

Dimension of Poly(2-methacryloyloxyethyl phosphorylcholine) in Aqueous Solutions with Various Ionic Strength

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The dimension and intermolecular interaction of poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) in aqueous solutions with various ionic strength was investigated with static and dynamic light scattering. Although PMPC is a polyelectrolyte, its dimension and intermolecular interaction did not change in the aqueous solution of NaCl at 0–0.5 M.

The dimension and the intermolecular interaction of polyelectrolytes usually strongly depend on the concentration of added low-molecular-weight salt. The dimension of polyanions such as sodium poly(2-acrylamido-2-methylpropanesulfonate) (NaPAMPS)^{1,2} or sodium poly(styrene sulfonate) (NaPSS)³ and that of polycations such as benzyl-poly(2-vinylpyridine) bromide (Bz-PVPBr)⁴ are extended, and their repulsive intermolecular interaction is enhanced by decreasing salt concentration. On the other hand, the dimension of polyampholytes such as polysulphobetaine (PSB)⁵ usually shrink a little by decreasing salt concentration because of increased attractive interaction of positive and negative charges.

We investigated here the dimension and intermolecular interaction of a super-hydrophilic polymer, poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC) in aqueous solution with various salt concentration. PMPC is a polyampholyte with phosphorylcholine groups in its side chains, as shown in Figure 1.

Because of its excellent biocompatibility and ability as lubricant, PMPC is expected to be used as medical material such as artificial joints.⁶ As PMPC is exposed to wide range of salt concentration in physiological environment, the change of its dimension and intermolecular interaction with salt concentration will be important for its practical application.

PMPC was synthesized by atom transfer radical polymerization (ATRP)⁷ of which detailed procedure was described in the supporting information. Weight average molecular weight M_w of the sample used in this study was determined to be 1.96×10^5 by static light scattering described below. Molecular weight dispersity M_w/M_n was determined to be 1.50 by GPC.

Static and dynamic light scattering was carried out at 25 °C with ALV 5000/E/EPP using He–Ne laser as a light source.

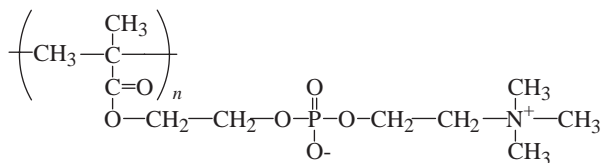


Figure 1. Chemical structure of PMPC.

Specific refractive index increment was measured for the PMPC pure water solution with Otsuka Electric DRM-1020 ($0.145 \text{ g}^{-1} \text{ cm}^3$). Specific refractive index increment of other solutions was determined by assuming a constant M_w value of PMPC in all the solutions.

Figure 2 shows typical auto-correlation function $g^{(2)}(t)$ for the aqueous solution of PMPC, where c_p , c_s , θ , $A(\tau)$, and Γ stand for the concentration of PMPC, that of added salt (NaCl), scattering angle, relaxation spectrum and first cumulant, respectively. The magnitude of scattering vector q is defined as $q \equiv (4\pi n/\lambda_0) \sin(\theta/2)$, where n and λ_0 are the refractive index of solvent and the wavelength of irradiation light, respectively.

Both $g^{(2)}(t)$ and $A(\tau)$ in Figure 2a show unimodal relaxation spectrum, although they are rather broad for the polydispersity. Almost the same shapes of $g^{(2)}(t)$ and $A(\tau)$ were also obtained for all the solutions measured in this study. This means that there were no large aggregates in the aqueous solutions of PMPC. Γ/q^2 in Figure 2b is independent of q^2 , suggesting that Γ reflects only translational diffusion of polymer chains.

Figure 3 summarizes the results of static and dynamic light scattering for the aqueous solutions of PMPC with various salt

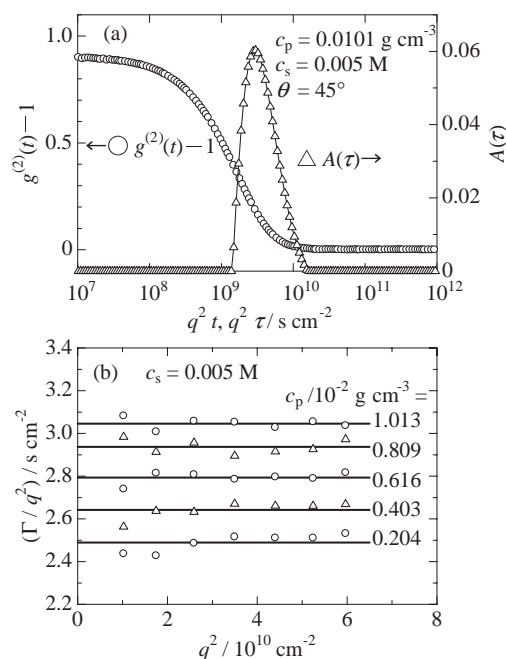


Figure 2. (a) Auto-correlation function and relaxation spectrum, and (b) angular dependencies of first cumulant divided by the square of the magnitude of scattering vector.

