COLLAPSE OF A SINGLE POLYSTYRENE CHAIN IN DIOCTYL PHTHALATE: EFFECT OF MOLECULAR WEIGHT

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Dedicated to Dr B. Sedláček on the occasion of his 60th birthday.

The use of a viscous solvent (dioctyl phthalate) made possible an investigation of the whole coil-globule transition of polystyrene chains in dilute solution. For values of the reduced temperature variable $\tau \sqrt{M}$ lower than -230 the globular polymer region was observed in which the radius R and the molecular weight M are related by $R \sim M^{1/3}$. The range of the Θ region where the expansion factor α is a linear function of $\tau \sqrt{M}$ was determined as $-50 < \tau \sqrt{M} < 50$. It was shown that within the whole temperature range investigated the expansion factor is a universal function of the variable $\tau \sqrt{M}$. The polymer dimensions at the Θ temperature are higher by some 15% in this solvent than in cyclohexane; also, the width of the transition region is much larger.

The collapse of a polymer coil or the so-called coil-globule transition has been investigated in a number of theoretical papers[1-7]. The transition may be continuous or discontinuous, depending on the chain rigidity[7]. For flexible polymers in the limit of infinite molecular weight the transition is a second-order one, and that, directly in the Θ-point[6]; for polymers with finite molecular weight (M_w) the transition is broader, and shifted to lower temperatures, the more so the lower the molecular weight of the polymer, or the higher its polydispersity.

Up to very recently, experimental studies of such transitions have been missing, due to interfering effects caused by intermolecular aggregation. Individual molecules can exist in the globular state only at such low concentrations[8] which could not be used experimentally. Owing to the development of experimental techniques this (basic difficulty has been overcome, and the collapse of the experimental coil could be intensively studied by a number of dynamic and static methods[9,10]. Experimental studies are usually carried out with polystyrene (PS) solutions in cyclohexane or cyclopentane. Polystyrene is used mainly because it is available in samples of very low polydispersity and in a broad range of molecular weights.

Of hydrodynamic measurements, one should mention sedimentation measurements PS–cyclopentane, $M_w = 3\cdot8 - 20 \cdot 10^6$) (ref.[11]) and viscosity measurements (PS–cyclohexane, $M_w = 8\cdot2 \cdot 10^4 - 6\cdot7 \cdot 10^6$) (ref.[12]), both carried out within a broad range

of temperature. Of other methods, the scattering ones greatly contributed to the investigation of the collapse.

The coil-globule transition was observed for the first time by using time averaged light scattering from solutions of polystyrene with an extreme molecular weight, $M_w = 4.4 . 10^7$, where the transition region is very narrow[13]. More complete results are provided in ref.[14] (PS–cyclohexane, $M_w = 1 - 30 . 10^6$). In the low-molecular weight range, where, basically, the methods of time averaged light scattering cannot be used, the small-angle neutron scattering technique was successfully employed (PS––cyclohexane, $M_w = 29\ 000$)[15].

The development of photon correlation spectroscopy made possible the determination of characteristic dimensions also at extremely low concentrations[16]. Tanaka and coworkers used this method successfully in a study of the collapse of the polystyrene coil in cyclohexane[16,17] ($M_w = 2.7 . 10^7$), and of polyacrylamide in a water––acetone mixture[18] ($M_w = 5 - 6 . 10^6$). The effect of molecular weight was studied by Adam and coworkers (PS–cyclohexane[19], $M_w = 1.7 . 10^5 - 1.2 . 10^6$).

We have shown in our preceding paper[20] that a viscous solvent (dioctyl phthalate) considerably extends the concentration range in which one can successfully examine the collapse of the polymer coil by means of time averaged light scattering. It should be pointed out, namely, that in viscous solvents dynamic processes (aggregation) are so much slowed down that the necessary measurements can be carried out also at temperatures lower than those corresponding to the binodal. The study is mainly concentrated on an investigation of the effect of molecular weight on processes of the collapse of polystyrene coils in dioctyl phthalate. The results are interpreted in terms of the scaling theory of polymers.

