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Temperature effects in hydrodynamic properties of comb-like polymer with laterally attached mesogenic units

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Abstract

The specific temperature effects in hydrodynamic properties (intrinsic viscosity, sedimentation velocity and translational diffusion) of *side*-on comb-like polymers with molecular weights from 5.70×10^5 to 3.02×10^6 were observed in dilute solution in two different solvents, benzene and chloroform, over a temperature range from 2 to 73°C. The viscosity temperature coefficient $\mathrm{d}\ln[\eta]/\mathrm{d}T$ was found to be negative in sign in chloroform ($-0.007\ \mathrm{K}^{-1}$) and positive in benzene ($+0.005\ \mathrm{K}^{-1}$). Increase in temperature leads to intensification of the excluded volume effects in real benzene solution of the polymer and to weakening of those in chloroform. Simultaneously, increase in temperature leads to decreasing unperturbed dimensions of the macromolecule chain in both the solvents. This effect is more pronounced in benzene ($\mathrm{d}\ln\langle h^2\rangle/\mathrm{d}T = -0.005\ \mathrm{K}^{-1}$, where $\langle h^2\rangle$ is the mean-square end-to-end distance) than in chloroform ($-0.001\ \mathrm{K}^{-1}$). Origins of the temperature effects are discussed with relation to the lateral structure of the macromolecule where every monomer unit contains the threecyclic mesogenic moiety which is laterally (with the middle part) attached to a side chain consisting of 11 carbon atoms. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Sedimentation; Diffusion; Viscometry

1. Introduction

The temperature dependence of hydrodynamic properties (e.g., intrinsic viscosity) reflects the change in the dimensions of the macromolecules in solution when the intensity of the interactions between nearest neighbour parts of the macromolecule (short-range interactions) or between its distant parts (long-range interactions) is a function of temperature.

In the same solvent at various temperatures, the change in the energy of the interactions between the polymer chain and the solvent molecules usually plays a main part and, hence, so does the change in polymer–polymer long-range interactions. On the other hand, solvents with different chemical nature can profoundly affect the short-range interactions with change in the degree of coiling of an isolated macromolecule in solution. The latter effect is expected to be more pronounced for the flexible-chain macromolecules rather than for semiflexible and rigid-chain ones.

Many works on temperature investigations were aimed at the separation of the long-range interaction effects from the short-range ones and, thus, at determination of the main conformational parameters of the polymer molecule [1–3]. Mutual interactions between the side chains in the comb-like macromolecule provide one of the known physical origins of equilibrium rigidity of the macrochain. Steric factors here are mainly responsible for the hindrance to intramolecular motions. Therefore, the temperature effects are different, for instance, for polymethyl methacrylate and its derivatives with the side chains of various volume dimensions [4–8]. The effect (the longer the side chain the higher the temperature coefficient of the unperturbed dimensions) was observed for vinyl polymers as well as for other ones, e.g., for series of polyesters [9]. One can expect that additional specific interactions (dipole–dipole, etc.) between the side chains (from direct contacts or the interactions through a solvent) influence sufficiently the temperature effects.

In the present work, hydrodynamic methods (translational diffusion, sedimentation velocity, and viscometry) were used to investigate the temperature effects in the solution properties of the comb-like *side*-on polymer PLMA. In every monomer unit of this polymer, a threecyclic mesogenic group with linkage ester bonds is attached by the

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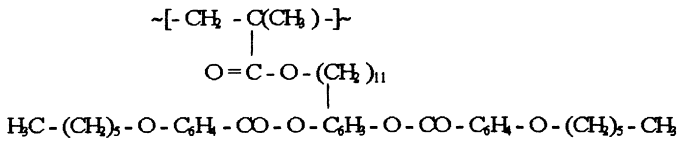
middle part to a side chain, consisting of 11 carbon atoms, in the macromolecule with a methacrylic backbone:



PLMA

Measurements were carried out in two solvents, benzene and chloroform, over a wide temperature range limited by the boiling and freezing temperatures of the solvent. The aim was to investigate the nature of the chain flexibility of the macromolecules with lateral chemical structure through the peculiarities of the temperature effects in hydrodynamic properties of the *side*-on polymer in solution.

