



Variation with temperature of the thickness of an adsorbed polymer layer in the collapsed state

Ph. Déjardin

► To cite this version:

Ph. Déjardin. Variation with temperature of the thickness of an adsorbed polymer layer in the collapsed state. Journal de Physique, 1983, 44 (4), pp.537-542. 10.1051/jphys:01983004404053700 . jpa-00209629

HAL Id: jpa-00209629

<https://hal.science/jpa-00209629>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification

Physics Abstracts

68.45 — 36.20 — 61.40

Variation with temperature of the thickness of an adsorbed polymer layer in the collapsed state

Ph. Déjardin (*)

CNRS, Centre de Recherches sur les Macromolécules, 6, rue Boussingault, 67083 Strasbourg Cedex, France

(Reçu le 13 juillet 1982, révisé le 19 novembre, accepté le 17 décembre 1982)

Résumé. — Des mesures d'épaisseur hydrodynamique L_H en dessous de la température θ du système polystyrène/*trans*-decaline mettent en évidence l'état effondré de la couche de polymère adsorbé. Pour trois échantillons de polystyrène ($M_w \simeq 10^6$; $M_w = 6 \times 10^5$; $M_w = 4 \times 10^5$), on observe la loi de puissance $L_H \sim \left(\frac{\theta - T}{T}\right)^\alpha$ avec des valeurs de l'exposant α ($-0,87$; $-0,83$; $-0,80$) plus proches de 1,0 que de $1/3$. Ces résultats sont en faveur de macromolécules adsorbées interdépendantes. Les tentatives pour rendre compte d'un facteur logarithmique $\left[\ln\left(\frac{T}{\theta - T}\right)\right]^\beta$ donnent des valeurs de β comprises entre $-0,39$ et $-0,65$, à comparer avec $-0,636$, valeur prévue par la théorie de De Gennes pour une chaîne non adsorbée, près de la température θ .

Abstract. — The behaviour of the hydrodynamic thickness L_H , below the θ -temperature for the system polystyrene/*trans*-decalin, is consistent with the presence of a collapsed adsorbed polymer layer. For three samples of polystyrene ($M_w \simeq 10^6$; $M_w = 6 \times 10^5$; $M_w = 4 \times 10^5$), one observes a power law dependence $L_H \sim \left(\frac{\theta - T}{T}\right)^\alpha$ with values of α ($-0,87$; $-0,83$; $-0,80$) close to 1.0 rather than to $1/3$. These results are consistent with an interdependent macromolecule model. Attempts to obtain a logarithmic factor $\left[\ln\left(\frac{T}{\theta - T}\right)\right]^\beta$ give values of β between $-0,39$ and $-0,65$, to be compared with the value $-0,636$ obtained theoretically by De Gennes, for a chain surrounded by solvent near the θ -temperature.

1. Introduction. — The coil-globule transition of a flexible polymer chain in dilute solution has been the matter of several theoretical [1-4] and experimental [5-8] studies. The authors are mainly interested in the description of the polymer chain in the collapsed state, in other words, the globule. Recently more complex systems have been studied :

(i) the collapse of a polymer chain in a melt of incompatible polymer chains [9],

(ii) the collapse of one polymer coil in a mixture of solvents [10]. The last problem was again presented in a review article [11] where the mean-field theory (Flory-Huggins) and the more recent scaling approach were both applied to the single polymer chain in one solvent. For the condensation of a single coil

DNA, mean-field theory has been developed by Frisch and Fesciyan [12] and Post and Zimm [13]. The main difference between DNA and a chain like polystyrene, for our purposes, is their flexibility. Rigid polymers like DNA should experience a more abrupt transition than flexible polymers like polystyrene.

