

Dimensions of Poly(Styrene) in the Vicinity of the Theta Point

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Dedicated to Prof. Dr. H.-J. Cantow on the occasion of his 60th birthday

Summary

The decrease of the mean-square radius of gyration of a high molecular weight polystyrene dissolved in cyclohexane with decrease of temperatures to far below θ was observed by conventional light scattering techniques. The experiments were performed in the region of the coil-globule transition of the polymeric chain. The transition was reversible upon repeated heating and cooling of the sample. Aggregation occurred at temperatures below the sharp decrease of the polymer dimensions.

Introduction

The conformation of a polymer chain in solution as the solvent quality decreases has been of considerable interest to many theorists and experimentalists over a long period. STOCK-MAYER (1960) suggested that even atactic chain molecules must collapse to a rather dense form (very small α) if the net attraction between their parts becomes sufficiently large. Currently both mean-field theories (e.g. SANCHEZ, 1979) and scaling theories (e.g. DAUD and JANNINK, 1976) agree in the exponential behaviour of the conformations of a polymer chain expressed in terms of the mean-square radius of gyration $\langle S^2 \rangle$ or expansion coefficient α as a function of the reduced temperature $\tau = |T - \theta| / \theta$:

$$\alpha \sim \langle S^2 \rangle^{1/2} \sim \tau^{1/5} \quad \text{for } T > \theta \quad \text{and} \quad (1)$$

$$\alpha \sim \langle S^2 \rangle^{1/2} \sim \tau^{-1/3} \quad \text{for } T < \theta \quad . \quad (2)$$

Experimental observations of the dimensions of polymer chains far below θ aiming to observe the entire coil-globule transition seemed to be prohibitively difficult. Extremely small polymer concentrations are required to ensure the observation of a single polymer chain shrinking without aggregation (e.g. CUNIBERTI and BIANCHI, 1974; NIERLICH et al., 1978). The best previous light scattering measurements of the dimensions of polystyrene in cyclohexane by SLAGOWSKI, TSAI and McINTYRE, 1976 allowed to observe the onset of the coil-globule transition between 308.6 K and 307.2 K. Recently SWISLOW et

al. (1980) reported experimental observations of the coil-globule transition in a single polystyrene chain in cyclohexane by means of photon correlation spectroscopy. The transition occurred at 305 K with a width of 5 K for a $2.6 \cdot 10^7$ g/mole molecular weight sample with a sharp decrease in hydrodynamic radius from 125 nm to 50 nm. Photon correlation spectroscopy allowed even with a low signal-to-noise ratio at polymer concentrations as low as 10^{-7} g/cm³ measurements of the hydrodynamic radius via the translational diffusion coefficient.

SUN et al. (1980) used polymer correlation spectroscopy to determine the radius of gyration from the angular dependence of relative scattering intensity extracted from the autocorrelation function assuming a Gaussian coil for the polymer. The observed transition is in good agreement with the prediction by mean field theory. The phase separation curve determined by the same authors illustrated the competition between the intra- and intermolecular interaction. Recently KAJIWARA and BURCHARD (1982) demonstrated by theoretical assumptions following an estimate by KONINGSVELD et al. (1974) that a coil-globule transition can be observed only if the probability P of finding an isolated coil is very close to unity.

Following the same lines of argumentation like KAJIWARA and BURCHARD (1982) we calculate using

$$P \approx \exp(-1/2 N^{1/2} \phi_2) \quad (3)$$

with $P = 0.99$, i.e., allowing a 1% overlapping of coils, the volume fraction $\phi_2 \leq 4.5 \cdot 10^{-5}$ and the maximum concentration $c_{max} = 4.9 \cdot 10^{-5}$ g/cm³ for a linear polystyrene of molecular weight $2.2 \cdot 10^7$ g/mole. We found it worthwhile to carry out conventional light scattering experiments with this polymer dissolved in cyclohexane under careful conditions in order to observe the decrease of dimensions directly to temperatures as low as possible without aggregation.

Experimental

The cyclohexane used as solvent was stirred for several weeks over sulfuric acid to remove olefinic impurities. After predrying the solvent was refluxed with Li-dispersion and benzophenone for three days and carefully distilled into cells. The solutions were prepared by this method individually on a weight/weight basis and contained within tightly closed light scattering cells. The cells were shaken for three days at 313 K. Pure polystyrene material had been prepared before by filtering a solution, phase separating and freeze-drying of a sample from Toyo Soda with nominal molecular weight $2.07 \cdot 10^7$ g/mole. Solutions with concentrations in the range of $1 - 5 \cdot 10^{-5}$ g/cm³ were prepared. Benzene standard for light scattering was prepared in the same manner as described for cyclohexane before.

The measurements were performed using a Sofica photo goniometer equipped with an external lamp housing and a 500 W mercury high pressure lamp at $\lambda_0 = 436$ and 365 nm in the angular range from 20° to 150° with respect to the primary beam of vertically polarized light. The measurements were made at temperatures from 321.9 K down to 303.9 K. At temperatures below 303.9 K a sharp increase in the intensity of the light scattered at small angles indicated aggregation and the measurements were not used. Upon repeated heating and cooling the measurements could be reproduced within high accuracy.

Results and Discussion

Figure 1 shows the mean square radius of gyration $\langle S^2 \rangle_z$ as a function of temperature T . The solid line connects the experimental points and serves to guide the eye. A sharp drop of $\langle S^2 \rangle_z$ to less than a third of its value at good solution behaviour at temperatures above 318 K is being observed and the decrease of $\langle S^2 \rangle_z$ with temperature decreasing further below 305 K is somewhat smaller. This observation compares favourably to the observations of SUN et al. (1980).