2. Experimental

The preparation of PLMA samples and their molecular characterization in benzene solution at 26°C have already been described [10]. Unfractionated samples were investigated only because their fractionation was drastically complicated with the associative phenomena. Molecular weight M and heterogeneity index of the samples are listed in Table 1.

Benzene (‘UV’ mark) with density $\rho_s = 0.8724$ g/cm^3, viscosity $\eta_s = 0.583 \times 10^{-2}$ g/cm s and refractive index $n_D = 1.5011$, and chloroform (chemically pure grade) with $\rho_s = 1.480$ g/cm^3, $\eta_s = 0.536 \times 10^{-2}$ g/cm s, $n_D = 1.4423$ at 26°C were used as the solvents.

Methods used for measurements of solution viscosity, sedimentation velocity, and diffusion of the PLMA molecules were described previously [10]. Intrinsic viscosity $[\eta]$ was determined from extrapolation $[\eta] = \lim(\eta_{sp}/c)_{c \to 0}$ made according to Huggins equation $\eta_{sp}/c = [\eta] + [\eta]^2 k_H c$, where η_{sp} is specific viscosity of the solution, c the concentration, and k_H the Huggins constant. The sedimentation coefficient s was calculated with a correction for the pressure effect observed in the ultracentrifuge field. This effect was evaluated with the equation $s^p = s(1 - \mu p)$, where s^p and s are the sedimentation coefficients at a pressure of p and at atmospheric pressure, respectively. The literature data [11] were used for the parameter μ characterising the solvent compressibility. All data were evaluated via unweighted linear regression analysis.

Table 1
Molecular characteristics of PLMA samples as calculated from sedimentation, diffusion and GPC data

Sample no.	$M_{sD} \times 10^{-6}$ (g/mol)	M_z/M_w		M_w/M_n	
		Sed.	GPC	Sed.	GPC
IV	3.02	2.1	2.28	3.8	2.73
III	2.39	—	2.02	—	3.22
I	1.01	—	3.52	—	5.77
II	0.57	—	3.01	—	4.51

Refractive index increment $(dn/dc)_{546}$ was determined from the area under the diffusion curve to be equal to 0.078 cm^3/g in chloroform and 0.045 cm^3/g in benzene.

3. Results and discussion

3.1. Solution molecularity

Hydrodynamic properties of the polymer in solution in different solvents can differ because of the specific effects of solvent nature on the dimensions of the isolated macromolecule, and also as a result of associative phenomena such as complex formation, aggregation, and gel formation. The latter phenomena depend strongly on the solvent, side chain structure and the macrochain tacticity [12–15]. They cause obvious difficulties to molecular characterization of the polymer, which can result in the apparent value of molecular weight greatly exceeding that of an individual macromolecule.

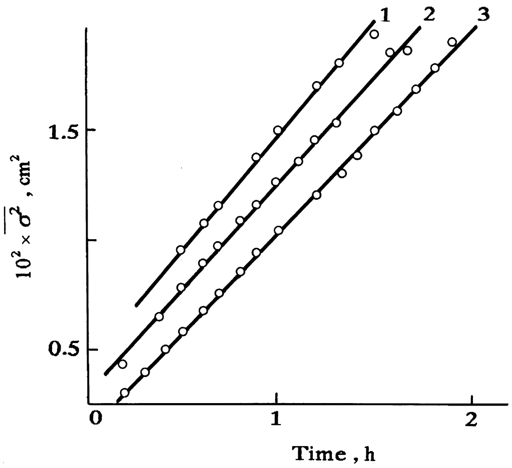


Fig. 1. Variation in the dispersion of diffusion curve $\overline{\sigma^2}$ with experimental time for PLMA sample IV in chloroform (curves 1, 2) and benzene (curve 3) at 26°C, and average solute concentration $\bar{c}(\times 10^2)$ = (1) 0.138; (2) 0.065 and (3) 0.10 g/cm^3.

