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

Chi Wu[**], Mei Li and Xiao-hui Wang

*Department of Chemical Physics, The Open Laboratory for Bond Selective Chemistry,
University of Science and Technology of China, Hefei 230026, China
Department of Chemistry, The Chinese University of Hong Kong, Shatin, N. T., Hong Kong, China*

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 Gaussain coil are recovered, but not other properties (e.g. the hydrodynamic radius) related to the non-Gaussain 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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[**] Corresponding author: Chi Wu (吴奇), E-mail: chiwu@cuhk.edu.hk

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 ~34.5°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

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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