In this article we are concerned with the collapse of adsorbed layers of polystyrene from *trans*-decalin solutions. To our knowledge, this is the first study of the collapse of adsorbed polymers. Here our purpose is to attempt to extend single chain results to the problem of adsorbed polymers, mainly to study the dependence of the hydrodynamic thickness L_H of the adsorbed layer on the parameter $\tau = \frac{\theta - T}{T}$

where T is the temperature and θ is the Flory Theta temperature of the polymer-solvent system [14].

L_H is also dependent on the molecular weight

(*) Present address : University of California, San Diego, Department of Chemistry, B-017, La Jolla, California 92093 USA.

through the amount of polymer adsorbed per unit area. This dependence is not studied here.

2. Theoretical background. — For a single chain in the globule state, the mean-field theory [2, 3] leads to the law :

$$R \sim N^{1/3} \tau^{-1/3}, \quad (1)$$

where R is the radius of the collapsed chain having N statistical units. With τ fixed the volume V of the sphere ($V \sim R^3$) is proportional to N ; the concentration of monomer inside the globules is independent of molecular weight.

The scaling approach gives the same result. However, De Gennes [1] has proposed a logarithmic factor, by using renormalization group calculations

$$V \simeq R^3 \sim N \tau^{-1} \left[\ln \left(\frac{1}{\tau} \right) \right]^{-7/11}. \quad (2)$$

Here we are dealing with adsorbed polymers, and the isotropic shape of the isolated globule in solvent is lost. An adsorbed long flexible polymer is generally viewed as a succession of adsorbed trains in direct contact with the surface and loops and tails protruding into the solution. The thickness of the adsorbed layer is dependent primarily on the structure of the loops and of the tails. The contribution of the trains is negligible, except for very short chains. The subject studied here is not that of a polymer completely adsorbed with all monomers in direct contact with the surface. Although we are dealing with adsorption experiments, we are not justified in considering a collapse in two dimensions, as was studied theoretically by Khokhlov [15]. What we are measuring, on the contrary, is essentially the change of the « third » dimension with temperature.

Let us assume that the concentration of monomer inside the adsorbed layer varies with temperature in the same way that the concentration inside the isolated globule surrounded by solvent does. Schematically, for an adsorbed polymer layer, we have to consider two extreme cases (Fig. 1) :

(i) the macromolecules interpenetrate intimately and their volumes can vary only jointly. The variation of the volume of the whole layer is a consequence of the variation in only one dimension. Therefore

$$V \sim L_H \sim \tau^{-1}, \quad (3)$$

(ii) the adsorbed macromolecules are juxtaposed and their volumes vary independently. For each chain the variation of the volume is a consequence of the variations in all three dimensions. By giving the same relative variation to each of the three dimensions, we obtain :

$$3 \frac{dL_H}{L_H} = \frac{dV}{V} = - \frac{d\tau}{\tau}.$$

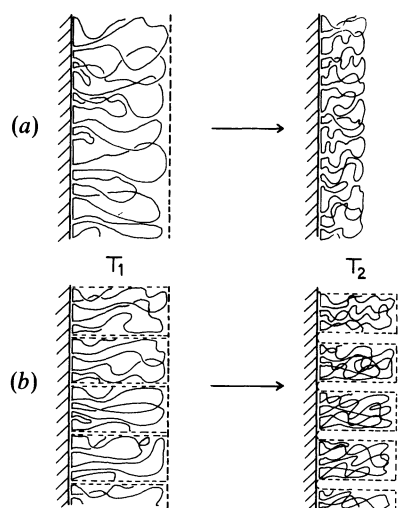


Fig. 1. — Schematic representation of the contraction of an adsorbed layer with temperature ($T_2 < T_1$) for two models, (a) the adsorbed macromolecules interpenetrate and cannot contract individually, (b) the adsorbed macromolecules are juxtaposed and can contract individually. The volume variation is the same for the two models but the thicknesses of the layers are not the same at temperature T_2 , although they are at T_1 .