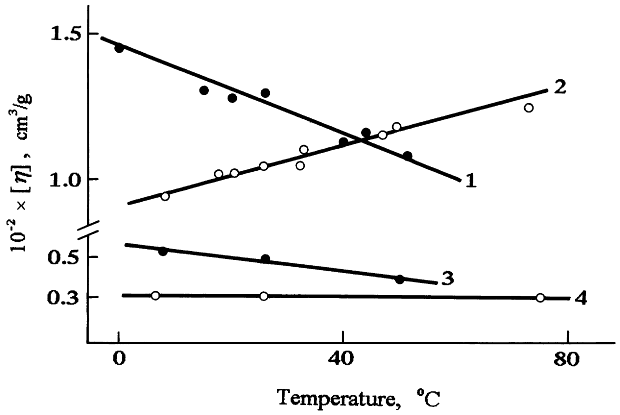


Fig. 2. Temperature dependence of $[\eta]$ in chloroform (curves 1 and 3) and benzene (curves 2 and 4) for PLMA samples IV (1, 2) and II (3, 4). Solid curves are calculated with $d\ln[\eta]/dT = -0.007\ K^{-1}$ (curve 1) and $+0.005\ K^{-1}$ (2).

To check the molecular dispersity of the polymer solution, diffusion of one PLMA sample was investigated in both benzene and chloroform at 26°C. Fig. 1 shows that dispersion of the diffusion boundary, $\overline{\sigma^2}$ increases in proportion to experimental time, t, in both the solvents. This is typical for a homogeneous sample. Therefore, the diffusion coefficient D was evaluated from the slope of linear approximation of the data points: $D = (1/2)\ d\overline{\sigma^2}/dt$. It is equal 1.38×10^{-7} cm²/s in chloroform and 1.27×10^{-7} cm²/s in benzene. At a low average solute concentration used, $c = 0.1 \times 10^{-2}$ g/cm³, the concentration dependence $D(c)$ was negligible [10], and D did not differ (within experimental error) from the value extrapolated to zero concentration: $D_0 = \lim D_{c \to 0}$. The D values thus obtained reflect, first, the difference in the solvent viscosity. Therefore, the product $(D\eta_s)^3[\eta]$ is discussed below.

In fact, for a real solution of uncharged particles, the product $(D\eta_s)^3[\eta]M$ is known to be insensitive (invariant) to a change in a solvent (when the temperature is retained) [16]. Consequently, the product $(D\eta_s)^3[\eta]$ should be very sensitive to change in M. The experimental value of $(D\eta_s)^3[\eta]$ obtained at 26°C in chloroform (5.15×10^{-26} cm^6 s^{-6} g^2) is close to that in benzene (4.22×10^{-26}), the difference being referred to uncertainty in determination of D (7%). Thus, comparison of diffusion–viscosity properties in different solvents shows that the apparent value of the molecular weight determined at 26°C in chloroform coincides practically (within experimental error) with that obtained in benzene. We may conclude, therefore, that PLMA forms real (molecularly dispersed) solution in both the solvents at concentrations used at 26°C.

3.2. Temperature dependence

In spite of high M, intrinsic viscosities, $[\eta]$, of PLMA samples are low. Nevertheless, zero shear viscosity is sensitive to temperature in both the solvents used, as is shown in Fig. 2 for PLMA samples IV (high M) and II (low M). The $[\eta]$ value drops in the solvent chloroform and increases in benzene with increasing T. The viscosity temperature coefficient $k_\eta \equiv d\ln[\eta]/dT$ is negative in chloroform ($-0.007\ K^{-1}$) and positive in benzene ($+0.005 K^{-1}$). In elucidating the origins of this temperature dependence, the retention of molecularity of PLMA solution at various temperatures (different from 26°C) should be firstly proved. For this purpose, the sedimentation data have been analysed in detail.

