdot 10^{-2} (\bar{v}/K_o) (1/3 - v) \alpha_\eta^{-3}]. \quad (A6)$$

By means of this equation, we carry out model calculations of the dependence of α_η^3 vs $M^{1/2}$ for several combinations of χ and v with typical values being substituted for V_1 , \bar{v} and K_o .

Figure 6 shows that curves with fixed values of χ and different values of v are almost identical. Noticeable, though small, differences can be seen only at very low molecular weights. The slopes of the curves are governed by the χ value. A horizontal dependence can be found only for $\chi = 0.5$, and by no variation in the v value can it be transformed into a dependence with a non-zero slope.

Thus, unlike phase equilibria, the dependence of α_η^3 (or $[\eta]/M^{1/2}$) on $M^{1/2}$ does not seem to be significantly affected by the ternary interaction parameter v .

The authors wish to thank Dr J. Strohalm for SEC data and Mrs D. Švábová for technical cooperation.

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Translated by the author (M. B.).