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A SANS-Based Evaluation of the Chain Dimension Temperature Dependence of Poly(ethylethylene) under Θ-Conditions

A. Zirkel and D. Richter

Institut für Festkörperforschung, Forschungszentrum Jülich GmbH,
D-52425 Jülich, Germany

L. J. Fetters*

Corporate Research Laboratories, Exxon Research and Engineering Company,
P.O. Box 998, Clinton Township, Annandale, New Jersey 08801-0998

D. Schneider and V. Graciano

Brookhaven National Laboratory, Upton, Long Island, New York 11973

N. Hadjichristidis

Department of Chemistry, University of Athens, Athens, Greece

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ABSTRACT: The unperturbed chain dimensions of atactic near-monodisperse poly(ethylethylene) were evaluated in different Θ-solvents over the temperature range 10−80 °C. Radii of gyration, measured by small angle neutron scattering (SANS), were found to increase with increasing temperature and led to a value of 0.4×10^{-3} deg^{-1} for $d \ln \langle R^2 \rangle_0 / dT$; behavior which replicates that seen in the melt state via SANS and thermoelastic measurements. Those findings are contrary to those from intrinsic viscosity measurements.

Introduction

The experimental evaluation of unperturbed chain dimensions and their temperature dependences has historically been done in dilute solution via light scattering or intrinsic viscosity measurements under Θ conditions, the Flory temperature, at which excluded volume effects are screened out and the second virial coefficient is zero. These conditions, though, may only lead to an approximation of the unperturbed state.[1−3] Furthermore, even under Θ-conditions, the local chain conformations may be influenced by so-called specific solvent effects,[4−6] a situation at odds with the assumed concept that Θ-solvents serve only to provide a noninteracting environment, other than their capacity to eliminate long range excluded volume effects. An accompanying assumption is that the behavior of an isolated chain under Θ-conditions mimics that of the melt state.

Small angle neutron scattering (SANS) allows the evaluation of the radius of gyration, $\langle R_G \rangle_0$, in the realistic environment of the polymer melt. This is feasible as the result of a gift from nature; the scattering lengths of hydrogen and deuterium differ considerably, thus providing the needed contrast. For alternating poly(ethylene−propylene) and polyethylene good agreement with regard to chain dimensions and the corresponding temperature coefficients, $\kappa = d \ln \langle R^2 \rangle_0 / dT$, was obtained between Θ-condition measurements[7,8] and those in the melt state.[9−11] In contrast, recent SANS results from melt systems[12,13] have revealed prominent discrepancies between those findings and those from Θ-condition measurements.[7,14−16] The polymers involved were atactic polypropylene (PP), polystyrene (PS), atactic poly(ethylethylene) (a-PEE), and poly(methyl methacrylate) (PMMA). Θ-solvent measurements led to negative values of κ for the first three polymers[7,14,15] and positive values for PMMA.[16] SANS melt-based measurements[12,13] gave $\kappa \cong 0$ for a PP, PS, and PMMA and a positive value for PEE. This combination of findings demonstrates that prominent errors in κ can result from Θ-based results relative to what is found in the melt state.

It was thus of interest to evaluate κ, of one of the above polymers under Θ-conditions via SANS. The material chosen was a-PEE $[-CH_2-CH(CH_2CH_3)-]$ since that polymer exhibited a minus to positive sign change of the temperature coefficient in going from dilute solution Θ-conditions to the melt state. Both R_G and the corresponding intrinsic viscosity values were determined in each Θ-solvent. Discrepancies were found.

