

THE Θ -STATE OF A SINGLE HOMOPOLYMER CHAIN IN SOLUTION*

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Abstract It has been an established practice to estimate the Θ -temperature of a polymer solution from the disappearance of the interchain interactions ($A_2 = 0$). Recently, in studies of the temperature dependence of the chain conformation in solution, we found that the change of the chain conformation clearly underwent three different stages which could be viewed as the "gas", "liquid" and "solid" states in terms of the freedom of the "blobs" on the chain. The transition temperature between the first and second stages corresponds nicely to the Θ -temperature determined by the conventional method. It reveals, for the first time, that the Θ -temperature can be deduced from the conformation change of a single polymer chain in solution, which is important not only in conception, but also in practice.

Keywords Θ -state, Coil-to-globule transition, Poly(*N*-isopropylacrylamide)

It is known that in a good solvent, the effect of chain segment exclusion prevails over the effect of segment contacts and the chain expands in solution and its end-to-end distance is larger than that for its Gaussian coil, while in a poor solvent, the polymer coil contracts^[1]. Under some conditions, the effects of the segment exclusion and segment contact on the average end-to-end distance cancel each other exactly. These conditions are termed as the Θ -conditions and the solution is considered to be pseudo-ideal^[2].

Note that the segment interaction can be either interchain or intrachain because when one segment interacts with another, they do not "know" whether they are from two different chains or from two distant segments on the same chain. In a pseudo-ideal solution, only some long-range properties, such as the radius of gyration and virial coefficients, related to a Gaussian coil are recovered, but not other properties (e.g. the hydrodynamic radius) related to the non-Gaussian short-range distribution of intersegmental distance^[3]. The variation of solution temperature is probably the easiest way to make a polymer solution pseudo-ideal. Conventionally, measurements of at least four polymer solutions with different concentrations and at no less than four temperatures can lead to temperature dependence of the second virial coefficient (A_2), from which the Θ -temperature is estimated from the point of $A_2 = 0$. Typically, the error of each A_2 measurement is more than 10%. Therefore, the conventional method is not only time consuming, but also inaccurate.

Recently, in the study of the coil-to-globule transition of linear poly(*N*-isopropylacrylamide) (PNIPAM) chains in deionized water, we found that the decrease in the ratio of the radius of

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gyration ($\langle R_g \rangle$) to the hydrodynamic radius ($\langle R_h \rangle$) clearly underwent three different stages, as shown in Fig. 1, where $\langle R_g \rangle$ and $\langle R_h \rangle$ were determined respectively from the angular dependence of the excess absolute time-averaged scattered light intensity (i.e. the Rayleigh ratio, $R_w(q)$) and the Laplace inversion of the time correlation function measured by using a modified commercial LLS spectrometer (ALV/SP-125) equipped with a multi- τ digital time correlator (ALV-5000) and a solid-state laser (ADLAS DPY425II, output power ~ 400 mW at $\lambda_0 = 532$ nm)^[4]. The PNIPAM/water system has a lower critical solution temperature (LCST), i.e. at lower temperatures, water is a good solvent and the PNIPAM chain expands like a random coil, while at temperatures higher than $\sim 32^\circ\text{C}$, the PNIPAM chain collapses into a globule. It is interesting to note that in Fig. 1, the transition temperature between the first and second stages, $\sim 30.5^\circ\text{C}$, corresponds very nicely to the known Θ -temperature ($\sim 30.6^\circ\text{C}$) estimated by the conventional method.

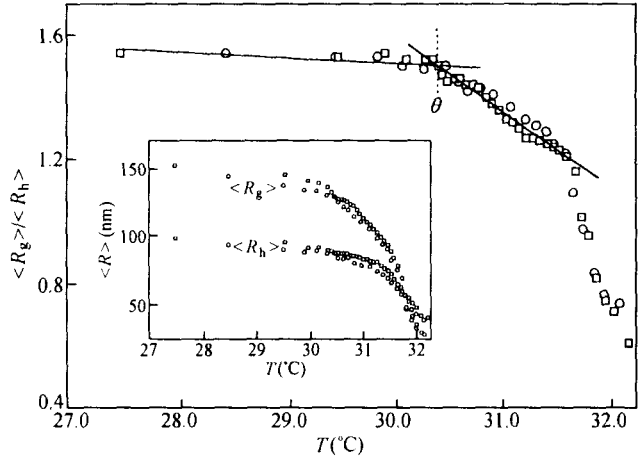


Fig. 1 Temperature dependence of $\langle R_g \rangle / \langle R_h \rangle$ for linear poly(*N*-isopropylacrylamide) chains in water
“□”: $M_w = 1.08 \times 10^7$ g/mol and “○”: $M_w = 1.21 \times 10^7$ g/mol
The inset shows the temperature dependence of both $\langle R_g \rangle$ and $\langle R_h \rangle$.

