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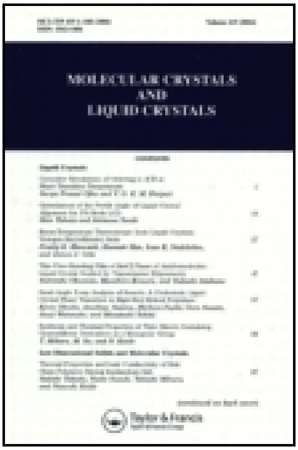

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Transition Behavior of Polyelectrolyte Brushes Depending on Polymer Chain Density

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Transition Behavior of Polyelectrolyte Brushes Depending on Polymer Chain Density

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Brush layers of polyelectrolytes, ionized poly(L-lysine) (PLL) or poly(L-glutamic acid) (PLGA), at desired densities were prepared by the Langmuir-Blodgett (LB) deposition of amphiphiles bearing PLL or PLGA segments as hydrophilic groups, and subjected to the surface force measurements. Abrupt changes in the surface force, the surface potential, and the transfer ratio of the brush layers were observed at a critical density. The present data is in good agreement with our previous report on the jump in the compressibility of the brushes, and supports the existence of the density dependent transition of polyelectrolytes in solutions.

Keywords: polyelectrolyte; brush layer; transition behavior; density dependence; transfer ratio; surface potential

INTRODUCTION

Polyelectrolytes are attracting increasing attention in materials science because of their importance in such applications as functionalized gels[1] and the components of novel molecular architectures[2]. However, the behavior of polyelectrolytes in solutions is complex, thus it is still poorly understood[3]. Two dimensionally organized brush layers have been adopted to simplify the complex behavior of

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polyelectrolytes, charged polymers with counterions, and investigated by surface force[4-6], neutron scattering[7] and x-ray scattering measurements[8].

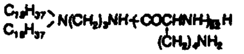
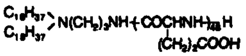
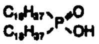
One of the characteristic phenomena for polyelectrolytes is the condensation of counterions around them, which occurs when the average intercharge distance on a single polyelectrolyte is less than the Bjerrum length for monovalent counterions[3]. This is an intra-chain transition behavior. Recently, we have measured the surface forces between opposed brush layers of ionized poly(L-glutamic acid) (PLGA) and found the density dependent transition in the compressibility at a critical chain density, i.e. a critical inter-chain distance[6].

In the present work, we studied this transition using brush layers of poly(L-lysine) (PLL) and PLGA, and found abrupt changes in other properties, i.e., the transfer ratio and the surface potential, of brush layers at the same critical density.

EXPERIMENTAL SECTION

Polyelectrolyte amphiphiles bearing hydrophobic anchors (dioctadecyl groups) at their terminals and PLL segment (polymerization degree = 52), 2C18PLL(52), or PLGA segment (polymerization degree = 48), 2C18PLGA(48), were synthesized following a previous procedure[9,10]. 3-(N,N-Dioctadecylamino)propylamine (DOPA, used as a diluent for PLL monolayer) was synthesized as reported[9]. Dioctadecylphosphoric acid (DOP, used for PLGA) was purchased from Sogo Pharmaceutical Co. Table 1 lists the chemical structures of these compounds.

TABLE 1 Polyelectrolyte amphiphiles, diluents, and solvents for spreading monolayers.

	polyelectrolyte amphiphile	diluent	solvent for spreading
PLL layer	 $(C_{18}H_{37})_2N(CH_2)_3NH(COCH((CH_2)_4NH_2)NH)_{52}H$ 2C18PLL(52)	 $(C_{18}H_{37})_2N(CH_2)_3NH_2$ DOPA	benzene : DMSO = 1 : 1
PLGA layer	 $(C_{18}H_{37})_2N(CH_2)_3NH(COCH((CH_2)_2COOH)NH)_{48}H$ 2C18PLGA(48)	 $(C_{18}H_{37}O)_2P(O)OH$ DOP	benzene : DMF = 7 : 3

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Polyelectrolyte brushes were prepared by the Langmuir-Blodgett (LB) method. In order to vary the polyelectrolyte content in the brushes, mixed monolayers of polyelectrolyte amphiphiles and diluents (1:0 ~ 1:16) were prepared. The spreading solvents for the monolayers are also shown in Table 1. The surface pressure - molecular area (π - A) isotherm measurement and the LB deposition were carried out using a film balance (FSD-50) and a lifter (FSD-21) system (USI System).