Therefore

$$L_H \sim \tau^{-1/3}. \quad (4)$$

One intermediate case is the adsorbed macromolecules are juxtaposed with many points of contact between them, without interpenetration. Here, most probably, although the macromolecules are juxtaposed, their volumes will vary jointly as for the case (i).

By writing L_H , in the relations (3) and (4), we assume for the two cases that the hydrodynamic thickness is a good approximation of the thickness used to determine the volume; that is, the concentration of monomers is high, and the functional form of the concentration distribution does not vary with temperature over this range. The interaction between one monomer and the wall is assumed to be constant.

Our experimental results, given in section 4, are consistent with the model of interpenetrating macromolecules. In the adsorbed layer, the concentration of monomers is high. This high concentration should favour the interpenetration of macromolecules, as it occurs in semi-dilute solutions [16]. It is proper here to verify whether the interface could modify this phenomenon.

3. Experimental conditions. — **3.1 HYDRODYNAMIC THICKNESS MEASUREMENTS.** — An experimental system [17] has been designed in which the flow rate of fluids through porous media is determined by recording the passage of a meniscus in front of two photodiodes in a horizontal precision glass capillary.

The flow rate of pure solvent is first determined as a function of temperature for a given pressure difference. The solvent is then replaced by the solution (0.1 % w/w) which is circulated through the porous medium until the flow rate becomes constant. A constant value was reached after about one week. This long time seems to indicate that adsorbed polymers, when adsorbed from θ -solutions, reach their equilibrium conformation only slowly. Similar observations were made by Priel and Silberberg [18] using precision viscometry. After adsorption is complete, the solution is withdrawn from the cell and replaced by pure solvent, the flow rate of which is subsequently measured; it was very stable indicating no detectable desorption of the adsorbed polymer. The temperature is then decreased. For each temperature, from the flow rates before adsorption (J_v^0) and after adsorption (J_v), one can deduce a value for the hydrodynamic thickness L_H , by assuming Poiseuille's law holds in the pore :

$$L_H = R_p \left[1 - \left(\frac{J_v}{J_v^0} \right)^{1/4} \right], \quad (5)$$

where R_p is the radius of the pore. The precision of J_v/J_v^0 is better than 0.5 %, leading to a determination of L_H with a precision of $\pm 10 \text{ \AA}$.

We verified that the hydrodynamic thickness L_H and the differential pressure were independent in the range 0.2 to 20 mmHg [19].

We have previously performed experiments where the adsorption had occurred in good solvent conditions (*trans*-decahydronaphthalene at 40 °C) and measured the variation of the thickness when the temperature decreased, in the presence of pure solvent [20]. This procedure is the one described and studied theoretically by De Gennes [21]. However, we did not measure the same thickness as initially when we came back to the adsorption temperature. On the contrary, in the experiments described here, we could reproduce the value of the thickness at the θ -temperature after the measurements at the lowest temperatures.

3.2 POROUS MEDIA. — We used Pyrex sintered glass disks analogous to those used by Rowland

Table I. — Characteristics of the polystyrene samples and corresponding pore radii R_p of the sintered glass discs.

Fraction	M_w (GPC) (^a)	M_w (l. s.) (^b)	M_w/M_n	$R_p/\mu\text{m}$
1	1.5×10^6	1.3×10^6	1.5	0.77
3	5.9×10^5	6.2×10^5	1.24	0.72
4	4.0×10^5	4.6×10^5	1.21	0.71

(^a) Gel permeation chromatography in tetrahydrofuran.

(^b) Light scattering experiments in benzene for the fraction 1 and 4, in tetrahydrofuran for fraction 3.

and Eirich [22] for the adsorbent. According to the manufacturer, the size distribution is narrow and has a sharp cutoff at 0.85 μm . We assigned this value to the average hydrodynamic conduct radius of the most permeable disk of six and introduced corrections to this value (Table I) for all other disks according to the Poiseuille's law $J_v^0 \sim R_p^4$ [19].