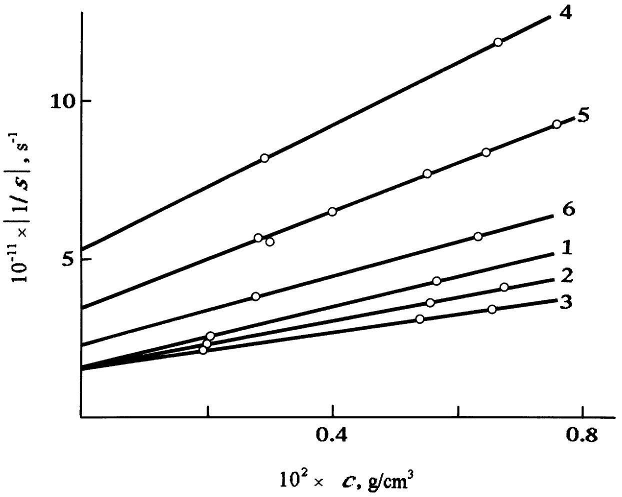


Fig. 3. Linear approximation of the 1/s absolute value plotted against concentration for PLMA in chloroform (curves 1–3) and benzene (curves 4–6) at temperatures of 8 (1, 4), 26 (2, 5), and 47°C (3, 6).

The sedimentation coefficient s is positive in sign in the solvent benzene (due to the positive buoyancy factor, $1 - \bar{v}\rho_s > 0$, $\bar{v}$ being the partial specific volume) and negative in chloroform (because of $1 - \bar{v}\rho_s < 0$). The absolute s value was found to be sensitive to the both c and T. The data are presented in Fig. 3 as $1/s$ plotted against c. The data points can be well approximated by a linear function described by $1/s = (1/s_0)(1 + k_s c)$, where $s_0 = \lim s_{c \to 0}$. Curves 1–3 (data obtained in chloroform) have evidently the same intercept (the same $1/s_0$ value), whereas in benzene (curves 4–6) the intercepts strongly differ one from another. The results are collected in Table 2. Intrinsic sedimentation coefficient $[s]$ was evaluated by

$$[s] = s_0\eta_s/(1 - \bar{v}\rho_s) \quad (1)$$

Simultaneously, the ratio $k_s/[\eta]$ exhibits a slight increase in

Table 2
Sedimentation characteristics of PLMA sample IV at different temperatures

Solvent	T (°C)	$s_0 \times 10^{13}$	k_s (cm³/g)	$[s] \times 10^{15}$ (g/cm)	$\bar{v}$ (cm³/g)
Benzene	8	19	185	—	—
	26	28	211	7.8	0.903
	47	43.5	235	—	—
Chloroform	8	− 62.5	296	—	—
	26	− 62.5	240	9.1	0.924[a]
	47	− 62.5	185	—	—

[a] The value estimated from sedimentation velocity data (see text)

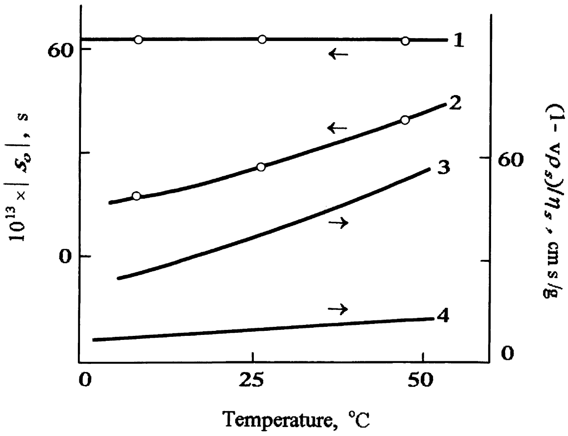


Fig. 4. Temperature dependence of $|s_0|$ (curves 1, 2) and $(\eta_s/1 - \bar{v}\rho_s)^{-1}$ (curves 3, 4) for PLMA sample IV in chloroform (1, 4) and benzene (2, 3). Solid curves smoothly connect the data points.

benzene and decrease in chloroform with increasing T. However, the average value of the ratio $k_s/[\eta]$ remains close to 1.9. This value is characteristic of the many non-draining macromolecules in a thermodynamically good solvent [17].