THEORETICAL

Depending on the thermodynamic quality of the solvent, the polymer chain may be present in a dilute solution either in the swollen (I), unperturbed (I'), or collapsed (IV) state. The numbers in brackets denote the individual regions of the universal temperature — concentration diagram[21,22] (i.e., $\tau \sqrt{M}$ vs $c \sqrt{M}$) (Fig. 1) in which c is the concentration, $\tau = (T - \Theta)/T$ is the reduced temperature and T is the absolute temperature. In these reduced variables the diagram for the given polymer–solvent pair is universal, i.e. independent of molecular weight[21]. The thermodynamic quality of a one-component solvent is determined predominantly by its temperature. The scaling theory[21,22] gives the following relations for the dimension (radius of gyration R_G) of the polymer chain in a dilute solution:

range I: $R_G \sim M^{3/5} \tau^{1/5}$,   (1a)

range I': $R_G \sim M^{1/2}$,   (1b)

range IV:
$$R_G \sim M^{1/3} |\tau|^{-1/3} \; . \tag{1c}$$

From homogeneity arguments[23], it can be derived that the coil expansion factor $\alpha_G = R_G(\tau)/R_G(0)$ should be a universal function of the single reduced variable $\tau \sqrt{M}$. We have, indeed,

range I:
$$\alpha_G \sim \frac{M^{3/5}\tau^{1/5}}{M^{1/2}} = (\tau \sqrt{M})^{1/5} \; , \tag{2a}$$

range I':
$$\alpha_G \cong 1 + k(\tau \sqrt{M}), \quad k = \text{const.}, \tag{2b}$$

range IV:
$$\alpha_G \cong \frac{M^{1/3}|\tau|^{-1/3}}{M^{1/2}} = (|\tau| \sqrt{M})^{-1/3} \; ; \tag{2c}$$

universality must be maintained also in the transition between the individual ranges.

Range IV, in which coils possess dimensions below the unperturbed dimension, is restricted by the coexistence curve — binodal (which is also universal in the $\tau \sqrt{M} - C \sqrt{M}$ diagram[21]) and which, particularly at lower temperature, is very narrow on the concentration axis. As has been shown[20], by using a viscous solvent which slows down nucleation, it is possible to displace the dynamic coexistence curve towards higher concentrations (to the metastable region).

In terms of the classical theory[24,25], the rate of nucleation is given by

$$J(t) \sim (D/t)^{1/2} \exp(-y^2/4Dt), \tag{3}$$

where D is the diffusion coefficient, t is time and y is the number of particles in the critical agglomerate. A typical shape of dependence (3) is shown in Fig. 2. It can be seen that after the system has been put in the metastable state at a time 0 nucleation cannot be observed immediately, but only after some induction period $t_i \sim y^2/4D$; this time is the longer, the smaller the diffusion coefficient of the particles, and thus the higher the viscosity of the solvent, η. According to the Stokes–Einstein relation,

$$D = kT/6\pi\eta R \; , \tag{4}$$

where R is the hydrodynamic radius of the coil. Also, the asymptotic rate of nucleation for large t values is proportional to $\sqrt{D}$, i.e., it is the smaller, the higher the viscosity of the solvent.

EXPERIMENTAL

The measurements were carried out with polystyrene standards manufactured by Toyo Soda and Pressure Chemicals; the respective characteristics are given in Table I. Dioctyl phthalate,

dried and redistilled twice *in vacuo*, was used as the viscous solvent. The Θ temperature of this solvent for polystyrene is 22°C (ref.[26]), the refractive index (n_D^{20}) is 1·4848; the viscosity (η_{20}) is 0·074 Pa s; the temperature dependence of viscosity measured with a capillary viscometer and supplemented by literature data[27] is shown in Fig. 3. The solutions were prepared by weighing and dissolved with mild shaking at 60°C. The concentrations lay in the range 10^{-3} g cm^{-3} > > c > 6 . 10^{-5} g cm^{-3} and were at least 100 times lower than the overlapping (crossover) concentration $c^*(\Theta)$, *cf.* Table I. The lowest concentration was chosen so as to make the excess scattering of polymer approximately equal that from the solvent.

Time averaged light scattering was measured with a Sofica apparatus adapted for low temperatures. The immersion liquid was cooled in a stream of nitrogen vapour, controlled automatically with the heating unit of the apparatus. Thus it was possible to perform light scattering measurements in the temperature range between -40°C and 60°C. The light source was an ordinary mercury lamp, from which wavelengths 546 nm or 365 nm were selected by means of interference filters. In the latter case an antifluorescence filter was inserted before the photomultiplier.