3.3 POLYMER SAMPLES. — Polystyrene was prepared by radical polymerization followed by fractionation with a cyclohexane/methanol solvent/precipitant system. The characteristics of the fractions, numbered as in reference [19], are given in table I. The last two fractions have a ratio $M_w/M_n \approx 1.2$ while the first is very polydisperse ($M_w/M_n \approx 1.5$). Its molecular weight was determined to be 9.5×10^5 from dilute solution viscosity measurements in *trans*-decalin.

3.4 SOLVENT ; θ -TEMPERATURE. — *Trans*-decahydronaphthalene of analytical grade (Merck, 96 % content by GC) was used without further purification. Viscosity measurements in solution were carried out with an automatic recording capillary viscosimeter [23], between 20 °C and 25 °C, where θ -points are reported in the literature [24-28]. We have determined $\theta = 25.5 \text{ °C}$ by viscosimetry, somewhat higher than the values generally reported. This difference could be attributed to the use of unpurified solvent and/or to the presence of water. The adsorption experiments were made at 24.8 °C. At this temperature, the Mark-Houwink relationship was found to be

$$[\eta] = 0.084 M_w^{0.49}, \quad (6)$$

where the intrinsic viscosity of the polymer $[\eta]$ is expressed in ml.g^{-1} and M_w in daltons.

4. Experimental results and discussion. — In figure 2 $\ln L_H$ is plotted versus $\ln \tau$ for temperatures below

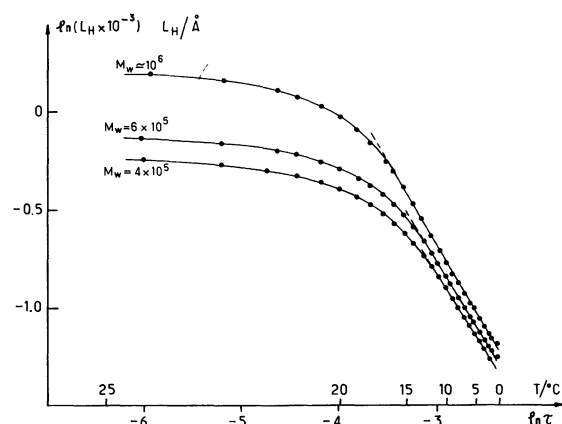


Fig. 2. — Variation of $\ln(L_H)$ versus $\ln \tau$. L_H is the hydrodynamic thickness. $\tau = \frac{\theta - T}{T}$. Adsorption experiments were made from dilute solutions (0.1 % w/w) in *trans*-decalin at 24.8 °C.

Table II. — Parameters of the experimental law $L_H = A\tau^\alpha$ for the three fractions used and higher limit of validity T_c . r = least square correlation coefficient.

Fraction	$A/\text{\AA}$	α	$T_c/^\circ\text{C}$	r^2
1	37.4	-0.87	16.2	0.998
3	38.3	-0.83	13.1	0.998
4	40.1	-0.80	12.1	0.999

the θ -temperature. At the lowest temperatures, the curve is fit by a straight line; L_H can be represented by a power law in τ

$$L_H = A\tau^\alpha. \quad (7)$$

The values of A and α are reported in table II. We can make two remarks :

(i) The three values of α are closer to 1.0 than to $\frac{1}{3}$ and suggest that the macromolecules are jointly adsorbed. Nevertheless the exponent α , lower than 1.0, is an increasing function of the molecular weight. This would indicate that the asymptotic behaviour derived for infinite chains, has not yet been attained. Previously Weill and Des Cloizeaux [29] and Akcasu and Han [30] have reported that in solution the asymptotic laws apply over a range which is much broader for the radius of gyration than for the hydrodynamic radius.

(ii) The difference $(\theta - T_c)$, where T_c is the upper limit of validity of the empirical relation (7), is a decreasing function of the molecular weight. This result is in accordance with the theory [2] about the width of the coil-globule transition for an isolated macromolecule, which has been predicted to scale like $N^{-1/2}$ (Fig. 3).