Experimental Section

Deuterated butadiene (Cambridge Isotopes) was polymerized in cyclohexane at 0 °C via the use of *tert*-butyllithium and *bis*(piperidino)ethylene to control the microstructure (~98% vinyl). The usual anionic polymerization protocols were followed.[17] Saturation using deuterium was accomplished by the use of palladium on barium sulfate. Size exclusion chromatography measurements involving both the parent polydiene and the polyolefin gave M_z/M_w of 1.03 and M_w/M_n of 1.04. The sample molecular weight was determined via low-angle-laser-light scattering (KMX-6) at 633 nm. An M_w of 5.2×10^{-4} was found. This corresponds to M_w of 4.7×10^4 of hydrogenous polymer of the same degree of polymerization. a-PEE has been shown[15] to possess Bernoullian chain statistics.

The SANS experiments were done on the H9B instrument at the Brookhaven National Laboratory, Upton, NY. The wavelength used was ≅7 Å, the wavelength spread $\Delta\lambda/\lambda$ was about 20%. The detector distance was fixed to 1.76 m covering a Q range of ≅ 0.01−0.15 Å^{-1}. A position sensitive two-dimensional ^{3}He detector with 128 × 128 pixels was used. Due to the isotropy of the SANS scattering pattern the data could be radially averaged in order to improve the signal to noise ratio. For all temperatures investigated the pure solvent was measured separately to allow for the subtraction of the incoherent scattering.

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The theta-solvents were isoamyl acetate, phenetole, and anisole, respectively. The concentrations of the deuterated polymer were chosen to remain below the overlap concentration which is estimated by $c^* \cong M_w/(4/3)\pi R_G^3 \cong 0.05$ g/mL. The scattering from a dilute polymer solution in the small Q range is given by[18]

$$c\Delta\varrho^2 \frac{d\Sigma}{d\Omega}(Q)^{-1} = \frac{1}{M_w}\left(1 + \frac{1}{3}Q^2 R_G^2\right) + 2A_2 c \qquad (1)$$

Here, c denotes the polymer concentration, $\Delta\varrho^2$ is the neutron scattering contrast, M_w is the weight average molecular weight of the polymer, A_2 is the second virial coefficient, R_G is the radius of gyration, Q is the scattering vector, and $d\Sigma/d\Omega\ (Q)$ is the differential scattering cross-section. Plotting the left-hand side vs $Q^2 + \text{const} \times c$ allows the direct determination of R_G and A_2 from the slopes of the $c \rightarrow 0$ extrapolation and the $Q \rightarrow 0$ extrapolation, respectively.

Results and Discussion

The Θ-temperature is traditionally given by the condition $A_2 = 0$. Thus the slope of $Q \rightarrow 0$ must vanish at Θ. All Θ-temperatures for the individual polymer–solvent systems were directly determined from the SANS experiments using eq 1. Previous attempts by static light scattering had given only a rough estimate of Θ because the differential refractive index increments dn/dc were very small (≅0.025 dL g^{-1}).

Figure 1 shows the phenetole data at three different temperatures. At 62 °C the $Q \rightarrow 0$ slope is positive, indicating that the system is above Θ. A_2 is very close to zero at 53.5 °C, which was taken to be the Θ temperature. At 50 °C, the slope becomes negative.

In order to visualize somewhat better how A_2 changes sign with temperature, only the $Q \rightarrow 0$ slopes are plotted in Figure 2 for all temperatures measured in the three Θ-solutions. The changing sign of the slopes as A_2 passes zero is clearly visible.

For the phenetole and the anisole systems, the Θ-temperatures were determined quite exactly to be 53.5 and 80.0 °C, respectively. In the case of the isoamyl acetate, the A_2 did not vanish within the errors of the experiment for the temperatures investigated. The Θ-temperature was estimated after the experiment to be about 10 °C. This result is markedly different from the result of Moraglio et al., who found Θ ~ 23 °C for the protonated system.[19] In part, this difference is due to the recognized influence of deuteration on Θ.[20]

