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Notes

Electrostatic Interaction of Anionic/Nonionic Polyelectrolyte Prototype Copolymer Brushes with Cationic Linear Polyelectrolyte

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Introduction

It is well-known that comb polymers with densely grafted side chains in a good solvent can adopt a wormlike cylinder brush conformations, in which the side chains are stretched in the direction normal to the backbone, owing to the excluded-volume interaction. The polymerization of macromonomers provides regular multibranched polymers with dense branching. More recently, Ishizu and co-workers established a novel synthesis of prototype amphiphilic copolymer brushes (see Figure 1) by alternating free-radical copolymerization of binary macromonomers.[1,2] They have also investigated their dilute-solution properties and aggregation behaviors in aqueous media.[3−6] As a result, such copolymer brushes were molecularly dissolved in a dilute solution and took geometrically anisotropic conformation such as cylinder with increasing aspect ratio. In the self-assembly process in water, hierarchical generation from small rods to large rods was observed, because such copolymer brushes exhibited phase-separated hydrophobic/hydrophilic domains. Among of them, polystyrene/poly(ethylene oxide) (PS/PEO) brushes can be easily converted to copolymer brushes composed of anionic/nonionic polyelectrolyte structure. Schlüter et al.[7] have also synthesized the prototype amphiphilic copolymer brushes by polycondensation of Suzuki-type dendron monomer (hydrophobic/hydrophilic side chains) with dibromic acid ester. Schmidt and co-workers obtained wormlike cylindrical brushes through radical copolymerization of macromonomers poly(4-vinylpyridine) and poly(methyl methacrylate).[8] Also, different routes to cylindrical brush polymers by “grafting from”[9−11] ATRP techniques were reported.

It is also well-known that dendrimers are systematically constructed to form regularly branched treelike structures and have active groups at the terminal positions. The binding of dendrimers to polyelectrolytes has been investigated.[12−14] The formation of complexes between cationic polyelectrolytes and carboxylated dendrimers occurred most readily for the 75th generation with high charge density[12] and at a critical pH.[13] The interaction of poly(propyleneimine) dendrimer with linear anionic polyelectrolyte was compared with that of DNA.[14] More recently, Imae et al.[15] have investigated the binding of poly(amino amine) dendrimer to sodium hyaluronate.

In this short communication, PS/PEO prototype brushes were synthesized by alternating free-radical copolymerization of PS and PEO macromonomers. These brushes were converted into sulfonated PS (PSS)/PEO brushes (anionic/nonionic polyelectrolyte prototype) by sulfonation. The electrostatic interactions of charged prototype brushes with cationic linear polyelectrolyte [quaternized poly(4-vinylpyridine) (P4VPQ)] were investigated by scanning electron microscopy (SEM) as a parameter of blend ratios.

Experimental Section

Materials. 4-Vinylpyridine (4VP) (Tokyo Kasei, Tokyo) was distilled under high vacuum. 2,2′-Azobis(isobutyronitrile) (AIBN), methyl iodide (CH_3I), dichloroethane, benzene, tetrahydrofuran (THF), ethanol (Tokyo Kasei, Tokyo), and chlorosulfuric acid (Kanto Kagaku, Tokyo) were used as received.

Free-radical copolymerizations of binary macromonomers (vinylbenzyl-terminated PS and methacryloyl-terminated PEO) were performed in benzene with the addition of $SnCl_4$ at 60 °C using AIBN as an initiator (see Figure 1). It was found from previous results that these copolymerization systems showed strong alternation.[5,6] Characteristics and dilute-solution properties of PS/PEO prototype brush CB11 are listed in Table 1.

Sulfonation of PS/PEO Prototype Copolymer Brushes. Sulfonation of PS/PEO copolymer brushes was carried out as follows. PS-grafted chains of PS/PEO brushes (0.5 g) were sulfonated in dichloroethane solution (20 mL) of 10 vol. % chlorosulfuric acid at room temperature for 1 day. After evaporating the solvent, the resulting product was neutralized with NaOH aqueous solution. This solution was placed in dialysis tubes and dialyzed against distilled water for 4 days. The solvent was evaporated and PSS/PEO copolymer brush was freeze-dried. It was recognized from the gel permeation chromatography (GPC) trace of PEO macromonomer that the hydrolysis of the PEO side chain did not occur under such sulfonation conditions. The degree of sulfonation ($QS = 36.6\%$) was determined by acid-alkaline titration with 0.05 M HCl aqueous solution.