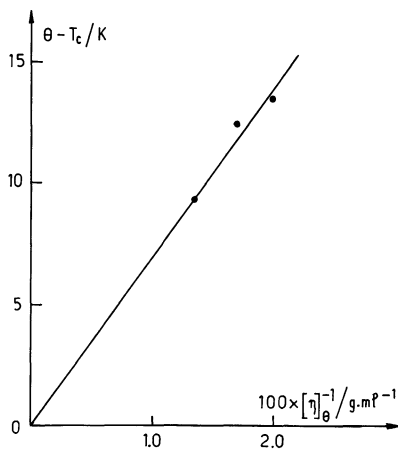


Fig. 3. — Difference $\theta - T_c$ versus the inverse of the intrinsic viscosity $[\eta]$ in θ solvent. $[\eta]_\theta^{-1}$ scales like $N^{-1/2}$, where N is the number of statistical units.

Since the values of α are close to 1.0, we have plotted, in figure 4, $\ln(L_H \tau)$ versus $\ln \left[\ln \left(\frac{1}{\tau} \right) \right]$,

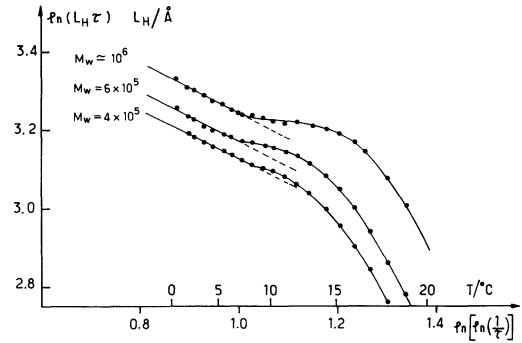


Fig. 4. — Variation of $\ln(L_H \tau)$ versus $\ln \left[\ln \left(\frac{1}{\tau} \right) \right]$ in the range of the lowest temperatures studied. The slopes of the straight lines are respectively -0.655, -0.64 and -0.62 for the molecular weights 10^6 , 6×10^5 and 4×10^5 .

in order to test the relation (2) given by De Gennes [1] for a chain near the θ -temperature. Extended to the adsorption problem, with the assumption of macromolecules jointly adsorbed, the relation (2) gives

$$L_H \sim \tau^{-1} \left[\ln \left(\frac{1}{\tau} \right) \right]^{-7/11}. \quad (8)$$

The preceding ranges of temperature, where empirical relations (7) hold, seem, as seen in figure 4, to split into two ranges below and above about 8°C . We observe, below 8°C , straight lines with slopes near the theoretical value -0.636.

In table III are reported the parameters B and β of the empirical relation

$$L_H = B\tau^{-1} \left[\ln \left(\frac{1}{\tau} \right) \right]^\beta, \quad (9)$$

determined both for the whole range $T < T_c$, and the range $T \lesssim 8^\circ\text{C}$.

It is difficult to decide whether this splitting is a fundamental result or an artifact of the experiments. It is noteworthy that the splitting is more pronounced

Table III. — Parameters of the experimental law $L_H = B\tau^{-1} \left[\ln \frac{1}{\tau} \right]^\beta$ for the three fractions used, in the range $T < T_c$ and in the range $T \lesssim 8^\circ\text{C}$. r = least square correlation coefficient. T_1 = higher limit of validity.

Fraction	$B/\text{\AA}$	β	$T_1/^\circ\text{C}$	r^2
1	38.3	-0.39	16.2	0.942
3	38.6	-0.47	13.1	0.967
4	40.3	-0.57	12.1	0.993
1	49.3	-0.655	7.4	0.985
3	45.2	-0.64	7.4	0.977
4	42.4	-0.62	8.3	0.994

at higher molecular weights and larger degrees of polydispersity (see Table I). As in solution experiments polydispersity should certainly be minimized to avoid confusion in the interpretation of experimental results. The author is aware that the experimental conditions were not ideal. However, one may note that the exponent β always has a reasonable order of magnitude and the right sign, regardless of the temperature range chosen.