3.3. Partial specific volume

Let us compare the s_0 values obtained at 26°C in different solvents. From the analysis of the diffusion data made above, the conclusion was made that the apparent value of molecular weight in benzene coincides with that in chloroform. In terms of Svedberg's equation, $M_{sD} = RT(s_0/D)/(1 - \bar{v}\rho_s)$, this conclusion means that the ratio $s_0/[D(1 - \bar{v}\rho_s)]$ has the same magnitude in benzene and chloroform. The s_0 and D values are determined here in both solvents, and the value of $(1 - \bar{v}\rho_s) = 0.211$ was obtained at 26°C in benzene [11]. Hence, the buoyancy factor for PMA in chloroform at 26°C can be calculated to be -0.367, which corresponds to $\bar{v} = 0.924\ \mathrm{cm^3/g}$. Note the higher $\bar{v}$ value thus obtained for PLMA in chloroform agrees quantitatively with the lower value of the PLMA refractive index in this solvent, as estimated with the experimental dn/dc value.

The s_0 is plotted against T in Fig. 4. Curves 1 and 2 present the data obtained for PLMA in chloroform and benzene, while curves 3 and 4 present the physical properties of benzene and chloroform, respectively. Curve 1 looks evidently like curve 4, and curve 2 repeats almost entirely the form of curve 3. Hence, the experimental $s_0(T)$ dependence is determined by the temperature dependence of physical characteristics of the solvent, rather than by a change in mass of a migrating particle. In fact, if the change in T would be accompanied by association of the macromolecules, then the product $([s]^3[\eta])^{1/2}$ (being proportional to the mass of a migrating particle [16]) should be changed by the corresponding ratio. However, this change was not experimentally observed.

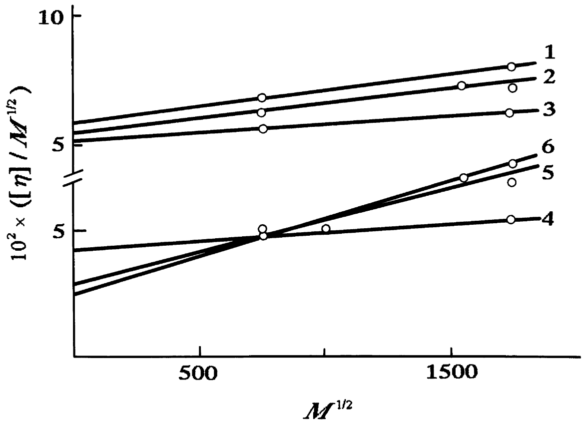


Fig. 5. Linear approximation of $[\eta]/M^{1/2}$ (with $[\eta]$ in cm^3/g) as a function of $M^{1/2}$ for PLMA in chloroform (1–3) and benzene (4–6) at temperatures of 8 (1), 26 (2, 5), 50 (3), 7 (4), and 75°C (6).

The small change in $([s]^3[\eta])^{1/2}$ detected at temperatures different from 26°C (15% distinction observed in benzene and 20% in chloroform, as estimated with assumption of $\bar{v}_T = \bar{v}_{26}$, where the subscript T denotes the temperature at which the given value was obtained) should be referred to the T dependence of partial specific volume of the polymer. We characterize now this effect. The following equation is valid [16] when the mass of a migrating particle is independent of T:

$$[s]_T = [s]_{26}([\eta]_{26}/[\eta]_T)^{1/3}$$

By substituting here the $[s]_{26}$ and $[\eta]$ values obtained at current temperature we obtain the $[s]_T$. Then, the $[s]_T$, s_o, η_s, and ρ_s quantities evaluated at the same current temperature were substituted into Eq. (1) to calculate the $\bar{v}_T$ value. The temperature coefficient $(1/\bar{v})\mathrm{d}\bar{v}/\mathrm{d}T$ was found to be negative in sign and equal to $-0.0013\ \mathrm{K^{-1}}$ in benzene and $-0.0019\ \mathrm{K^{-1}}$ in chloroform.