Temperature control was ±0.5 deg throughout the sample. Fortunately, R_G does not change very much near the Θ-regime.[21] Thus it was possible to average the data of the 7.0, 17, and 21 °C measurements in the case of the isoamyl acetate. R_G was extracted from the data by two different evaluation methods. First it was obtained from the Zimm plots according to eqn 1. The Zimm analysis, however, yields an apparent value for the radius of gyration which is bigger than the "true" value. The reason for this is that QR_G was greater than 1 for the majority of the data and hence the Zimm formula is not directly applicable. The apparent R_G can be corrected by a procedure outlined by Ullman which was applied to the data.[22,23]

The second evaluation method arises from the fact that near the Θ-point the chain statistics will be Gaussian because A_2 is very small. This can be checked by plotting the data in Kratky form. Then, A_2 can be neglected and equ 1 simplifies to

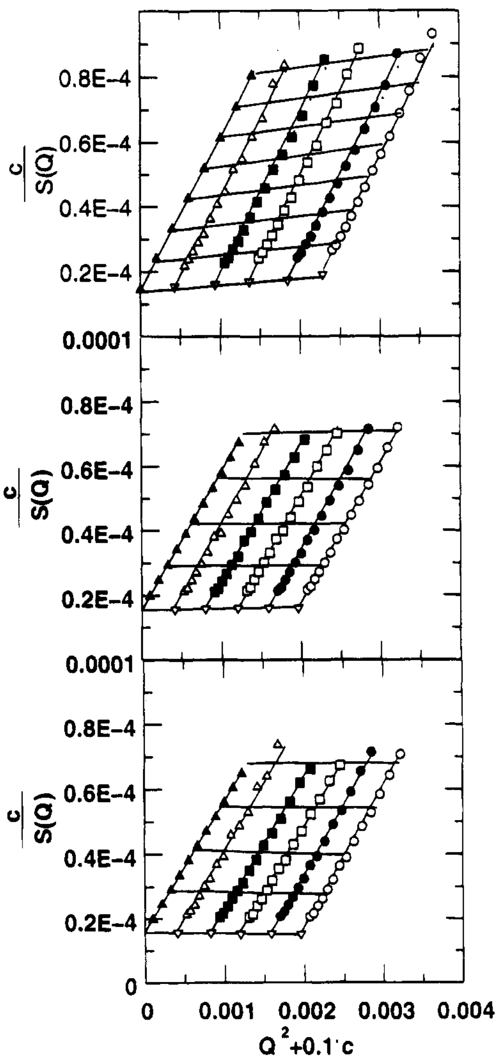

Figure 1. Phenetole data at three different temperatures in the Zimm format. The upper plot shows the data at T = 62 °C, the plot in the middle displays the data at T = 53.5 °C (Θ-temperature), and the lower plot shows those at T = 50 °C.

$$\frac{d\Sigma}{d\Omega}(Q) = c\Delta\varrho^2 M_w g_z(\xi) \qquad (2)$$

where $g_z(\xi)$ denotes the polydispersity corrected Debye function[24]

$$g_z(\xi) = 2\frac{[(1 + u\xi)^{-1/u} + \xi - 1]}{(1 + u)\xi^2} \qquad (3)$$

with $\xi = R_G^2 Q^2/(1 + 2u)$ and $u = M_w/M_n - 1$.

The advantage of eq 3 is that the whole Q range can be used in fitting the data.

In Figure 3 the results of the Ullman-corrected Zimm fits and of the Debye analysis are displayed. The R_G values are also shown in Table 1. Obviously, both methods yield almost identical radii of gyration. The temperature coefficient κ turns out to be 0.6×10^{-3} K^{-1} for the Debye analysis and 0.2×10^{-3} K^{-1} for the Zimm analysis. Taking the average of the two values, we arrive at 0.4×10^{-3} K^{-1}, a value which replicates that seen in the melt state via SANS and thermoelastic measurements.[12,25]

The melt data have recently been taken by using partially deuterated chains in a protonated matrix.[12] A

