Chain Uncoiling

Dynamic Critical Exponent in the Coil-Extended Chain Transition in a Non-Ideal Solvent

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SUMMARY

The behavior of dilute solutions of polystyrene (M ranging from $0,7.10^6$ to 4.10^6) in bromoform was studied in the Frank-Keller apparatus. The data obtained confirm the prediction of the non-linear theory of single-chain dynamics on a first order coil-extended chain phase transition in a longitudinal hydrodynamic field. The observed ratios of the measured streaming birefringence to its ultimate value attain 0,95 thus recording a practically complete uncoiling of the macromolecules. The dependence of the fundamental relaxation time on molecular weight is expressed by

$$\tau \sim (R_F)^\Psi$$

R_F being the Flory radius of the inperturbed chain in an athermic solvent, and Ψ the dynamic critical exponent equal to $2,82\pm0,15$. This value corresponds to data obtained for polystyrene in good solvents by various dynamic methods.

INTRODUCTION

The deformation of a macromolecular coil in solution leads to an increase in the polymer – solvent hydrodynamic interaction. This known fact tempted one of the present authors to predict as far back as in 1970 a possibility of either first or second order impermeable coil – extended chain phase transition (FRENKEL, 1970, 1977). This concept has been elaborated in the most perfect form by de Gennes (P. de GENNES, 1974, 1979), who has taken into account not only the change in the permeability of the macromolecular coil on deformation but also the non-linear dependence of the entropic force on the chain end-to-end distance.

The de Gennes theory predicts a first order transition in a longitudinal hydrodinamic field at $G\tau \approx 1$, G being the velocity gradient and τ the fundamental relaxation time of the chain undeformed by the field. This theory was qualitatively confirmed (MACKLEY, KELLER, 1975; FARREL et al., 1980; MILES et al., 1980).

EXPERIMENTAL

The aim of the present experimental study was to estimate the ultimate possible degree of uncoiling of a chain in a longitudinal hydrodynamic field, and to investigate the dependence of the fundamental relaxation time on molecular

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weigth. Solutions of polystyrene (PS) fractions with M ranging from $0,7.10^6$ to 4.10^6 (see table 1) were studied. The concentration of the solutions corresponded to the product $[\eta] \cdot C \approx 0,6$; Therefore the coil did not overlap in the solution (here $[\eta]$ is the intrinsic viscosity, cm^3/g; C the concentration, g/cm^3). Bromoform was used as solvent because its refraction index (n) coincides with that of PS. Thus, in contrast to the preceding studies (MACKLEY,KELLER,1975), we could measure correctly streaming birefringence (SBF) and consequently the degree of uncoiling.

RESULTS AND DISCUSSION

The hydrodynamic part of our device was analogous to that already described (MACKLEY,KELLER,1975) and consisted of two coaxial capillaries with orifices desposed towards each ether. On flowing of the solution in the capillaries, in the gap between them equal to $1,5 - 2$ their internal diameters, a longitudinal hydrodynamic field was generated. The internal and external diameters of the capillaries were 0,4 and 6 mm respectively. Their uniaxial disposition was attained by means of observing the formation of a birefringent disk, as already described (MACKLEY,KELLER,1975).

The device had an optical attachment corresponding to Brace's scheme with an analyzer fixed on the limb and a $1/4\lambda$ plate as a compensator. The attachment made it possible to measure the diameter of the anisotropic region occuring in the solution, and the phase difference between the ordinary and unordinary rays passing through this region. At relatively low gradients this region had the appearance of a cylindrical string. With increasing velocity gradient this region attained the shape of a paraboloid of revolution. In this case the measurements were performed on the o a b c line (fig.1).
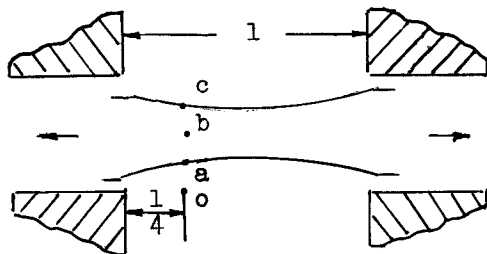

Fig.1. Schematic representation of the anisotropic string formed between the capillaries (vertical dimensions of the string are increased).