3.4. Unperturbed dimensions

Unperturbed dimensions of the isolated PLMA molecule were evaluated, and equilibrium rigidity of the chain was characterized from extrapolation of the hydrodynamic data to low M range where the excluded volume effects are negligible. The Burchard's plotting of $[\eta]/M^{1/2}$ versus $M^{1/2}$ was used as described by [18,19]

$$[\eta]/M^{1/2} = K_\theta + 2K_\theta(Z/M^{1/2})M^{1/2} \tag{2}$$

The parameter K_θ represents here the intramolecular short-range interactions limiting the chain coiling. It is defined as $K_\theta = \Phi_0(\langle h^2\rangle/M)^{3/2}$, where Φ_0 is Flory's coefficient in a θ – solvent, $\langle h^2\rangle$ is the mean-square end-to-end distance. The excluded volume parameter, Z, represents the intramolecular long-range interactions. In random-coil limit we may write $K_\theta = \Phi_o(A/M_L)^{3/2}$ where A is the length of the Kuhn's random link characterizing the equilibrium rigidity of the macromolecule backbone, and M_L is the mass per unit contour length of the polymer chain. Applicability of the

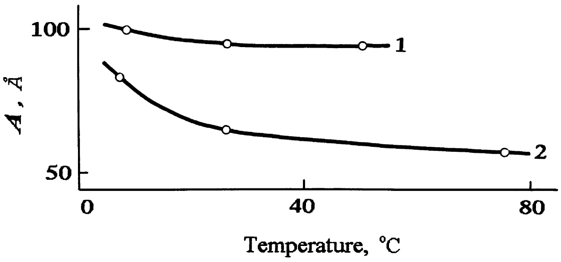


Fig. 6. Temperature dependence of the length A of the random link for the PLMA chain in chloroform (curve 1, points) and benzene (curve 2, points). Solid curves are calculated with d$\ln A$/dT equal to $-0.001\ \mathrm{K}^{-1}$ (1) and $-0.005K^{-1}$ (2).

method was discussed earlier [10]. The M_L was taken as the monomer unit mass, M_o, related to its length, λ, in the direction of the extended macromolecule: $M_L = M_o/\lambda$.

The plot (2) is shown in Fig. 5 for PLMA in chloroform (curves 1–3) and benzene (curves 4–6) at different temperatures. According to Eq. (2), the intercept (first term) was used to estimate the product $A\lambda$ and, thereby, the length of the random link A, applying [20] $\Phi_o = 2.86 \times 10^{23}\ \mathrm{mol}^{-1}$, and $M_L = 302.4 \times 10^8$ Da/cm.

The A thus obtained at different temperatures is plotted against T in Fig. 6 for PLMA in chloroform (curve 1) and benzene (curve 2). The result of increase in A seems obvious as the macromolecule is highly constrained to rotations due its comb-like structure. At higher temperatures, the system possesses enough energy to overcome rotation barriers and therefore the chain becomes more flexible as shown in both solvents. However, one can see, first, that the length A of the random link in chloroform is almost twice that in benzene over all the T-range investigated. Second, not only chain flexibility but also its growth along the temperature range in benzene is several times that in chloroform. The temperature coefficient of unperturbed dimensions, $k_A \equiv \mathrm{dln}\langle h^2\rangle/\mathrm{d}T = \mathrm{dln}\,A/\mathrm{d}T$ is equal $-0.005\ \mathrm{K}^{-1}$ for PLMA in benzene and $-0.001\ \mathrm{K}^{-1}$ in chloroform. Hence, in benzene solution, the PLMA macromolecule is more coiled, and degree of coiling increases along the temperature range more readily than that in chloroform. This result reflects the specific (and still unclear) influence of the solvent nature on the PLMA chain dimensions.