The diffusion coefficient (D_0) was determined by extrapolation to zero of the concentration of dynamic light scattering (DLS) with cumulant method (Otsuka Electronics Ltd.) at 25 °C in 0.4−5.6 mg/mL in aqueous solution for PSS/PEO copolymer brush. The scattering angle was in the range 30−150°. The value of the hydrodynamic radius (R_h) was estimated using the corresponding D_0 value. R_h is defined by the Stokes−Einstein equation, $R_h = kT/6\pi\eta_0 D_0$, where k, T, and η_0 indicate the Boltzmann constant, the absolute temperature, and the viscosity of the solvent, respectively.

Synthesis of Quaternized Poly(4-vinylpyridine). Poly(4-vinylpyridine)s (P4VP) were prepared by usual radical polymerization in ethanol at 60 °C initiated by AIBN ($M_w = 8 \times 10^5$). The molecular weight was determined by viscometry (intrinsic viscosity $[\eta]$ (mL/g) $= 25.0 \times 10^{-3} M_w^{0.68}$ in ethanol at 25 °C[16]). P4VP (1 wt % solution) was quaternized with CH_3I

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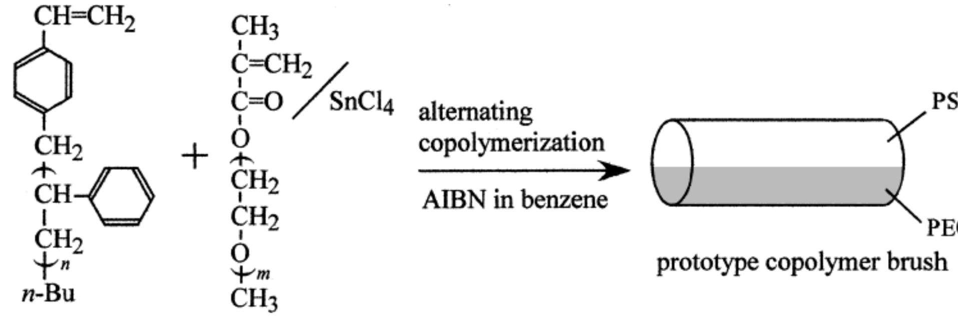

Figure 1. Reaction scheme to synthesis of prototype copolymer brushes.

Table 1. Characteristics and Solution Properties of PS/PEO Prototype Copolymer Brush

	M_n of macromonomers									
expt no.	PS−VB	PEO-MC	$10^{-6}M_w{}^a$	$M_w/M_n{}^b$	F^c	$DP_n{}^d$	$R_h{}^e$(nm)	$R_g{}^a$(nm)	$R_{g,c}{}^f$(nm)	R_g/R_h
CB11	4200	2100	4.45	1.43	0.48	975	14.2	30.0	6.2	2.11

[a] Determined by static light scattering (SLS) with Zimm mode in benzene at 25 °C. [b] Determined by gel permeation chromatography (GPC) in THF as the eluent at 38 °C. [c] PEO fraction in copolymer brush; determined by ^{1}H NMR in $CDCl_3$. [d] Degree of polymerization. [e] Determined by dynamic light scattering (DLS) with cumulant method in benzene at 25 °C. [f] Determined by small-angle X-ray scattering (SAXS) using cross-sectional Guinier's plot in benzene.

([4VP unit]/[CH_3I] = 1/1.3 mol/mol) in ethanol at room temperature for 1 day. The degree of quaternization (DQ) was determined by ^{1}H NMR in DMSO-d_6 [from the integration ratio of protons (δ 8.65 and 7.35 ppm) of the quaternized pyridine ring to protons (8.30−8.22 and 6.56 ppm) of pyridine ring]. The DQ values of quaternized P4VP (P4VPQ) samples were estimated to be 100 mol % under such conditions.