SBF was calculated from the well-known formula:

$$\Delta n = \frac{\lambda \Delta \delta}{2 \pi d}$$

λ being the wavelength (563 nm) of the linearly polarized light irradiating the solution (the orientation of the plane of polarisation was 45° to the axis of anisotropic region), d the diameter of the string estimated in the case of the paraboloidal shape as the distance between the points a and c

(the corrections for the diffraction widening were introduced in the measured values of d)

$$\Delta\delta = 4(\varphi - \varphi_o)$$

the phase difference of the ordinary and unordinary rays, φ_o the dark field angle measured with the limb, φ the angle corresponding to the disappearance of the illumination contrast in the vicinity of points b and o.

The ultimate SBF was determined according to Peterlin (PETERLIN,1966):

$$\Delta n_\infty = \frac{2\pi(n^2 + 2)^2}{9n}(\alpha_1 - \alpha_2)\,N'$$

$(\alpha_1 - \alpha_2)$ being the difference of polarizabilities of a PS segment assumed to be equal to $145.10^{-25}\mathrm{cm}^3$ (BARANOV,MAGARIC, 1963), N' the number of segments in 1 cm^3 of the solution.

The velocity gradient was calculated(MACKLEY,KELLER,1975) as

$$G = \frac{2Q}{1\pi r^2}$$

Q being the consumption of the liquid per second per one capillary, l the distance between the orifices of the capillaries, 2r their internal diameter.

The experimental data are plotted in fig.2 as the dependences of $\Delta n/\Delta n_\infty$ on G measured at 20°C for fractions of various molecular weights. It can be seen that with increasing G $\Delta n/\Delta n_\infty$ approaches 0,95.
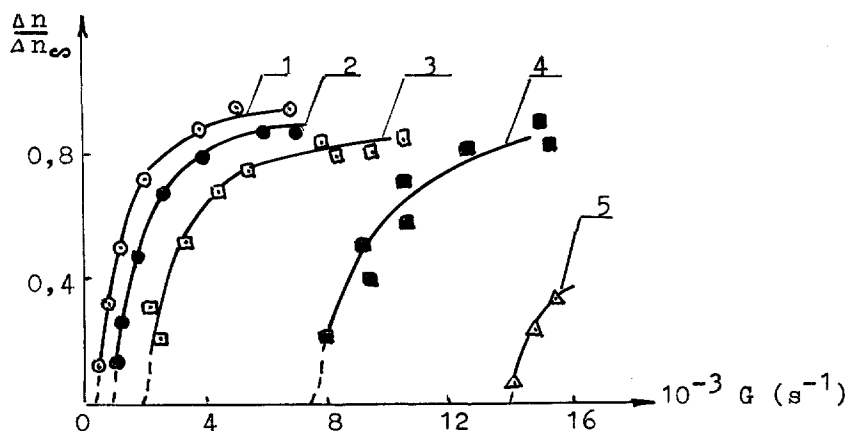

Fig.2. Dependence of $\Delta n/\Delta n_\infty$ on G for PS fractions of various molecular weights: 1 - 4,2; 2 - 3,95; 3 - 2,07; 4 - 1,1; 5 - 0,74.10^6.

This result must be treated as a direct indication of a practically complete uncoiling of the chains in the longitudinal field assumed but not proven unequivocally in the theory of orientational crystallization (BARANOV, 1977). This result

also confirms the previous suggestion on the possibility of a first order coil - extended chain phase transition. It should be mentioned that in a paper (FARREL et al., 1980) the limiting value of $\Delta n / \Delta n_\infty$ for dilute solutions in ortho xylene was found equal to 0,6.