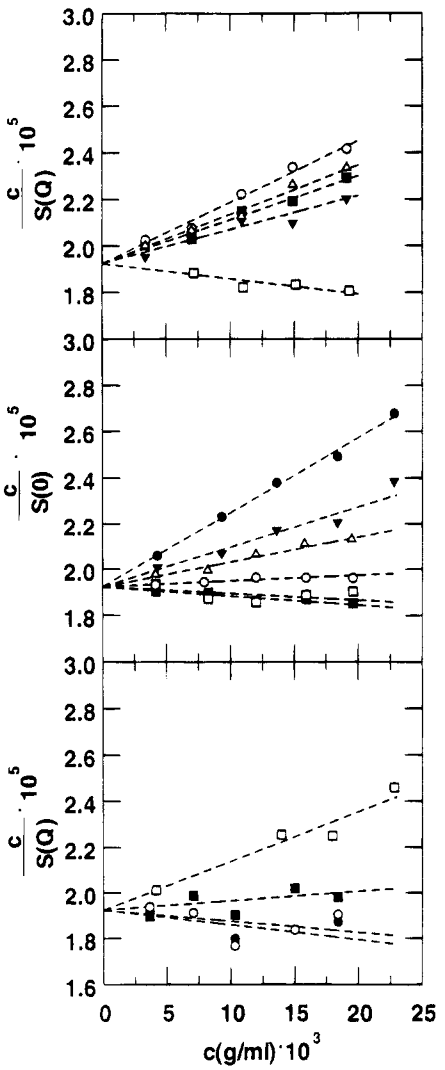

Figure 2. $Q \to 0$ slopes plotted for the three different Θ-solvents for all temperatures measured. The upper part of the figure shows the isoamyl acetate data, the part in the middle displays the phenetole data, and the lower part gives the anisole data. Individual temperatures: isoamylacetate (upper plot) (○) 25 °C, (■) 23 °C, (△) 21 °C, (▼) 17 °C, (□) 7 °C; phenetole (middle) (●) 67 °C, (▼) 62 °C, (△) 58 °C, (○) 53.5 °C, (□) 52.5 °C, (■) 50 °C; anisole (lower plot) (□) 86 °C, (■) 80 °C, (○) 79 °C, (●) 78 °C.

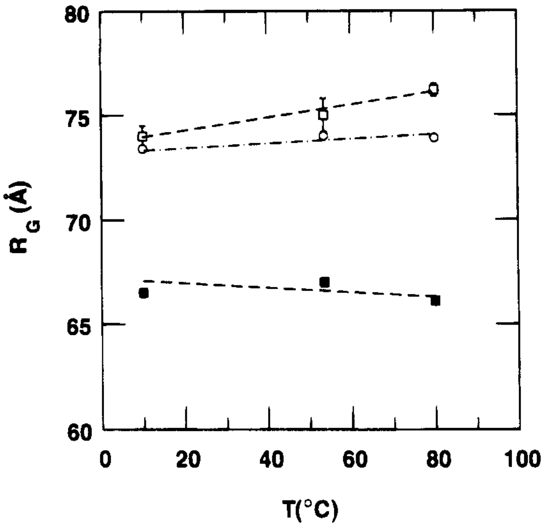

Figure 3. SANS-based radius of gyration vs temperature: (□) Debye analysis, (○) Zimm fits; R_G from intrinsic viscosity measurements under Θ-conditions (■).

Table 1. a-PEE Θ-Solvent and Melt Chain Dimensions via SANS

T (°C)	$R_G{}^{\mathrm{Zimm}}$ (Å)[a]	$R_G{}^{\mathrm{Deb}}$ (Å)	R_G (Å) (melt)[b]
10.0	73.4	74.5 ± 0.4	58.7
53.5	74.0	75.0 ± 0.8	59.6
80.0	73.9	76.2 ± 0.3	59.8

[a] Isoamyl acetate, 10 °C; phenetole, 53.5 °C; anisole, 80 °C. [b] Reference 12.