Binding of PSS/PEO Copolymer Brushes to Linear P4VPQ. Aqueous mixtures of PSS/PEO prototype brush (polymer concentration $C_0 = 0.005$ wt %) and P4VPQ prepared from the blend ratio: prototype brush/P4VPQ = 5/1 w/w. Aqueous solutions exhibited turbidity. However, no precipitates were observed for any of the sample specimens. This means that copolymer brushes formed some kind of binding structure due to electrostatic binding with P4VPQ. The size distribution of aggregates was determined by the cumulant method on DLS at 25 °C in a 0.017 mg/mL aqueous solution. The scattering angle was in the range 30−90°.

The direct observation of binding products was carried out by the use of field emission gun scanning electron microscopy (FE-SEM S-800: Hitachi) with a tilt angle of 30°. The preparation procedure of SEM specimens was performed as follows. A few drops of the aqueous solution were placed onto a glass plate and spin-coating was conducted immediately at 3000 rpm for 5 min.

Results and Discussion

It was also mentioned in the previous results on DLS[5,6] that prototype copolymer brushes showed strong angular dependence ($\Gamma_e q^{-2}$ vs q; $qR_h < 1$, where Γ_e is the first cumulant) with increasing the aspect ratio and the translational diffusion coefficient D(C) had a constant value against polymer concentration. The PS/PEO brush CB11 (R_h = 14.2 nm) also showed the similar results. These facts suggested that the brush CB11 with wormlike shape was molecularly dissolved in the dilute benzene solution. On the other hand, the ratio R_g/R_h is a sensitive fingerprint of the inner density profile of macromolecular architectures. This parameter was calculated for various macromolecular architectures. The calculated values of R_g/R_h are 0.775 and >2 for a hard sphere of uniform density[17] and for a monodisperse rigid rod,[18] respectively. The observed value of R_g/R_h for PS/PEO brush is 2.11. Then, this copolymer brush takes a relatively compact shape in a good solvent.

We consider the molecular size of PS/PEO brush CB11 in the solution. Assuming a polydisperse rodlike shape and neglecting $R_{g,c}$, R_g is given by the following relation

$$R_g = L_w/\sqrt{(5/27)} \quad \text{for the Schulz−Zimm length distribution} \quad (L_w/L_n = 1.5) \tag{1}$$

where L_w denotes the length of a rodlike molecule. Equation 1 allows one to evaluate the rod length as L_w = 69.7 nm. The cross-sectional diameter d is calculated from $R_{g,c}$ as

$$d = (\sqrt{8})R_{g,c} \tag{2}$$

by assuming a constant electron density across the cylinder. Since eq 2 yields d = 17.5 nm, the aspect ratio L_w/d (3.98) is significantly larger than 2.5. Accordingly, the shape of the prepared CB11 is much more similar to a cylindrical shape as sketched in Figure 1.

Subsequently, the PS/PEO prototype copolymer brush CB11 was converted into a PSS/PEO brush (CB11S) by sulfonation using chlorosulfuric acid. The CB11S (QS = 36.6%) was soluble in water. This copolymer brush also showed a strong angular dependence on DLS data in water, and the mutual diffusion coefficient $D(C)$ has an almost constant value ($D_0 = 2.67 \times 10^{-8}$ cm^2/s) in the range 0.4−5.6 mg/mL of polymer concentration. This suggests that the copolymer brush is molecularly dissolved at such a polymer concentration. The value of R_h was estimated to be 45.7 nm. This value is somewhat larger than that (R_h = 14.2 nm) for PS/PEO prototype brush CB11 in benzene, even if considering electric double layers by charge effect. Both polymer components (PSS and PEO) are soluble in water. It seems therefore to lead intermolecular cross-linking (formation of n-mer of CB11S) during sulfonation process.