The data presented here show that SBF practically does not occur up to a certain critical value of G different for each fraction. This corresponds to the non-linear theory of single - chain dynamics in the longitudinal field. The value of $G_{crit.}$ can be determined by extrapolating the dependence of Δn on G to zero value of Δn. According to de Gennes, the fundamental time can be then determined as

$$\tau \cong \frac{1}{G_{cr.}}$$

The determined values of τ for fractions of different molecular weights are presented in table 1. Using the least-squares method one obtains

$$\tau = 10^a \cdot M^b$$

$a = -(14,10 \pm 0,05)$ and $b = (1,7 \pm 0,1)$.

It should be mentioned that according to dynamic scaling (DE GENNES, 1980) we have

$$\tau \sim \frac{\eta_0 \ A^3 \ N^x}{kT}$$

A being the length of the segment, η_0 the solvent viscosity, k Boltzmann's constant, T the absolute temperature, $x = 3/2$ in an ideal solvent and 9/5 in an athermic solvent. The value of the exponent 1,7 found for the dependence on M (or N) is in accordance with the known fact that the PS-bromoform pair is closer to an athermic than to an ideal system. This follows, in particular, from the dependence of $[\eta]$ on M for PS in bromoform (BARANOV, MAGARIC, 1963):

$$[\eta] = 0,52 . 10^{-4} \cdot M^{0,76}$$

In a θ-solvent $[\eta] \sim M^{0,5}$, in an athermic solvent - $M^{0,8}$.

According to (DE GENNES, 1979) the relation between τ and N can be expressed in the form:

$$\tau \sim (R_F)^{\xi}$$

ξ being the dynamic critical exponent, $R_F = AN^{3/5}$. In our case (fig.3) $\xi = 1,70/0,6 = 2,83$. This value is a fact accord with the ξ values determined for PS in good solvents by various dynamic methods (DE GENNES, 1979).

TABLE 1

M.10^{-6}	G	$\tau.10^3$	$\tau.10^3$cal-culated	C g/dl
4,20	700	1,43	1,36	0,107
3,95	1030	0,97	1,21	0,142
2,07	2300	0,435	0,404	0,182
1,10	8200	0,125	0,14	0,311
0,74	14400	0,07	0,07	0,388
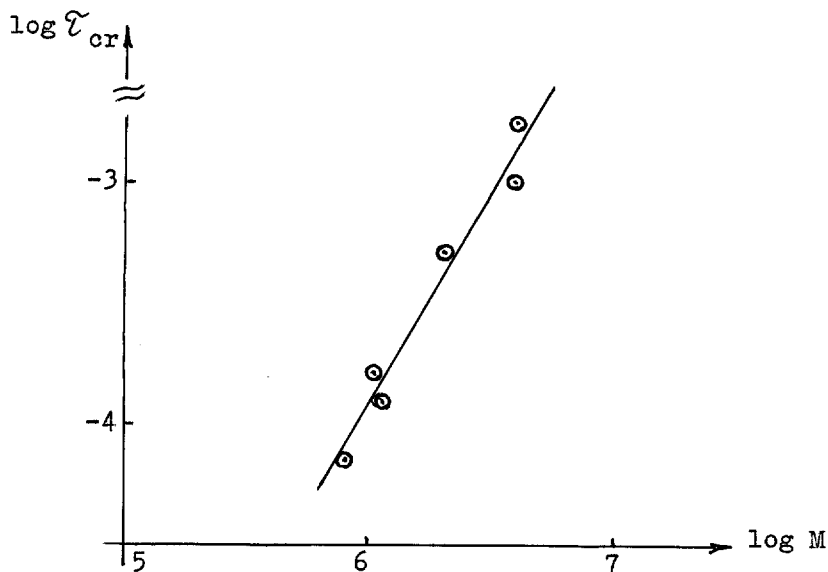
Fig.3. Dependence of $\log \tau_{cr.}$ on $\log M$.

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