From a fundamental point of view, one has to consider, for an adsorbed macromolecule, a loop size distribution which is as broad, in θ -solvent [31] as in good solvents [32]. Thus, to describe properly the crossover from the coil state to the collapsed state of an adsorbed polymer layer, we should probably consider this distribution.

The parameter B appears to be nearly constant with molecular weight over the whole range $T < T_c$. The same conclusion holds for the values of A (Table II). In the restricted range $T \lesssim 8^\circ\text{C}$, B seems to be an increasing function of the molecular weight, this is not very surprising since B is dependent on the amount adsorbed per unit area, which has been found generally to be an increasing function of the molecular weight [22, 33, 34]. Although the dependence of the hydrodynamic thickness on molecular weight at the θ -temperature has been studied [19], our results suggest such a study with collapsed layers would be ill advised. At the θ -temperature, the variations of the hydrodynamic thickness with molecular weight are much higher than in the collapsed state, because of the contraction of the largest loops when the temperature is decreased. We need to use better porous materials, with regular geometry, in order to deduce valuable information, by deleting the inaccuracy of the pore radii. Moreover we first need a constant value for the exponent β .

5. Conclusions. — We have studied the contraction of an adsorbed polymer layer in the collapsed state, after adsorption from solutions in a θ -solvent. The dependence of the hydrodynamic thickness L_H on

the parameter $\tau = \frac{\theta - T}{T}$ suggests that the macromolecules are jointly adsorbed on the wall and cannot contract individually.

Moreover, the attempts to obtain the logarithmic factor theoretically predicted by De Gennes give exponents close to the one predicted : -0.39 in the worst case. -0.62 to -0.65 in the better ones, which should be compared with -0.636 .

Taking advantage of the quasi-irreversibility of the adsorption, the study of the collapse of an adsorbed polymer layer could be a suitable method to characterize its structure. If confirmed by using better materials than those we have presented above, the law $L_H \sim \tau^\alpha$, with α close to -1.0 , should permit a verification of the logarithmic factor given by De Gennes [1]. Furthermore, the values of the parameter B in relation (9), for molecular weights high enough to have a constant value of β , should be reliable on the amount adsorbed per unit area.

Finally, one can remark that the experimental conditions which are favourable for the observation of collapsed polymers are totally opposite in solution to those in the adsorbed state. In the former case, one has to use *extremely dilute* solutions (concentration as low as $10^{-7} \text{ g. ml}^{-1}$ [35]) in order to have isolated macromolecules and to avoid phase separation by increase of temperature in a range as large as possible. As a result, the technique must be very sensitive. In the latter, one has to use *dilute* solutions (concentration $\simeq 10^{-3} \text{ g. ml}^{-1}$, range of the pseudo-plateau in the adsorption concentration isotherm), in order to cover the whole surface and to avoid entirely isolated macromolecules, in order to make easier the explanation of the results.

Acknowledgments. — The author is grateful to Professor B. H. Zimm for a critical remark, to Dr. L. Leibler and Dr. M. Benmouna for fruitful discussions, and wishes to express his thanks to Dr. J. Conrad for the reading of the manuscript and to Ms. S. Hosmer for the typing.