The miscibility of 2C18PLL(52)-DOPA in mixed monolayers was characterized by Brewster angle microscopy (NL-EMM633K, Nippon Laser & Electronics Lab.) of the surface morphology. Uniform monolayers were observed for all mixed monolayers at $\pi = 25$ mN/m except for the mixing ratios of 1:1 (mole fraction of polyelectrolyte amphiphile, $x = 0.5$) and 1:2 ($x = 0.33$). In the case of $x = 0.5$, the monolayer was uniform at $\pi = 20$ mN/m. For measurements of the surface forces and transfer ratios, only uniformly mixed monolayers were used, and the data obtained at $x = 0.33$ was excluded. The ideal mixing of the monolayers of 2C18PLGA(48)-DOP was established in a previous report[6].

To prepare the brush layers for the surface forces measurement (Figure 1), mixed monolayers were transferred onto hydrophobic mica at pH 4 (HNO_3 was used for pH adjustment) for PLL, or at pH 10 (KOH) for PLGA. The deposition pressure was 20 or 25 mN/m for the PLL (see the caption of Figure 2) and 30 mN/m for the PLGA layers. The chain number density of the polyelectrolyte per nm^2 of the LB films, Γ, was calculated using the molecular area and transfer ratio.

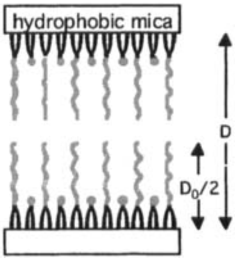

FIGURE 1 Schematic drawing of opposed brush layers.

The surface force measurements[11] were carried out using a Surface Forces Apparatus Mark 4 (ANUTECH) or NL-SF001 (Nippon Laser & Electronics Lab.). Separation distances, D, between the surfaces (Figure 1) were measured using the fringes of equal chromatic order (FECO). The measured force, F, normalized by the mean

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radius, R, of the surface curvature is proportional to the free energy of interaction, G_f, per unit area between two flat surfaces, $F/R = 2\pi G_f$ (Derjaguin approximation)[11].

RESULTS AND DISCUSSION

Behavior of Mixed Monolayers on the Aqueous Subphase

The transfer ratios of the mixed monolayers onto hydrophobic surfaces are plotted versus the mole fraction, x, of a polyelectrolyte amphiphile in Figure 2; A is for PLL and B for PLGA. Both plots can be divided into two regions. One is the low-density region, $x \leq 0.2$ for PLL and $x \leq 0.11$ for PLGA, where the transfer ratio linearly decreases with increasing x, and another is the high-density region where the transfer ratio is constant ($0.2 < x$ for PLL, and $0.33 < x$ for PLGA). These results indicate the presence of two states of mixed monolayers, and are in good accord with our previous observation of the transition in the compressibility modulus of the PLGA brushes at a critical chain density, $\Gamma = 0.20 \pm 0.07$ chain/nm^2 which lies between $x = 0.11$ and 0.33[6]. Figure 2B shows an irregular point at $x = 0.2$ which corresponds $\Gamma = 0.29$ chain/nm^2. It is understandable that behavior of the monolayers becomes irregular near the critical point between two states. We also observed an irregular force profile between the PLGA brushes deposited under this condition[12], suggesting the presence of a phase separation.