Interestingly, the difference in the A values obtained in benzene and chloroform reduces with decreasing T. Curves 1 and 2 in Fig. 6 demonstrate the tendency to their convergence at low T, approaching, thereby, the characteristics of the PLMA chain equilibrium flexibility that may be expected to be independent of solvent nature.

Inhomogeneity of the polymer samples was taken into account as described previously [10]. In this way, the first term in Eq. (2) is not K_θ but $K_\theta q_\eta$. Polymolecularity correction factor q_η was evaluated [10] to be about 0.90 for the samples with the inhomogeneity indices given in Table 1. This correction affects slightly the absolute A value (~10% growth) but does not influence the T effects discussed herein.

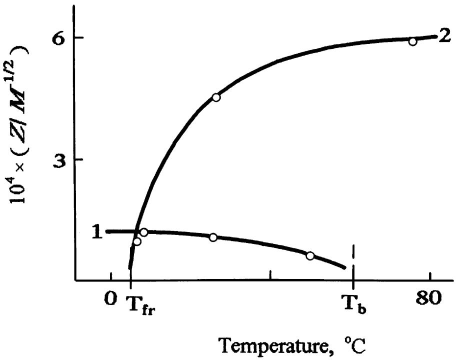


Fig. 7. Temperature dependence of $Z/M^{1/2}$ (Z is the excluded volume parameter) for PLMA in chloroform (1) and benzene (2). T_{fr} and T_{b} are, respectively, the freezing temperature of benzene (melting) and the boiling temperature of chloroform.

3.5. Excluded volume effects

The slope of the $[\eta]/M^{1/2}$ *versus* $M^{1/2}$ plot depends on the thermodynamic quality of the solvent and, hence, on temperature. It can be used, therefore, for estimation of the excluded volume parameter Z by Eq. (2). The $Z/M^{1/2}$ thus obtained is plotted against T in Fig. 7. The same value of $Z/M^{1/2}$ (intersection of curves 1 and 2), i.e., the same excluded volume effects, are observed in the different solvents at a temperature close to 8°C. These effects increase in benzene and decrease in chloroform with increasing T. At $T > 8$°C, the excluded volume effects themselves and their temperature dependence are both evidently much more pronounced in benzene than in chloroform. This observation is in agreement with higher flexibility of the PLMA molecule in benzene solution (discussed above) and, hence, its higher susceptibility to the excluded volume effects (in accordance with the proportionality $Z/M^{1/2} \sim A^{3/2}$ predicted theoretically for the worm-like chains [21]).

The decreasing slope of this dependence (decreasing $Z/M^{1/2}$) indicates the approach to the θ point. For PLMA in chloroform (Fig. 7, curve 1) this effect was observed with increasing T, and in benzene (curve 2) with decreasing T. However, the θ temperatures are evidently inaccessible in both solvents under atmospheric pressure. Fig. 7 shows that zero value of $Z/M^{1/2}$ is accessible in benzene (curve 2) at a temperature close to that of the solvent freezing temperature (T_{fr}), and in chloroform (curve 1) at the solvent boiling temperature (T_{b}), or even at a higher one.

In other terms, a lower critical solution temperature was observed in the PLMA in benzene solution to be close to T_{fr}, whereas in chloroform, an upper critical solution temperature is close to T_{b}. Unfortunately, no explanation is yet evident as to the chemical causes which would affect the nature of the different phase diagrams of the polymer in the two solvents. However, a macromolecule is known to have its unperturbed dimensions at both critical solution temperatures. The approach to these dimensions is observed with