Next, we studied the binding behaviors of PSS/PEO prototype brushes to linear P4VPQ (starting material P4VP; $M_w = 8 \times 10^5$) in an aqueous solution, varying the blend ratio and polymer concentration. When anionic PSS domains of PSS/PEO brush molecules abundantly bind on quaternized 4VP groups (cationic sites), P4VPQ chains should become elongated and brush-P4VPQ complexes take a rod shape, because the cross-sectional diameter of the complex becomes greater. A

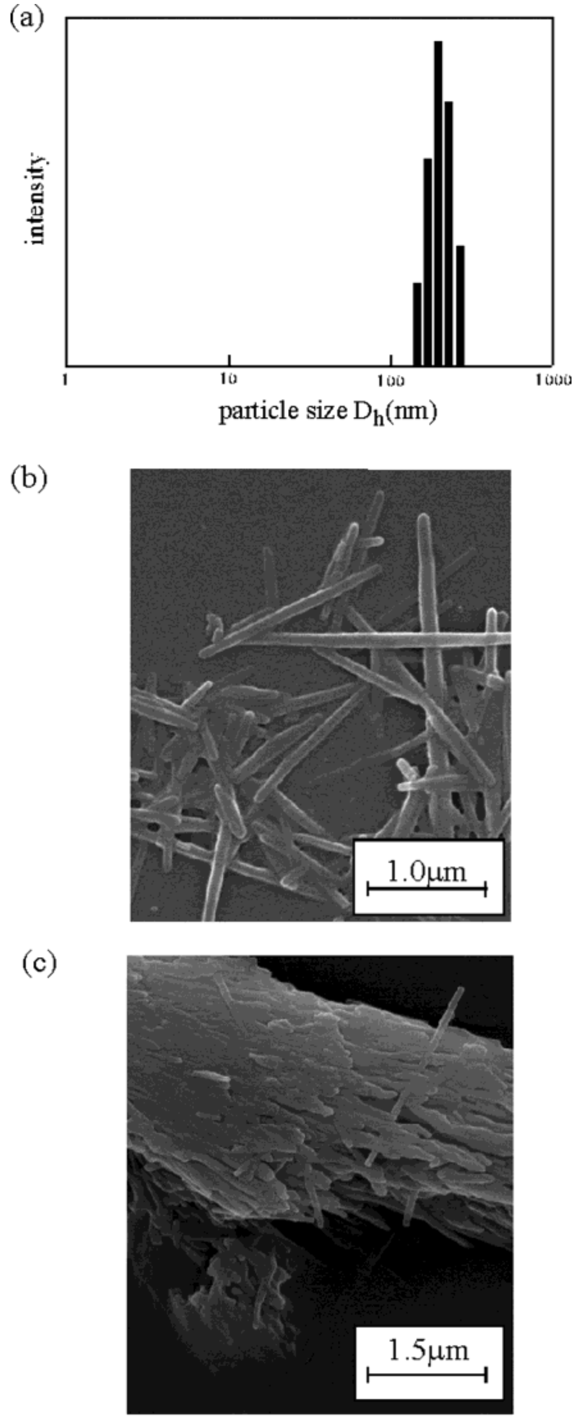

Figure 2. Hydrodynamic diameter distribution of CB11S brush aggregate/P4VPQ complex in water (a) and FE-SEM photograph [prepared from 0.005 wt % of CB11S/P4VPQ: 5/1 (w/w) aqueous solution] (b and c).