Zimm plot was used to make sure that no residual isotope effects due to the h/d exchange were present. No concentration dependence of R_G was detected in the limits of the errors. The R_G values were obtained from a Debye and a Zimm analysis as in the present paper. This allows for a direct comparison between the melt data and the Θ-solution data.

The absolute values of the unperturbed chain dimensions are larger in the Θ-solvents isomyl acetate, phenetole, and anisole than in the melt, Tables 1 and 2 and Figure 4. Furthermore, there exist similar differences in the desired unperturbed chain dimensions from the octanol Θ-solvent series[15] and those used by us and Moraglio and co-workers[20,26,27] (Table 2). It should also be noted that the octanol-based chain dimensions[15] are in semi-accord with those found in the melt.[12]

These findings demonstrate the influence of specific solvent effects on local chain statistics. Although the chain exhibits Gaussian statistics, the local rigidity is enhanced by the presence of the solvent molecules. Bahar[6] argued that such an influence would be larger if the substituents were comparable in size with the solvent molecules than if only small side groups were present. This could be a qualitative explanation for the good agreement of the unperturbed dimensions in the melt and in Θ-solvents for polyethylene and poly(ethylene–propylene), where no large side groups occur and thus specific solvent effects should be small.[10,11]

The result of a positive temperature coefficient in the Θ-solutions by SANS is in strong disagreement with the findings from intrinsic viscosity measurements (Table 3). The latter gave negative κ values for all Θ-solvent families investigated.[15,20,26–28] To extract R_G from intrinsic viscosity data, one makes use of the Mark–Houwink relation:

$$[\eta]_\Theta = K_\Theta M^a \tag{4}$$

with $a = 0.5$ under Θ-conditions. K_Θ is given by

$$K_\Theta = \Phi^s \left(\frac{\langle R_G{}^2 \rangle_0}{M} \right)^{3/2} \tag{5}$$

Here, $\Phi^s = 3.67 \times 10^{24}$ mol^{-1} is the Flory–Fox parameter.

These results prompted us to investigate our system of PEE-d_8 in the protonated Θ-solvents by intrinsic viscosity in order to have a direct comparison to our SANS data. The results are shown in Figure 3. Again, a negative temperature coefficient is found, though smaller in absolute value than those found in former experiments.[15,20,26–28]

A long standing conjecture[29] pertaining to the Flory–Fox hydrodynamic parameter is of its universality, i.e., that it is independent of temperature and solvent type. The experimental value generally exhibited is that given above, e.g., for polystyrene in cyclohexane at 34.5 °C.[30] However, deviations from that value are found for

Table 2. Intrinsic Viscosity Relations and Chain Dimensions for a-PEE

solvent[a]	temp (°C)	$10^3 K_\Theta$ (dL g$^{-3/2}$ mol$^{1/2}$)	$\langle R^2 \rangle_0/M$ (Å^2 mol g^{-1})	C_∞[b]	refs
TOL	−46	1.325	0.655	7.8	20, 26−28[c]
IAA	23	1.153	0.596	7.1	20, 26−28
PT	61	1.063	0.565	6.8	20, 26−28
AN	83	1.082	0.572	6.8	20, 26−28
OPE	141	0.991	0.539	6.4	20, 26−28
IAA, PT, AN	10−80	1.062	0.565	6.6	this work
3-Oct	5.0	0.889	0.502	5.9	15
2-Oct	21.0	0.822	0.476	5.6	15
1-Oct.	53.0	0.749	0.448	5.3	15
		SANS			
IAA	10		0.688[d]/0.709[e]	8.1/8.3	this work
PT	53.5		0.699[d]/0.718[e]	8.2/8.4	this work
AN	80		0.697[d]/0.741[e]	8.2/8.7	this work
melt[f]	25		0.442	5.2	12
melt	54		0.459	5.4	12
melt	75		0.472	5.5	12
melt	143		0.468	5.5	12