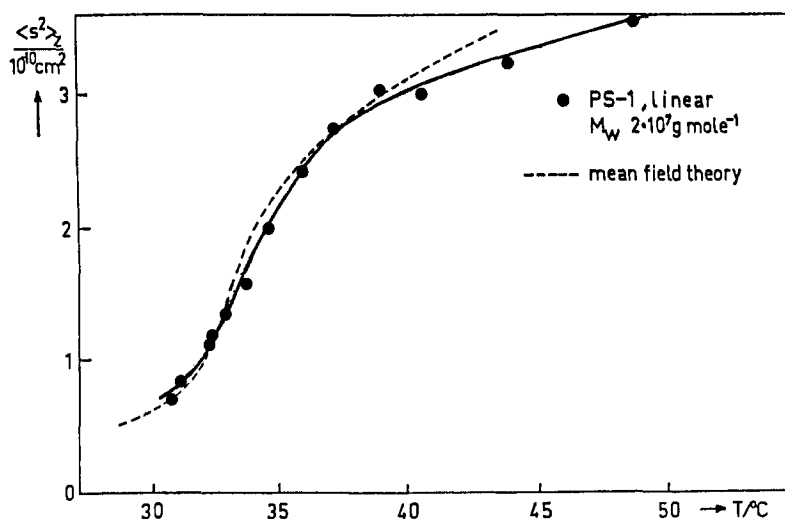


Fig. 1 : Decrease of mean square radius of gyration of polystyrene ($M_w 2.2 \cdot 10^7$ g/mole) in cyclohexane with decrease of temperature in the vicinity of θ . The solid circles present the data from this work. The broken line presents the curve obtained from eq. (4) using the parameters $\alpha_{min} = 3.1 \cdot M_w^{-1/6}$, $\sigma = 2.14$ and $N = 7.2 \cdot 10^{-4} \cdot M_w$.

The experimental points were fitted as indicated in fig.1 using the equation (4) given by SUN et al. (1980) derived from the mean field theory as presented by SANCHEZ (1979) :

$$\frac{14\phi_S}{3N} (1 - \alpha^2) = \sigma \left(\frac{\theta}{T} - 1 \right) \phi_S^2 - \frac{2}{3} \phi_S^3 - \frac{1}{2} \phi_S^4 \quad (4)$$

following the notation by SUN et al. (1980).

Fig. 2 presents a log-log plot of $\langle S^2 \rangle^{1/2}$ vs. reduced temperatures $|T-\theta|/\theta$. The slope of -0.36 agrees, within experimental error, with the predictions of both mean field theory and scaling theory as mentioned earlier.

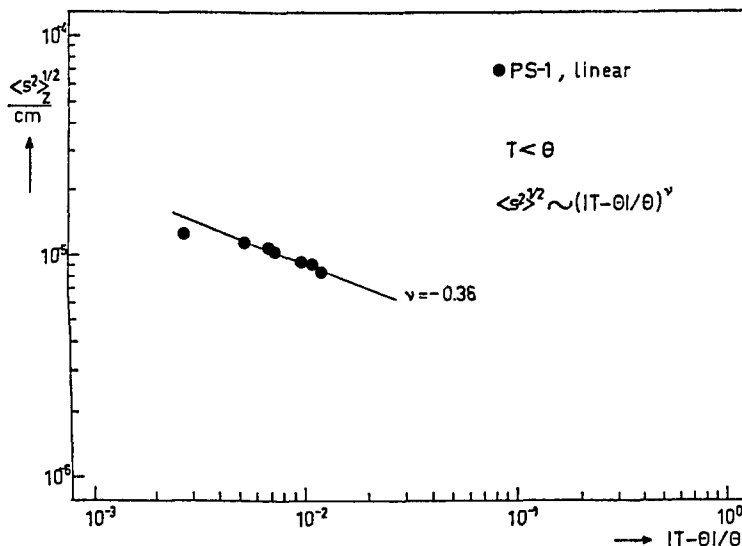


Fig. 2 : Plot of the radius of gyration as a function of reduced temperature $|T-\theta|/\theta$ for $T < \theta$. Theoretical predictions ask for a slope of $-1/3$.

We conclude from our experiments carried out under conditions as described above that it is indeed possible to perform classical light scattering experiments well into the region below θ described as the region of coil-globule transition by SUN et al. (1980). Our further work (EISELE et al.) will examine the shape of the polymer molecule as temperature is decreased in the range of the coil-globule transition and compare the decrease in dimensions for linear and branched polymeric structures.

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References

- C.CUNIBERTI and U.BIANCHI, *Polymer* 15, 346 (1974)
M.DAOUUD and G.JANNINK, *J.Phys. (Paris)* 37, 973 (1976)
M.EISELE, L.J.FETTERS, K.KAJIWARA and D.NERGER, in prep.
R.KONINGSVELD, W.H.STOCKMAYER, J.W.KENNEDY, L.A.KLEINTJENS
Macromolecules 7, 73 (1974)
K.KAJIWARA and W.BÜRCHARD, *Macromolecules* 15, 660 (1982)
M.NIERLICH, J.P.COTTON, B.FARNOUX, *J.Chem.Phys.* 69, 1379 (1978)
I.C.SANCHEZ, *Macromolecules* 12, 980 (1979)
E.SLAGOWSKI, B.TSAI, D.McINTYRE, *Macromolecules* 9, 687 (1976)
W.H.STOCKMAYER, *Makromol.Chem.* 35, 54 (1960)
S.T.SUN, I.NISHIO, G.SWISLOW, T.TANAKA, *J.Chem.Phys.* 73, 597
(1980)
G.SWISLOW, S.T.SUN, I.NISHIO, T.TANAKA, *Phys.Rev.Let.* 44, 796
(1980)

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