Polymer solutions were kept at given temperature for 30 minutes prior to light scattering measurements. The results of light scattering measurements near the Θ temperature were evaluated by using the classical Zimm plot; in measurements at lower temperatures the angular dependence of the intensity of scattered light was analyzed[20]. Our main interest in this study is concentrated on the determination of the radius of gyration of the polymer at low temperatures.
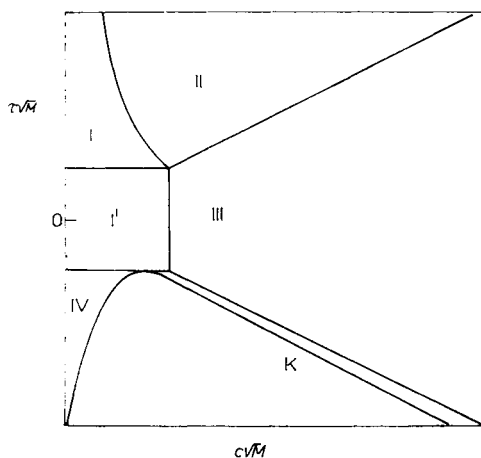

FIG. 1

Schematic universal temperature-concentration diagram for a polymer solution. I region of good solvent, dilute solution; II region of good solvent, entangled solution; I′ region of Θ solvent, dilute solution; III region of Θ solvent, entangled solution; IV region of poor solvent, dilute solution; K coexistence curve
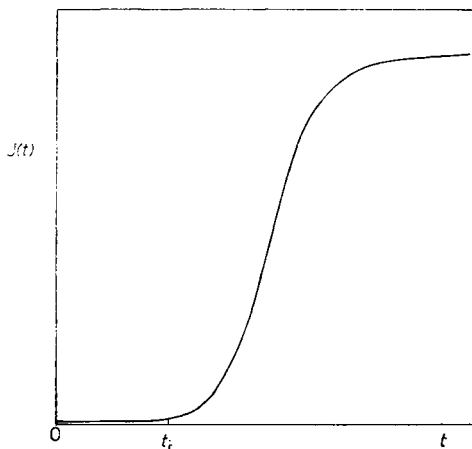

FIG. 2

Typical dependence of the nucleation rate $J(t)$ on time; t_i is the induction period

RESULTS AND DISCUSSION

According to ref.[26], the Θ temperature of the system under investigation is 22°C, which has been corroborated by the zero value of the second virial coefficient A_2 at this temperature obtained in our earlier measurements[20]. Another confirmation of the Θ temperature which is very important for further estimation of the reduced

Characteristics of the polystyrene standards. Manufacturers: Pressure Chemicals (PC), Toyo Soda (TS)

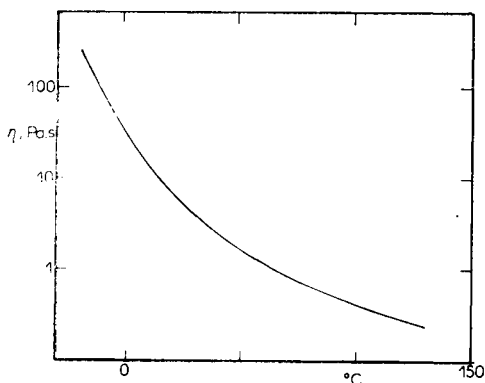| $M_w \cdot 10^{-6}$	M_w/M_n	$c^*(\Theta)$, g/cm^3	Manufacturer
0·77	1·01	$4·5 \cdot 10^{-3}$	TS
1·26	1·05	$3·6 \cdot 10^{-3}$	TS
1·80	1·20	$3·0 \cdot 10^{-3}$	PC
2·00	1·3	$2·8 \cdot 10^{-3}$	PC
2·89	1·09	$2·3 \cdot 10^{-3}$	TS
3·84	1·05	$2·0 \cdot 10^{-3}$	TS
6·77	1·14	$1·5 \cdot 10^{-3}$	TS
20·6	—	$8·8 \cdot 10^{-4}$	TS

FIG. 3

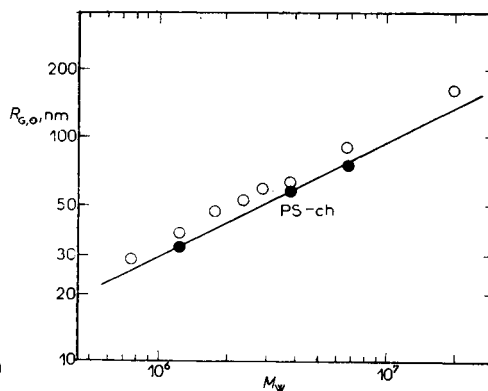Temperature dependence of the viscosity of dioctyl phthalate