[a] TOL = toluene; IAA = isoamyl acetate; PT = phenetole; AN = anisole; DPE = *p*-diphenyl ether; 3-Oct = 3-octanol; 2-Oct = 2-octanol; 1-Oct = 1-octanol. [b] C_∞ $[\langle R^2 \rangle_0/M] m_0 l_0^{-2}$. For the data of refs 20 and 26−28, $m_0 = 28.00$. For the a-PEE samples of refs 12 and 15 and this work, $m_0 = 27.44$. These different values are occasioned by the presence of a small amount of the 1,4 enchainment in the parent polybutadienes used in the latter refs. l_0^2 was taken as 2.3409 Å^2. [c] The data of refs 20 and 26−28 was treated by the Burchard−Stockmayer−Fixman extrapolation procedure to correct for small deviations from true Θ: Burchard, W. *Makromol. Chem.* **1960**, *50*, 20. Stockmayer, W.; Fixmann, M. *J. Polym. Sci.* **1963**, *1C*, 137. [d] Via Zimm analysis. [e] Via Debye analysis. [f] Selected values from ref 12.

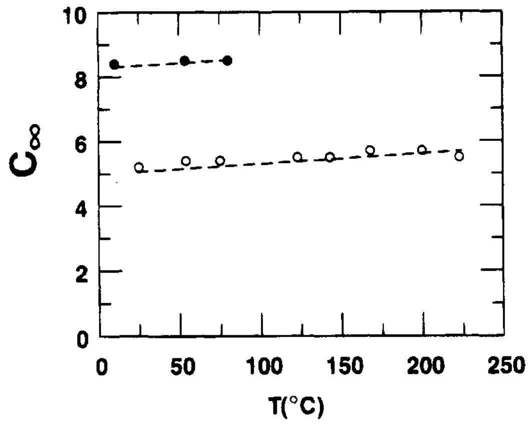

Figure 4. Comparison of C_∞ for the results in the melt (○) and in the Θ-solvents (●).

Table 3. Chain Dimension Temperature Coefficients for a-PEE

method	temp range (°C)	103κ (K^{-1})	ref
[η]	−46 to +141	−1.0	20, 26−28
[η]	5−53	−2.3	15
[η]	10−80	-0.1_2	this work
SANS (solution)	10−80	0.2_1[a]	this work
	10−80	0.61[b]	
		0.41 (av)	
SANS (melt)	25−223	0.40	12
thermoelastic	140−200	0.50	25

[a] Via Zimm analysis. [b] Via Debye analysis

Table 4. Apparent R_G Values via Intrinsic Viscosity Measurements under Θ-Conditions

solvent	temp (°C)	[η][a] (dL g^{-1})	[η][b] (dL g^{-1})	R_G[c] (Å)
IAA	10	0.250	0.230	66.5
PH	53.5	0.230	0.235	67.0
AN	80	0.235	0.227	66.1

[a] Calculated values via the results of Moraglio et al.;[20,26−28] see Table 2. [b] Normalized values of d-PEE (∼97% d) to h-PEE. [c] Calculated via eqs 4 and 5 and the normalized values of [η].

polystyrene in cyclopentane—UCST and LCST[31,32]—where Φ^s is about 2.3×10^{24} mol^{-1} and in 1-chloro-*n*-undecane and diethyl malonate[32,33] where the value of 2.9×10^{24} mol^{-1} is observed. Polyisobutylene yields a value of ca. 4.1×10^{24} mol^{-1}.[34,35] Deviant values have also been reported for atactic poly(methyl methacrylate) and poly(dimethylsiloxane).[34] The use of the measured R_G values of a-PEE in the Θ-solvents used in this work, Table 1, and the normalized intrinsic visosities, Table 4, yields Φ^s values of $(2.53−2.67) \times 10^{24}$ mol^{-1} over the temperature range 10−80 °C.