blend solution ($C_0 = 0.005$ wt %) of CB11S with P4VPQ [CB11S/P4VPQ: 5/1 (w/w)] showed turbidity, but we observed no precipitates. This blend ratio corresponds to a molar ratio of CB11S into P4VPQ of ca. 2:1. Figure 2a shows the size distribution of such binding product by means of DLS. Single narrow peak is observed at $D_h = 266.1$ nm. Parts b and c of Figure 2 show FE-SEM photographs of the binding product. Textures indicate the flux of large rigid rods or a single rod (diameter = ca. 130 nm). This rod diameter is too large, under the assumption that single PSS/PEO brushes bind with P4VPQ by electrostatic interaction. It is reasonable that PSS/PEO brush aggregates bind with P4VPQ molecule. In this illustration, there are several P4VPQ chains inside the aggregates, because the feed molar ratio of CB11S into P4VPQ was 2:1. It can be therefore speculated that there are several P4VPQ chains inside the aggregates. It is found from both photographs that these semiflexible P4VPQ chains changed to stretched conformation by electrostatic interaction during binding process. The complex formation of CB11S with P4VPQ can be speculated as follows. Anionic PSS domains of brush molecules abundantly bind on P4VPQ chains in the first stage. Two cases can be considered at the next stage: (1) intermolecular aggregation among such complexes (complex **1**) and (2) PEO shells lead to fusion with PEO domains of CB11S brushes. By repeating these aggregation process, supermicelles are formed as sketched in Figure 3 (complex **2**). In this illustration, we sketch that PSS is inside and PEO is outside of the aggregated structure. However, it is possible to consider that these large rods are stabilized by highly grafted PSS chains. We can also assume other structures of the complexes: they are coiled in middle of the filament such that the core of the filament consists of a string of many coiled P4VPQ chains. As mentioned in the Introduction, Imae et al.[15] have investigated the binding of poly(animo amine) dendrimer to sodium hyaluronate (NaHA). They concluded that the structure of NaHA changed to a rodlike one by the electrostatic interaction with dendrimers. Our results were very similar to their investigations. So, we assumed in this work that the P4VPQ chains were stretched by the electrostatic interaction with PSS/PEO copolymer brushes.

The information for the aggregated structure has been left unsolved in this work. Beyond more than ca. 0.1 wt % of the polymer concentration of blend mixtures, we observed the precipitate (may be network formation) in such a system, which is due to intermolecular binding between PSS/PEO brush and P4VPQ. In the case of high blend fraction of PSS/PEO brushes, we also observed the precipitate in aqueous solution. The solubility of the PSS/PEO brush (CB11S) in water was poor in relatively high concentration. Therefore, this precipitate seemed to correspond to prototype brushes. We are investigating the morphology of aggregated structures. The information obtained will be reported in the near future.

Conclusions

Amphiphilic prototype copolymer brushes were synthesized by alternating free-radical copolymerization of

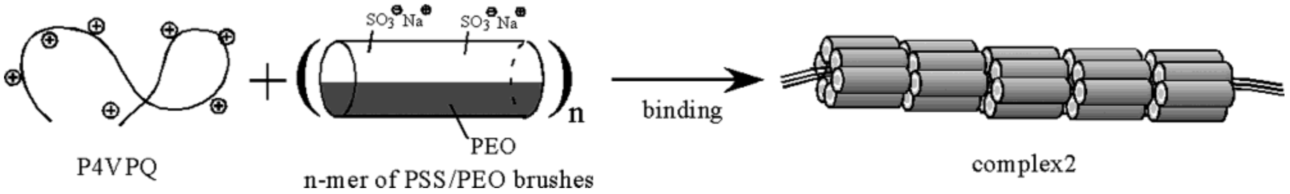

Figure 3. Illustration in binding process of PSS/PEO brush with P4VPQ by electrostatic interaction in water.

PS−VB with PEO-MC/$SnCl_4$ complex. These brushes could be converted into PSS/PEO (anionic/nonionic polyelectrolyte) brushes by sulfonation. The value of R_h for CB11S (45.7 nm in water) was larger than that (R_h = 14.2 nm in benzene) for CB11, even if considering electric double layers by charge effect. It seemed to lead to intermolecular cross-linking (formation of the *n*-mer of CB11S) during the sulfonation process. We studied the binding behaviors of PSS/PEO brush to linear cationic P4VPQ in an aqueous solution. As a result, rod-shaped prototype brush aggregate/P4VPQ complexes were formed, since PSS/PEO brushes abundantly bound to P4VPQ due to electrostatic interaction.

Supporting Information Available: Text giving information on the synthesis and dilute solution properties of PS/PEO prototype copolymer brushes, a table of properties for CB12, and figures showing the angular dependences and *D*(*C*) vs C for CB11, CB12, and CB11S, a Guinier plot for CB11, and hydrodynamic diameter distribution aand FE-SEM photograph of CB11. This material is available free of charge via the Internet at http://pubs.acs.org.

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