FIG. 4

Dependence of the radius of gyration R_G of polystyrene on molecular weight M_w in dioctyl phthalate (○) and cyclohexane (literature data ——— and our control measurements ●)

temperature τ consists in the determination of the dependence of the radius of gyration on molecular weight. Values of R_G obtained for all polymers from Table I are given in Fig. 4. One can see that the proportionality $R_G \sim M^{1/2}$ does hold, namely,

$$R_G(\Theta) = (0.026 \pm 0.002) M_w^{0.51 \pm 0.03} \text{ nm} .$$ (5)

On the other hand, the values of the radius of gyration are systematically higher by some 15% than for the system polystyrene–cyclohexane represented in Fig. 4 with a solid line. This line represents reported data and can be described by the relation

$$R_G(\Theta) = 0.03 M_w^{0.5} \text{ nm} .$$ (6)

The 15% deviation mentioned in this study is attributed to steric hindrances caused by large planar molecules of the solvent which impede the chain to have unperturbed dimensions, but on the other hand have no effect on the Gaussian character of the chain leading to the relation $R_G(\Theta) \sim M^{1/2}$.

The dynamic coexistence curve, the shift of which to higher concentrations was documented in our preceding paper[20], has now been obtained down to $-33°C$, i.e. in the temperature range 50 degrees below the Θ temperature, cf. Fig. 5. The slope of the curve at low concentrations suggests that, in principle, for $c \sqrt{M} < 0.1$ nucleation cannot take place in real time.

The dependence of the radius of gyration of polymers having molecular weights (M_w) $2.00 . 10^6$, $3.84 . 10^6$, and $6.77 . 10^6$ as a function of temperature is shown
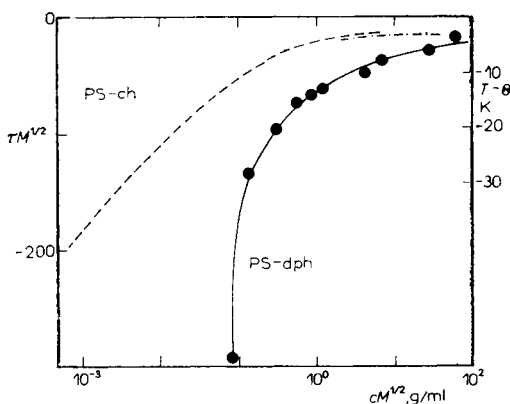

FIG. 5

Comparison of the coexistence curves for polystyrene in cyclohexane (------) and dioctyl phthalate (———)
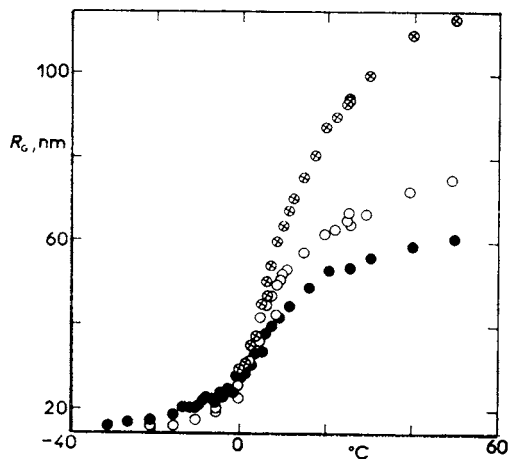
FIG. 6

Temperature dependence of the radius of gyration R_G of polystyrene in dioctyl phthalate for polymers having molecular weights $6 \cdot 77 \cdot 10^6$ (⊙), $3 \cdot 84 \cdot 10^6$ (○) and $2 \cdot 00 \cdot 10^6$ (●)
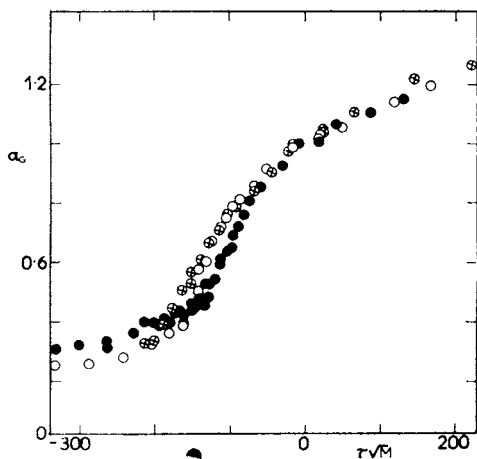

