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Effect of added-salts on structure of poly(L-glutamic acid) in aqueous solution

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Introduction

It is well-known that poly(L-glutamic acid)(PLGA) exhibits the helix-coil transition in aqueous solution[1,2]. However, it is unclarified how the local structure depends on added salt species, such as Cl^- and F^-. In the present work, the effect of added salt on the structure of PLGA in aqueous solution was analyzed with small-angle X-ray scattering(SAXS) data in a higher scattering vector.

Experimental

PLGA-Na(Mw=9.8×10^4) was purchased from Sigma-Aldrich Co. Sample solution for SAXS was prepared by adjusting the degree of ionization α of PLGA to 0.80 and 0.86 and dissolving it in 0.2M NaCl and 0.2M NaF, respectively. Polymer concentration was 0.01 gcm^{-3}. SAXS measurement was performed at PF beam-line BL-10C. The sample cell was made of stainless steel and had quartz windows of 20 μm thickness at an interval of 1 mm.

Result and Discussion

The SAXS profile for all samples show no peak or broad hump in a low q range owing to electrostatic interaction between different polymer chains, and the excess scattering intensity of the sample over the solvent was determined after transmission corrections.

Fig. 1 shows the Kratky plot, $P(q)q^2$ vs q, for all samples where $P(q)$ was evaluated by $I(q)/I(0)$, and $I(0)$ is the scattering intensity extrapolated to q=0, which was determined by Guinier approximation. The solid curves in the plots (A), (B) and (C) are theoretical ones computed with $P(q)$ of wormlike chain[3] assuming the contour length of a polymer chain is 1990Å and the persistence length 5.9-6.0Å.

It is seen that the plot of (A) for random-coil chain and (D) for helical chain is well compatible with theoretical prediction that the plot for a random-coiled chain should be represented a convex curve, whereas the plot for a helical chain by a straight line passing through an origin. In the plots (A) and (B), the agreement between the observed and the theoretical curve is fairly satisfactory except in low q range, where the observed data downward deviates from the theoretical one. The reason for such a downward deviation might be due to fairly broad molecular weight distribution of the sample and/or possible excluded-volume effect.

On the other hand, the plot (C) slightly deviate upwards from the theoretical curve in q range lower than 0.05 Å^{-1}. This means that the conformation of PLGA at α=0.80 in 0.2M NaF might be represented by a swollen gel having a network structure. That is, the conformation of PLGA at α=0.80 in NaF aqueous solution might be far apart from the conformation of a worm-like chain.

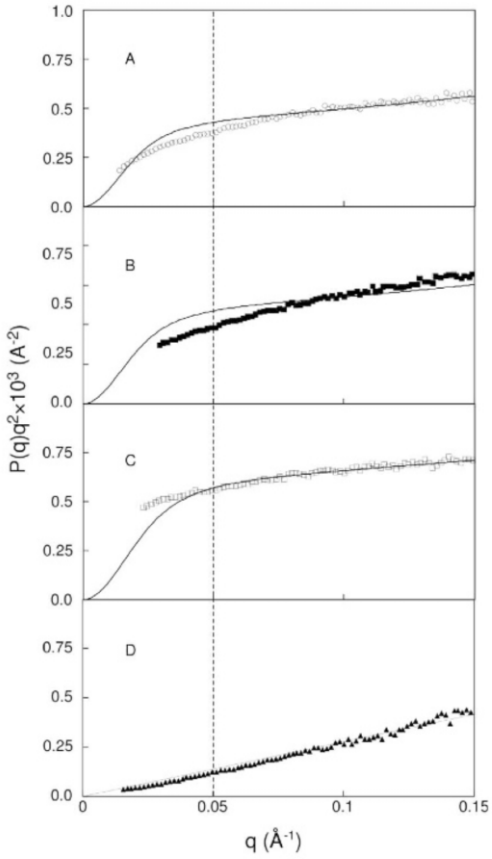

Fig. 1 Kratky plot for PLGA(Cp=0.01gcm^{-3}, 298K). (A): PLGA in 0.2M NaCl, α=0.86, (B): in 0.2M NaCl, α=0.25, (C): in 0.2M NaF, α=0.80 and (D) in N-methylacetamide at 333K, α=0, Cp=0.026 gcm^{-3}.

References

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