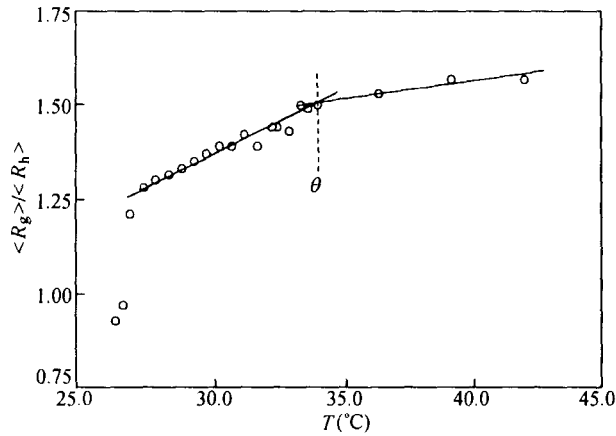


Fig. 2 Temperature dependence of $\langle R_g \rangle / \langle R_h \rangle$ for linear poly(styrene) chains ($M_w = 1.56 \times 10^6$ g/mol) in cyclohexane

With this finding, we examined a complete different system, polystyrene in cyclohexane, which has a known Θ -temperature ($\sim 34.5^\circ\text{C}$). Figure 2 shows that the decrease of $\langle R_g \rangle / \langle R_h \rangle$ for

polystyrene in cyclohexane also follows the three-stage process, but in an opposite direction because here the solution has an upper critical solution temperature (UCST). Again, the transition temperature between the first and second stages is located at $\sim 34.5^\circ\text{C}$. This clearly demonstrates that what we observed in Fig. 1 for PNIPAM in water is not an isolated incident. The transition temperature between the first and second stages corresponds to the Θ -temperature. Physically, it reflects a balance between the intrachain segment exclusion and segment contacts.

At this moment, we do not have direct evidence on what exactly happened at each stage. Qualitatively, we can follow a general description of de Gennes^[5] and Chu *et al.*^[6], as shown in Fig. 3. The speculation is that in the first stage, some "blobs" were formed along the chain backbone as the solvent quality decreased, due to the short-range segment contacts. However, we should not view or mistake each blob as a domain made of collapsed chain segments, but as a density (or entropy) fluctuation along the chain. At this stage, the solvent is still good and the long-range attraction among different blobs should be very weak, so that each blob could move independently even though they are interconnected by the chain backbone and behave like molecules in gas. At the second stage, the solvent became a poor solvent so that the blobs were attracted to each other and lost some freedom. The blobs acted like molecules in liquids, resulting in the crumpling of the polymer chain. At the third stage, the solvent became so poor that the blobs gradually condensed together and lost their mobility just as molecules in solids. In terms of the mobility of the blobs, the three-stage process in Figs. 1 and 2 can be viewed as the "gas-to-liquid" and "liquid-to-solid" transitions.

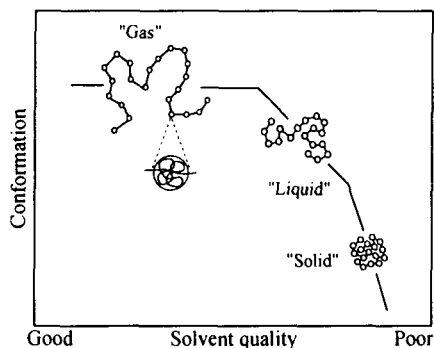


Fig. 3 Schematic of the "blob" on a polymer chain and the "gas", "liquid", and "solid" states of the blobs in terms of their mobility

Recently, an excimer study of the concentration dependence of $\langle R_g \rangle$ for polystyrene in toluene showed that the double logarithmic plot of $\langle R_g \rangle$ versus concentration changed its slope at the Θ -concentration^[7]. In comparison with this study in the extremely dilute solution, each chain shrinks as the temperature changes, so that the intrachain segment concentration increases, resulting in an increase of the segment contact. The point at which the intrachain segment exclusion balances the intrachain segment contacts is the Θ -temperature or the Θ -concentration depending on how one views it. In comparison with the excimer study, the only difference is that the segment interactions here are purely intrachain.

Summarizing, we found that the Θ -temperature can be determined from the conformation change of individual polymer chains in dilute solution. Instead of a set of solutions used in the conventional method, the present method requires only one polymer solution. Moreover, in this novel method, the Θ -temperature is experimentally determined by its definition, i.e. at which the effects of segment exclusion and segment contact cancel each other exactly, not only $A_2 \rightarrow 0$. Finally, we like to state that the observation of the third stage is much more difficult because

polymer chains often precipitate before reaching the third stage. However, the determination of the transition temperature between the first and second stages is fairly easy and it is not necessary to use a polymer sample with an ultrahigh molar mass and a very narrow distribution sample.

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