FIG. 7

Dependence of the expansion factor of the radius of gyration α_G on the reduced temperature variable $\tau \sqrt{M}$ for polymers having molecular weights $6 \cdot 77 \cdot 10^6$ (⊗), $3 \cdot 84 \cdot 10^6$ (○), and $2 \cdot 00 \cdot 10^6$ (●)
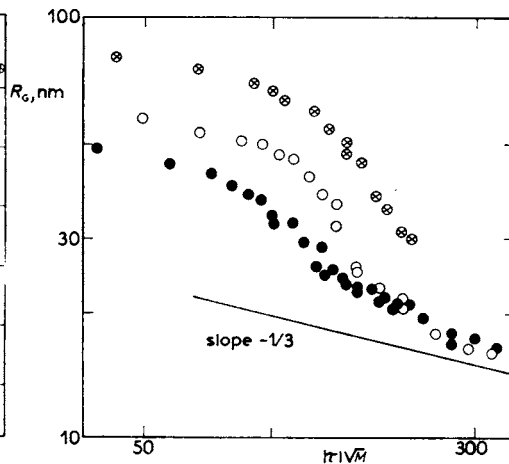
FIG. 8

Dependence of the radius of gyration R_G of polystyrene in dioctyl phthalate on the reduced temperature variable $\tau \sqrt{M}$ in the logarithmic coordinates for polymers having molecular weights $6 \cdot 77 \cdot 10^6$ (⊗), $3 \cdot 84 \cdot 10^6$ (○) and $2 \cdot 00 \cdot 10^6$ (●)

in Fig. 6. All three curves have the same character; the largest change in dimension at collapse occurs at the highest molecular weight. This is natural, because the ratio of dimensions of the swollen (R_s) and collapsed (R_c) coil is

$$\frac{R_s}{R_c} = \frac{aM^{3/5}}{aM^{1/3}} = M^{4/15} \tag{7}$$

(a is the proportionality constant characteristic of the given pair polymer–solvent), assuming that the persistent chain length is temperature-independent. The same results are shown in Fig. 7 as the dependence of the expansion factor α_G on the reduced temperature variable $\tau\sqrt{M}$. Agreement between the curves of molecular weights $3\cdot84 \cdot 10^6$ and $6\cdot77 \cdot 10^6$ is fairly good. Slight deviations observed for the polymer having the molecular weight $2\cdot00 \cdot 10^6$ are attributed to polydispersity of this sample. It may also be mentioned that within the whole temperature range the expansion factor of the coil, α_G, is a universal function of the variable $\tau\sqrt{M}$. The temperature dependence of the expansion factor in the range I' is adequately described by ($2b$)

$$\alpha_G = 1 + 1\cdot65 \cdot 10^{-3}\tau\sqrt{M} \tag{8}$$

for $-50 < \tau\sqrt{M} < 50$.

For the evaluation of the exponent in region IV (Eq. $2c$) the log-log representation of data is useful, cf. Fig. 8. The curve for molecular weight $6\cdot77 \cdot 10^6$ does not extend to sufficiently deep temperatures, but for other curves it can be seen that the globular region with the expected exponent $-1/3$ is reached only for reduced temperatures $\tau\sqrt{M} < -230$.

The whole coil-globule transition region is wider in this system (in the reduced variables) than for other polymer–solvent systems. For instance, in the polystyrene––cyclohexane system the region I' is restricted by the reduced temperature $|\tau|\sqrt{M} = 10$ (ref.[19]), and the globular state is reached below the temperature $\tau\sqrt{M} = -40$ (ref.[12]). The extension of the transition region in the case of the system PS–dioctyl phthalate is probably due to the relatively higher rigidity of the polystyrene coil in this solvent. The cause of such higher rigidity, similarly to the case of the Θ dimensions, is seen in steric hindrances due to large planar molecules of the solvent.

The coil-globule transition was observed for three polystyrene samples having molecular weights $2\cdot00 \cdot 10^6$, $3\cdot84 \cdot 10^6$ and $6\cdot77 \cdot 10^6$ in dioctyl phthalate.

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