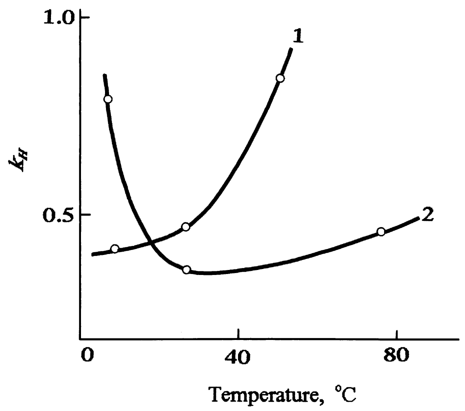


Fig. 8. Temperature dependence of Huggins's constant for PLMA in chloroform (1) and benzene (2).

increasing temperature in chloroform, and with decreasing temperature in benzene. In qualitative agreement with this conclusion, the Huggins constant presented in Fig. 8 increases abruptly with increasing T in chloroform (curve 1), and with decreasing T in benzene (curve 2).

4. Conclusions

In the present work, probably for the first time, a situation was observed where the viscosity temperature coefficient, k_η, was opposite in sign in various solvents within the same T range, whereas that of unperturbed dimensions of the macromolecule, k_A, was of the same sign. The positive (in sign) k_η was observed for PLMA in benzene, i.e., in the solvent where the equilibrium flexibility of the macromolecule is twice that in chloroform where the k_η is negative.

The molecular dispersity of the PLMA solutions in benzene and chloroform, and previous reliable characterization [10] of molecular dimensions for PLMA over a relatively wide M range, favoured the possibility of distinguishing the influence of temperature on long-range interactions (excluding volume effects) and on short-range interactions which determine the unperturbed dimensions of the macromolecule in solution. Consequently, origins for temperature dependences of PLMA hydrodynamic properties were established.

The temperature coefficient of unperturbed dimensions of the PLMA molecule in solution was negative in sign in both solvents, as was observed earlier for some methacrylic *end*-on comb-like polymers with the bulky side chains only [6,7]. True, the k_A value close to zero was more often observed [8], being positive in sign for the *end*-on macromolecules with the short side chains [4,5]. At the same time, monotonic change in the chain flexibility along the temperature observed herein is typical for the comb-like polymers because non-monotonic conformational changes caused by the change in T were only rarely mentioned [6].

The experimental data obtained in the work allows us to analyse correlation of short- and long-range interactions in the PLMA chains in solution. Additional coiling of the PLMA molecule with increasing T caused by the weakening short-range interactions must lead to falling $[\eta]$ values. On the other hand, simultaneously, $[\eta]$ in benzene has to grow due to increasing long-range interactions. Experimental observations for PLMA in benzene, of growth in $[\eta]$, shows that the excluded volume effects predominate over the weakening short-range interactions in the chain in this polymer–solvent system. The opposite effects were observed for PLMA in chloroform. The origins of the higher hindrance to intramolecular rotation (higher potential barriers) in the PLMA main chain in solution in chloroform are still not clear and have to be referred to the specific nature of the solvent.

The last question is complicated by the fact that the low-molecular weight model compound with a chemical structure coincident completely with that of the mesogenic group in the PLMA monomer unit, is soluble neither in benzene nor in chloroform. Nevertheless, peculiarities in molecular properties of the PLMA in dilute solution mentioned above are undoubtedly caused by the mesogen unit structure as well as by the manner of the mesogenic group attachment to the molecule backbone.

In fact, for poly(trityloxyethyl methacrylate), where the cluster-like threecyclic side group is attached to exactly the same main chain by a similar spacer, the intrinsic viscosity measured in benzene does not depend on temperature at all [22]. For another comb-like polymer, where just the same (as in PLMA) mesogen is attached to the main chain directly by its end [23] (*end*-on polymer) k_η was observed to be opposite in sign in benzene and chloroform [24]. It was shown also that the A value determined for this polymer in chloroform is approximately three times those in benzene. At the same time, it was surely concluded that both the solvents are θ solvents for this *end*-on polymer, in contrast to the results of the present work on solution properties of the side-on one, PLMA.

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