The octanol-based K_Θ values in conjunction with the value of $\Phi^s = 3.67 \times 10^{24}$ mol^{-1} yield chain dimensions in general accord with what is observed in the melt; Table 2. However, variations in Φ^s could account for the fact that the true K_Θ is masked *in both* the octanol family[15] and the Θ-solvents used by Moraglio et al.[20,26-28] This could also rationalize the observations that Θ-solvent evaluations have led to disparate values of κ, of both signs, for atactic and isotactic polypropylene and the atactic versions of polystyrene and poly(methyl methacrylate),[36] SANS evaluations of the melt state show that $\kappa \cong 0$ for these materials, a value only infrequently encountered from the K_Θ-based intrinsic viscosity Θ-solvent measurements.

The Zimm model[37] for Θ-solvents projects that

$$[\eta]_\Theta = 0.425 N_a M^{-1} [n^{0.5} l_0]^3 \qquad (6)$$

The Flory−Fox parameter is then derived as

$$\Phi^s = 6.246 N_a = 3.76 \times 10^{24}\ \text{mol}^{-1} \qquad (7)$$

a value close to the generally accepted experimental one. The foregoing results would seem to call for a reexamination of our understanding of intrinsic viscosity under Θ-conditions.

Summary

The temperature dependence of the unperturbed dimensions of atactic poly(ethyl−ethylene) in three different Θ-solvents was investigated by SANS over the temperature range of about 10−80 °C. An increase of the radii of gyration with temperature was found, leading to a value of $\cong 0.4 \times 10^{-3}$ K^{-1} for the temperature coefficient. This value agrees with that seen in the melt state via SANS and also by thermoelastic measurements. The absolute values for C_∞ are much larger in some Θ-solvents than in the melt, showing a pronounced influence of the solvent molecules on the local stiffness of the polymer chain.

Our finding of a positive temperature coefficient is in strong disagreement with intrinsic viscosity experiments which invariably give negative values for κ. In order to obtain a direct comparison to our SANS data in the Θ-solvents, we measured the same systems with intrinsic viscosity. The result was again a negative temperature coefficient, demonstrating that there is a basic flaw in going from the intrinsic viscosities to R_G. The nature of this masking event remains to be elucidated.

References and Notes

(1) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1974.

(2) Freed, K. F. *Renormalization Group Theory of Macromolecules*; Wiley: New York, 1987. des Cloizeaux, J.; Jannik, G. *Polymers in Solution: Their Modelling and Structure*; Oxford University Press: Oxford, 1984.

(3) Sanchez, I. C. *Macromolecules*, **1979**, *12*, 980.

(4) Lifsen, S.; Openheim, I. *J. Chem. Phys.* **1960**, *33*, 109.

(5) Crescenzi, V.; Flory, P. *J. Am. Chem. Soc.* **1964**, *86*, 141.

(6) Bahar, I.; Baysal, B. M.; Erman, B. *Macromolecules* **1986**, *19*, 1703.

(7) Mays, J. W.; Fetters, L. J. *Macromolecules* **1989**, *22*, 921.

(8) Flory, P. J. *Statistical Mechanics of Chain Molecules*; Interscience: New York, 1964.

(9) Butera, R.; Fetters, L. J.; Huang, J. S.; Richter, D.; Pyckhout-Hintzen, W.; Zirkel, A.; Farago, B.; Ewen, B. *Phys. Rev. Lett.* **1991**, *66*, 2088.

(10) Zirkel, A.; Pyckhout-Hintzen, W.; Fetters, L. J. *Macromolecules* **1992**, *25*, 954.

(11) Boothroyd, A.; Rennie, A. R.; Boothroyd, C. B. *Eur. Phys. Lett.* **1991**, *15*, 715.

