The $N^{1/3}$ dependence of polymer chain configuration in the collapsed-state region

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The intrinsic viscosity of polystyrene in cyclohexane is measured as a function of molecular weight at the critical temperature, 32.9°C. The results are plotted in the form of $[\eta]^{1/3}$ *versus* $N^{1/3}$ ($[\eta]$ = intrinsic viscosity, N = number of links in a polymer molecule). The scaling law for the collapsed state in the form of $R \sim N^{1/3}$ (R = end-to-end distance) seems to have been obeyed.

(Keywords: intrinsic viscosity; scaling law; collapsed state)

Introduction

Near a critical point, physical quantities of a material system are often shown to obey power laws. In the case of polymer solutions, the physical quantity of greatest interest is R, the end-to-end distance (or S, the radius of gyration), which is characteristic of the configuration of a flexible chain. The scaling variables of a power law are τ and N. The variable τ is the reduced temperature defined as:

$$\tau = \frac{\theta - T}{T}$$

where θ is the temperature T, at which the excluded volume effect vanishes. The variable N is the number of links in a polymer molecule estimated by the equation:

$$N = \frac{M}{M_0}$$

where M is the molecular weight of the polymer chain and M_0 is the molecular weight of the monomer. Since de Gennes discovered the similarity between the θ point in a polymer solution and the tricritical point of magnetization[1], the power law that describes the collapsed state of a polymer in solutions has been recognized as:

$$R \sim N^{1/3}\tau^{-1/3} \quad \text{for } \tau\sqrt{N} \gg 1$$

This condition is met at $T < \theta$.

Experimentally, there are some differences among the observable quantities R, S and R_H (the hydrodynamic radius). In the asymptotic region, however, they should all obey the same scaling law. More usually, these quantities are converted to α (the expansion factor), since, according to the mean field theory developed by Flory[2], the expansion factor α is better able to describe the configuration of a real chain.

Viscosity measurement was reported in a previous paper[3] and demonstrated that at constant N (namely, for a single polymer sample with $M = 3.2 \times 10^6$), the scaling law holds for the collapsed state:

$$\alpha \sim \tau^{-1/3}$$

In the present paper, we report the viscosity study of the scaling law:

$$R \sim N^{1/3}$$

keeping the temperature constant. We assume that if $\tau^{-1/3}$ is kept constant, the asymptotic regions would demonstrate equally well the behaviour of the globular state of the polymer chain. The critical temperature is chosen as 32.9°C for polystyrene in cyclohexane[3]. At this temperature, the excluded volume effect of the polymer segments changes direction and the chain collapses.

We further assumed that:

$$[\eta]^{1/3} \sim R$$

since the intrinsic viscosity $[\eta]$ is a measure of the chain volume. The plot of $[\eta]^{1/3}$ *versus* N is then similar to the plot of R *versus* N.

Experimental

Viscosity measurement was carried out as described previously[3]. Five samples of different molecular weights, manufactured by Toyo Soda, were obtained from Waters Associates. The polydispersity was 1.01–1.05, except for the sample with $M = 2.06 \times 10^7$ whose polydispersity was not given by the manufacturer.

Results and discussion

Table 1 gives the experimental data of intrinsic viscosity of polystyrene in cyclohexane at 32.9°C for five different molecular weights. The actual measurements covered the temperature range from 43°C to below the θ point (35°C), e.g. for $M = 3.78 \times 10^4$ down to 7°C and for $M = 2.06 \times 10^7$ down to 32°C. The value at

Table 1 Experimental data of the intrinsic viscosity of polystyrene in cyclohexane extrapolated at 32.9°C

M	$[\eta]$ (dl g^{-1})
3.79×10^4	0.162
3.55×10^5	0.508
1.09×10^6	0.893
3.84×10^6	1.68
2.06×10^7	3.15 (at 33°C)

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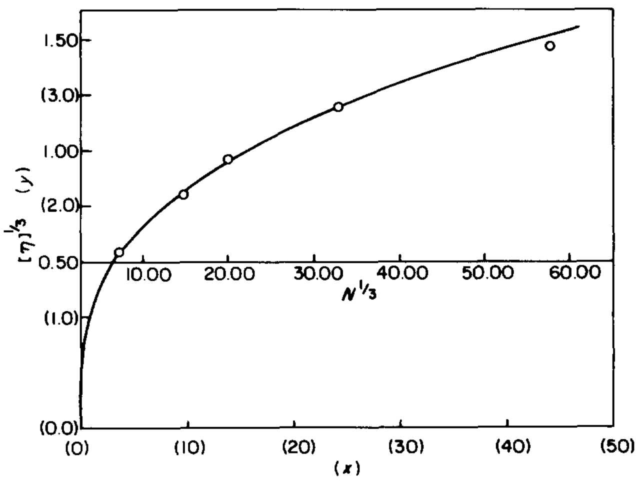

Figure 1 Intrinsic viscosity of polystyrene in cyclohexane at 32.9°C. The coordinates in parentheses represent (x, y) pairs; those without parentheses represent $(N, [\eta]^{1/3})$ pairs. The solid line represents $y = x^{1/3}$

32.9°C was extrapolated from the curve of the entire range.

In *Figure 1*, the solid curve is the plot of $y = x^{1/3}$. The experimental pairs $([\eta]^{1/3}, N)$ were adjusted to the same x–y coordinate scale. That is, the numerical values in parentheses represent the x–y scale, while those without parentheses represent the values of experimental pairs $([\eta]^{1/3}, N)$. They are plotted on the same graph. It is seen that the experimental points fall on the theoretical curve (x *versus* y), indicating that the relationship between R (in our case $[\eta]^{1/3}$) and N reasonably follows the law $R \sim N^{1/3}$. We also noticed that four experimental points fall on the curve while the fifth point is a little below the curve. Our interpretation is that if the molecular weight reaches 10^7, as this point represents, the entanglement of the chain is greatly increased. This influences the viscoelastic behaviour and introduces more error than for polymers of lower molecular weight. On the other hand, for lower molecular weight polystyrenes the effects of entanglements are less pronounced[4].

The observation reported here seems to confirm two points. First, the power law in terms of a physical quantity (here $[\eta]^{1/3}$) *versus* a scaling variable (here N) follows the power law with the critical exponent 1/3. Second, the estimation of 32.9°C as the critical temperature below which the chain collapses gains further support. For low molecular weight polystyrene (e.g. 3.84×10^4) in cyclohexane at 32.9°C, the chain is collapsed and for high molecular weight polystyrene (e.g. 2.06×10^7), the chain is totally collapsed. This qualitative description of the collapsed state and totally collapsed state was first suggested by Daoud and Jannink[5]. This point will be discussed in more detail elsewhere.

In conclusion, in the previous publication[3], we reported observation of the collapsed state of polystyrene in cyclohexane with τ as an independent variable, whereas in the present note N is the independent variable.

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