

Wide-angle X-ray Scattering from Aqueous Solutions of Non-ionic Polymers

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In the field of polymer solution science, small-angle X-ray (or neutron) scattering (SAXS or SANS) measurements have been made to determine the scattering function $P(k)$ as a function of the magnitude k of the scattering vector in the range of $k/\text{\AA}^{-1} \lesssim 2$ for a single polymer chain in solutions. The analyses of $P(k)$ on the basis of the Kratky–Porod wormlike chain or the helical wormlike chain model[1] lead to the molecular-level information of a polymer chain in solutions, the mean-square radius of gyration $\langle S^2 \rangle$, stiffness parameter λ^{-1} (or persistence length q), and diameter d of the cross section of the chain contour.

Recently, synchrotron radiation facilities have become readily available, enabling accurate measurements of X-ray scattering in a wider range of k . Hirai *et al.*[2] have measured X-ray scattering from aqueous solutions of proteins in the range of $0.01 \lesssim k/\text{\AA}^{-1} \lesssim 2.5$ and proposed a procedure for estimate the excess scattering intensity $\Delta\hat{I}(k)$ of solutions in such a high- k range, where $\Delta\hat{I}(k)$ is defined by

$$\Delta\hat{I}(k) = \Delta I_{\text{soln}}(k)/I'_{\text{soln}} - \Delta I_{\text{solv}}(k)/I'_{\text{solv}} \quad (1)$$

with $\Delta I_{\alpha}(k)$ ($\alpha = \text{soln}$ or solv) the (excess) scattering intensity of solution or solvent, respectively, and I'_{α} the scattering intensity of the higher peak corresponding the intermolecular correlation between solvent molecules in solution or solvent, respectively. By the use of their procedure, the hierarchical structure of proteins in solutions, from the mean-square radius of gyration to the packing structure of side chains, may be simultaneously elucidated.

In this study, the wide-angle X-ray scattering (WAXS) measurements were carried out for aqueous solutions of poly(*N,N*-diethylacrylamide) (PDEA), as a example of the systems exhibiting the normal lower-critical-solution-temperature (LCST) phase behavior ($\Theta = 29.5$ °C), and then examined the dependence on temperature of $\Delta\hat{I}(k)$ in the range of $1 \lesssim k/\text{\AA}^{-1} \lesssim 3$ obtained using with the procedure by Hirai *et al.* Figure 1 shows plots of $\Delta\hat{I}(k)$ against k for the aqueous solution of PDEA of weight-average molecular weight 1.77×10^5 with weight fraction 1.901 %. In the range of $1 \lesssim k/\text{\AA}^{-1} \lesssim 1.5$, the temperature dependence of $\Delta\hat{I}(k)$ is observed. The origin of this temperature dependence is elucidated by the molecular dynamics simulations using a full-atom model. The details will be explained on the day of the presentation.

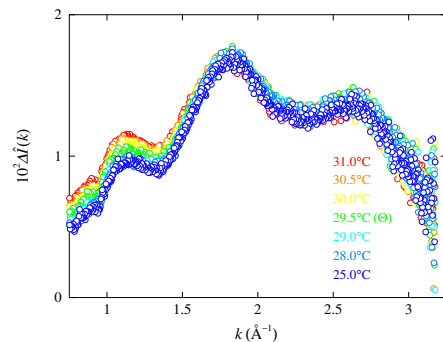


Figure 1. Plots of $\Delta\hat{I}(k)$ against k for the aqueous PDEA solution.

- [1] H. Yamakawa and T. Yoshizaki, *Helical Wormlike Chains in Polymer Solutions*, 2nd Ed. (Springer, Berlin, 20016).
- [2] M. Hirai, H. Iwase, T. Hayakawa, K. Miura, and K. Inoue, *J. Synchrotron Rad.*, **9**, 202 (2002).