(12) Zirkel, A.; Urban, V.; Richter, D.; Fetters, L. J.; Huang, J. S.; Kampmann, R.; Hadjichristidis, N. *Macromolecules* **1992**, *25*, 6148.

(13) Boothroyd, A. T.; Rennie, A. R.; Wignall, G. P. *J. Chem. Phys.* **1993**, *94*, 9135.

(14) Mays, J. W.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1985**, *18*, 2231 and references therein.

(15) Hattam, P.; Gauntlett, S.; Mays, J. W.; Hadjichristidis, N.; Young, R. N.; Fetters, L. J. *Macromolecules* **1991**, *24*, 6199 and references therein.

(16) Mays, J. W.; Nan, S.; Wan, Y.; Li, J.; Hadjichristidis, N. *Macromolecules* **1991**, *24*, 4469 and references therein.

(17) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *45*, 303.

(18) Higgins, J. S. *Polymer Conformations and Dynamics* Treatise on Material Science and Technology; Academic Press: New York, 1979; Vol. 15.

(19) Moraglio, G.; Gianotti, G.; Zopp, F. *Eur. Polym. J.* **1971**, *7*, 303

(20) Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.

(21) Daoud, M.; Jannik, G. *J. Phys.* **1976**, *37*, 973. Chains of finite molecular weight exhibit a temperature range, the Θ-region, over which chain dimensions are virtually insensitive to temperature fluctuations. That range can be evaluated as follows: $T - \Theta/\Theta \propto 1/\sqrt{N}$, where N denotes the degree of polymerization while the prefactor is of the order unity. For our a-PEE sample this range is about 10 deg. Thus temperature fluctuations of 0.5 deg will not introduce detectable changes in R_G. Experimental verification of the foregoing is available, e.g. see: Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4550. Miyake, Y.; Fujita, H. *Macromolecules* **1981**, *14*, 142. Stepánek, P.; Konák, C.; Sedlácek, B. *Macromolecules* **1982**, *15*, 1214.

(22) Ullman, R. *J. Polym. Sci., Polym. Lett. Ed.* **1983**, *21*, 521.

(23) Ullman, R. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 1477.

(24) Kirste, R. G.; Oberthür, R. C. In *Synthetic Polymers in Solution*; Glatter, O., Kratky, O., Eds.; Small Angle X-Ray Scattering; Academic Press: New York, 1982.

(25) Mark, J. E.; Flory, P. J. *J. Phys. Chem.* **1963**, *67*, 1396; *J. Am Chem. Soc.* **1965**, *87*, 1423.

(26) Moraglio, G.; Gianotti, G.; Danusoo, F. *Eur. Polym. J.* **1967**, *3*, 251.

(27) Moraglio, G.; Gianotti, G. *Re. Acond. Naz. Lincei* **1959**, *27*, 374.

(28) Danusso, F.; Moraglio, G.; Gianotti, G. *Re. Ist. Lamb. Sci. Lett.* **1960**, *A94*, 566.

(29) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; pp 616–617.

(30) Miyake, Y.; Einage, Y.; Fujita, M. *Macromolecules* **1978**, *11*, 1180.

(31) Berry, G. C.; Cassassa, E. F.; Liu, P-Y. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 673.

(32) Mays, J. W.; Hadjichristidis, N.; Fetters, L. J. *Macromolecules* **1985**, *18*, 2231.

(33) Li, J.; Wan, Y.; Xu, Z.; Mays, J. W. *Macromolecules*, in press.

(34) Konishi, T.; Yoshizaki, T.; Yamakama, H. *Macromolecules* **1991**, *24*, 5614.

(35) Fetters, L. J.; Hadjichristidis, N.; Lindner, J. S.; Mays, J. W. *J. Phys. Chem. Ref. Data* **1994**, *23*, 617.

(36) For example see Table 4 of ref 12 and Tables V and VI of ref 13.

(37) Zimm, B. M. *J. Chem. Phys.* **1956**, *24*, 269.

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