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Local structure of random-coiled poly(*L*-glutamic acid) in added salt solutions

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1 Introduction

Some of polypeptides exhibit the conformational transition, helix-to-coil transition, in aqueous solution. For example, poly(*L*-glutamic acid)(PLGA) shows the transition between the helical-state and random-coiled state by changing pH of solution. However, it is unclarified how the local structure of PLGA depends on added salt speices in aqueous solution.

2 Experiment

Sodium salt of poly(*L*-glutamic acid)(PLGA-Na) of Mw = 9.8×10^4 was purchased from Sigma-Aldrich Chemical Co. Sample solutions were prepared by adjusting the deree of ionisation α of PLGA to 0.8. Polymer concentration C_p was 0.01 g/mL and C_s of added salts concentration, LiCl, NaCl, KCl and CsCl were 0.1M.

SAXS measurements were performed using the small-angle X-ray scattering spectrometer installed at BL10C beam port Photon Factory of High Energy Accelerator Research Organization, Tsukuba, Japan. Scattered X-ray was recorded by an imaging plate system of R-AXIS VII from RIGAKU Co. Two-dimensional scattering data were circle-averaged about the beam center and data was registered over the modulus of the scattering vector q ranging from 0.1 to 4 nm ^{1}, where q is defined by $(4\pi/\lambda)\sin(\theta/2)$ and λ is the wavelength and θ is scattering angle. The details of the apparatus and the measurement are described elsewhere [1]. Since the size of X-ray beam at the sample position was so small compared with sample-to-detector distance that the system could be regarded as point-focusing system. The excess scattering intensity of the sample over the solvent was determined after transmission corrections for both solution and solvent.

3 Results and Discussion

The scattered intensity monotonically decreases with increasing q. Therefore, in the case of PLGA in added salt aqueous solutions of C_s=0.1M, the intermolecular interactions could be neglected. The mean-square radius of cross-section of PLGA chain $< R_{cs}^2 >$ was evaluated from cross-section plot. It was shown that $< R_{cs}^2 >^{1/2}$ was almost fixed at 0.4±0.05nm independently of added salt species. Fig. 1 shows the Kratky plot, $I_{thin}(q)q^2$ vs q, where $I_{thin}(q)$ is scattered intensity of a hypothetical chain with no cross-section. The solid line in Fig. 1 are theoretical scattering function $P(q)$ [2] [3] computed with excluded-volume effect assuming the contour length of the chain L_c = 199.0 nm estimated from molecular weight, M = 9.8×10^4 and the persistence length L_p = 0.3 0.54±0.05 nm, taking into account $< R_{cs}^2 >^{1/2}$.

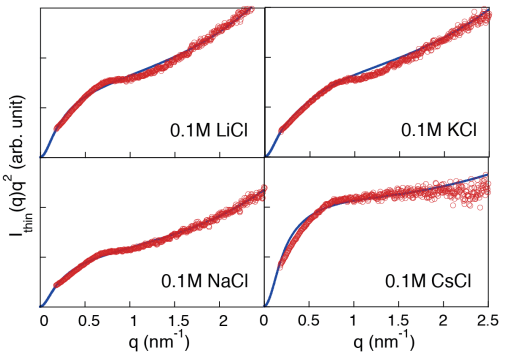

Fig. 1: Kratky plot of PLGA in several added salt solutions. Solid line shows the theoretical scattering function fot worm-like chain.

It is seen that the observed data is well mimicked by the theoretical curve. he persistence length of PLGA chain Lp thus evaluated is 0.54 nm for PLGA in LiCl, 0.54nm for PLGA in NaCl, 0.48 nm for PLGA in KCl, and 0.30 nm for PLGA in CsCl. The magnitude of L_p is comparable with an unpertubed effective bond-length of 0.8 nm [4]. These results might suggest that ionic radii of counter-ion condensed around PLGA chain affects the flexibility of the chain. That is, the chain flexibility was stiffer in the order of ionic radii of counter-ions, i.e., $Cs^+ < K^+ < Na^+ \leq Li^+$.

References

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