References

- [1] DE GENNES, P. G., *J. Physique-Lett.* **36** (1975) L-55; *ibid.* **39** (1978) L-299.
- [2] LIFSHITZ, I. M., GROSBERG, A. Yu., KHOKHLOV, A. R., *Rev. Mod. Phys.* **50** (1978) 683.
- [3] SANCHEZ, I. C., *Macromolecules* **12** (1979) 980.
- [4] STEPHEN, M., *Phys. Lett.* **53A** (1975) 363.
- [5] SUN, S. T., NISHIO, I., SWISLOW, G., TANAKA, T., *J. Chem. Phys.* **73** (1980) 5971.
- [6] PERZYNSKI, R., ADAM, M., DELSANTI, M., *J. Physique* **43** (1982) 129.
- [7] NIERLICH, M., COTTON, J.-P., FARNOUX, B., *J. Chem. Phys.* **69** (1978) 1379.
- [8] BAUER, D. R., ULLMAN, R., *Macromolecules* **13** (1980) 392.
- [9] JOANNY, J. F., BROCHARD, F., *J. Physique* **42** (1981) 1145.
- [10] BROCHARD, F., DE GENNES, P. G., *Ferroelectrics* **30** (1980) 33.
- [11] WILLIAMS, C., BROCHARD, F., FRISCH, H. L., *Ann. Rev. Phys. Chem.* **32** (1981) 433.
- [12] FRISCH, H. L., FESCIAN, S., *J. Polym. Sci. Polym. Lett. Ed.* **17** (1979) 309.
- [13] POST, C. B., ZIMM, B. H., *Biopolymers* **18** (1979) 1487.
- [14] FLORY, P. J., *Principles of Polymer Chemistry* (Cornell University Press, Ithaca and London) 1953.
- [15] KHOKHLOV, A. R., *Polymer* **22** (1981) 447.
- [16] DE GENNES, P. G., in *Scaling Concepts in Polymer Physics* (Cornell University Press, Ithaca, N.Y.) 1979.
- [17] DÉJARDIN, P., Thesis, Université Louis Pasteur, Strasbourg, France (1981).

- [18] PRIEL, Z., SILBERBERG, A., *Polymer Preprints* **11** (1970) 1405.
- [19] DÉJARDIN, P., VAROQUI, R., *J. Chem. Phys.* **75** (1981) 4115.
- [20] DÉJARDIN, P., not published.
- [21] DE GENNES, P. G., *Macromolecules* **14** (1981) 1637.
- [22] ROWLAND, F. W., EIRICH, F. R., *J. Polym. Sci. A1* **4** (1966) 2033; *ibid.* **4** (1966) 2401.
- [23] GRAMAIN, Ph., LIBEYRE, R., *J. Appl. Polym. Sci.* **14** (1970) 383.
- [24] INAGAKI, H., SUZUKI, H., FUJII, M., MATSUO, T., *J. Phys. Chem.* **70** (1966) 1718.
- [25] ROOTS, J., NYSTRÖM, B., *Europ. Polym. J.* **14** (1978) 773.
- [26] FUKUDA, M., FUKUTOMI, M., KATO, Y., HASHIMOTO, T., *J. Polym. Sci.* **12** (1974) 871.
- [27] NOSE, T., CHU, B., *Macromolecules* **12** (1979) 590.
- [28] NAKATA, M., HIGASHIDA, S., KUWAHARA, N., SAEKI, S., KANEKO, M., *J. Chem. Phys.* **64** (1976) 1022.
- [29] WEILL, G., DES CLOIZEAUX, J., *J. Physique* **40** (1979) 99.
- [30] AKCASU, A. Z., HAN, C. C., *Macromolecules* **12** (1979) 276.
- [31] HOEVE, C. A. J., DI MARZIO, E. A., PEYSER, P., *J. Chem. Phys.* **42** (1965) 2558.
- [32] DE GENNES, P. G., Preprint, *C.R. Hebd. Séan. Acad. Sci.* (1982).
- [33] KAWAGUCHI, M., HAYAKAWA, K., TAKAHASHI, A., *Polymer J.* **12** (1980) 265.
- [34] VAN DER LINDEN, C., VAN LEEMPUT, R., *J. Colloid Interface Sci.* **67** (1978) 48, 63.
- [35] SWISLOW, G., SUN, S. T., NISHIO, I., TANAKA, T., *Phys. Rev. Lett.* **44** (1980) 796.
-