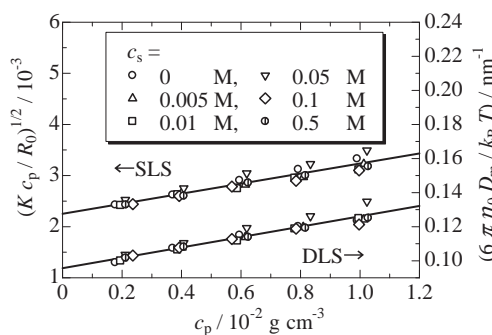


Figure 3. Plots of the results of static and dynamic light scattering vs PMPC concentration for the solutions with various salt concentration.

concentration, where K , R_0 , η_0 , D_m , k_B , and T stand for optical constant, excess Rayleigh ratio at $q = 0$, the viscosity of solvent, mutual diffusion coefficient, Boltzmann constant and temperature. The data points of both static and dynamic light scattering are essentially independent of the concentration of NaCl, and can be fitted by single lines.

In order to discuss the dependence of the dimension and intermolecular interaction of PMPC on the concentration of NaCl, second virial coefficient A_2 , concentration coefficient of diffusion coefficient k_D and hydrodynamic radius R_H were calculated as follows,

$$(Kc_p/R_0)^{1/2} = M_w^{-1/2} + A_2 M_w^{1/2} c_p + \dots \quad (1)$$

$$D_m = D_0(1 + k_D c_p + \dots) \quad (2)$$

$$R_H = k_B T / 6\pi\eta_0 D_0 \quad (3)$$

where D_0 is limiting diffusion coefficient. A_2 reflects the strength of excluded-volume effect, and its large positive value suggests that there is strong repulsive intermolecular interaction between polymer chains. If the shape of polymer chains does not change so much, large value of k_D also suggests the existence of strong repulsive intermolecular interaction. R_H indicates the hydrodynamic dimension of polymer chains, and its large value suggests that polymer chains have expanded form.

Figure 4 compares measured A_2 , k_D , and R_H of PMPC and those of other polyelectrolytes.¹⁻⁴ Their R_H and A_2 shown in Figure 4 are interpolated or extrapolated values for the same weight average degree of polymerization DP_w as that of PMPC used in this study ($DP_w = 662$). k_D of NaPSS and NaPAMPS shown in Figure 4 are the values of measured ones of NaPSS ($DP_w = 519$) and NaPAMPS ($DP_w = 539$).

R_H of NaPSS, NaPAMPS, and Bz-PVPBr decreased by increasing salt concentration, because the intramolecular repulsive interaction was moderated by screening effect of added salt. On the other hand, independence of the dimension of PMPC on salt concentration was observed, because the intramolecular interaction did not change so drastically, for MPC was electrically neutral as a monomer unit.

Even for typical polyampholyte PSB, aqueous solution of NaCl became poorer solvent by decreasing salt concentration and Θ solvent at $c_s = 0.06 \text{ M}$.⁵ On the other hand, A_2 and k_D

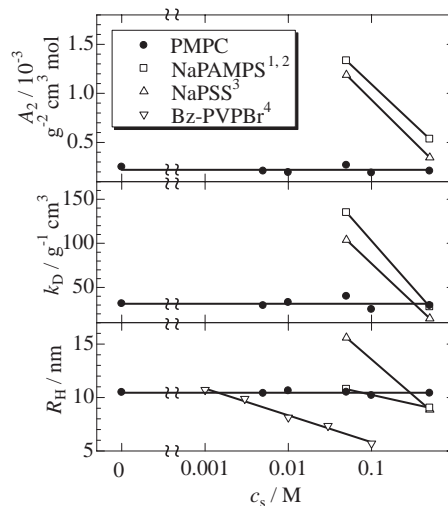


Figure 4. Salt concentration dependence of hydrodynamic radii, concentration coefficients of diffusion coefficients and second virial coefficients of PMPC and other polyelectrolytes.

of PMPC showed stable values ranging from $c_s = 0$ – 0.5 M , indicating that aqueous solution of NaCl with low ionic strength were also good solvent for PMPC.

There might be several factors influencing the difference in the dimension and intermolecular interaction of PMPC and PSB due to the presence of acid and base with different characteristics. We will clear the origin of the unique properties of PMPC by utilizing spectroscopic and scattering methods and zeta potential measurement in a near future.

In this paper, we confirmed the independence of dimension, intermolecular interaction and affinity to water of PMPC on ionic strength. This property may contribute usefulness of PMPC as medical material by certifying the stable performance under wide range of salt concentration.

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