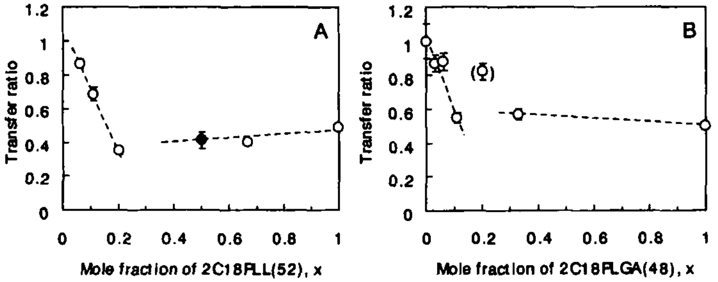

FIGURE 2 Plots of the transfer ratio versus mole fraction (x) of polyelectrolyte amphiphile of (A) PLL and (B) PLGA. The deposition ratio was 30 mN/m for PLGA and 25 mN/m for PLL but 20 mN/m for filled plot. Dashed lines are visual guides. Parenthesis in B shows an irregular point.

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Surface Forces between PLL Brushes.

The surface forces of the PLL brush layers were measured at various chain densities (Figure 3). The obtained force profiles consisted of a long-range ($D >$ ~40 nm) electrostatic repulsion and a short-range ($D <$ ~40 nm) steric repulsion. For Γ = 0.44 chain/nm^2, the repulsion at $D > 40$ nm can be fit by the diffuse electrical double layer theory[13] with the surface charge, σ, of 0.017 charge/nm^2 (constant-charge model) and with the surface potential, ψ, of 80 mV (constant-potential model). The experimental curve lies between these two calculated curves. Force profiles remained the same as that of Γ = 0.44 chain/nm^2 at densities higher than Γ = 0.27 chain/nm^2. However, the forces suddenly increased at Γ = 0.19 chain/nm^2 both in the double layer and the steric force regions.

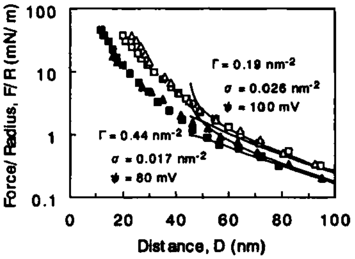

FIGURE 3 Force profiles of PLL brushes at $\Gamma = 0.44$ chain/nm^2 ($x = 1$, filled) and at $\Gamma = 0.19$ chain/nm^2 ($x = 0.11$, open). Different symbols show reproducibility of data. Lines were calculated curves using the diffuse electrical double layer theory.

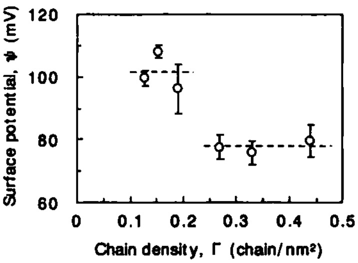

FIGURE 4 Plot of the surface potential for PLL brushes as a function of the chain density. Dashed lines show average surface potentials in each region.

The obtained surface potential for the PLL brush is plotted as a function of the chain density in Figure 4. The surface potential is nearly constant, ~80 mV, in the high-density region, $\Gamma \geq 0.27$ chain/nm^2, and jumps to a larger constant value, ~100 mV, for $\Gamma \leq 0.19$ chain/nm^2. Such a change in the potential has not been clearly found in the case of the PLGA brushes[6]. The transition of the PLGA brushes has been accounted for in terms of the change in the counterion binding to polyelectrolyte chains; strong binding at higher densities and relatively loose binding at lower densities. The jump in the surface potential shown in Figure 4 is in good agreement with this mechanism.

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We also observed, similarly to the PLGA brushes, the jump in the compressibility modulus for the PLL brushes at the critical density shown in Figure 4, which will be reported elsewhere.

This study demonstrates the density dependent jump in properties of polyelectrolyte brushes such as transfer ratio, surface force and surface potential, and supports the existence of the density (inter-chain distance) dependent transition of polyelectrolytes in solutions. We have proposed a counterion model to account for this transition[6]. Understanding this behavior should provide the foundation for studies on the complex properties of polyelectrolytes.

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