

SHORT COMMUNICATIONS

Water Soluble Bottlebrushes

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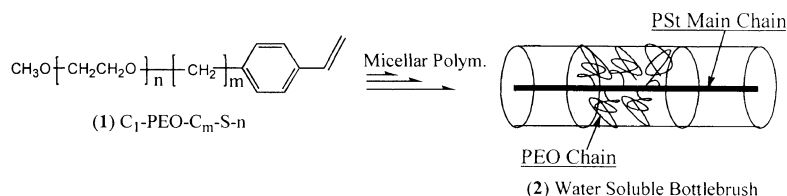
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Solution Properties /

Over the past decade, we have systematically studied the radical homo- and copolymerization of poly(ethylene oxide) (PEO) macromonomers (**1**) in homogenous and heterogeneous solutions as well as in organized self assemblies.^{1–4} Regular amphiphilic comb-shaped polymers (**2**) were prepared by organized, micellar homopolymerization of (**1**) in water.^{3–5} From structural point of view, a key characteristic of the polymacromonomer is that they have a much higher chain density around the main chain than ordinary linear polymers. Their conformational properties should thus be markedly different from linear chains due to the steric interaction between the adjacent branches.⁶ In 1992, we investigated molecular weight (MW) dependence of limiting viscosity for regular polymacromonomers (**2**) and found that at least in the MW range investigated, the exponent in the Mark–Houwink–Sakurada equation steeply approaches zero, when the degree of polymerization (n) of the side chain is higher than 44.⁷ The very low values of the exponent suggest that polymacromonomers (**2**) hydrodynamically behave as a non-draining sphere and/or constant segment density particles in tetrahydrofuran.

In remarkable contrast, in 1994, Tsukahara, Schmidt *et al.*^{8–11} reported that polymacromonomers prepared from methacrylate-terminated polystyrene macromonomer behave as semi-flexible polymers in dilute toluene solution⁹ and form lyotropic liquid crystals at a concentrated solution.^{10,11} Kuhn statistical segment length increases monotonously up to *ca.* 300 nm with branch chain length. They termed them, therefore, “molecular bottlebrushes”. Subsequently, diffusion and sedimentation experiments by Nemoto *et al.*¹² showed that their MW dependence is quantitatively described by the plate ellipsoid model. These results motivated us to investigate the MW dependence of radius of gyration, $\langle S^2 \rangle^{1/2}$, of polymacromonomers (**2**).¹³

Here we report the dimensional properties of water soluble bottlebrush polymers (**2**) prepared from *p*-alkylstyrene end-capped PEO macromonomers (**1**). These polymers were prepared in aqueous solution by free-radical micellar polymerization. PEO macromonomers with a sufficiently hydrophobic alkylstyrene end group self-assemble in water,¹⁴ and polymerization in these aggregates proceeds rapidly to high conversion and affords very high molecular weight regular amphiphilic polymers (**2**) having the unique structure of a hydrophobic backbone surrounded by a shell of hydrophilic PEO chains.

PEO macromonomers (C₁-PEO-C₄-S-50) (**1**) were prepared by reacting hydroxy-ended PEO with five-fold excess of sodium hydride and *p*-bromobutylstyrenes.⁵ The degree of polymerization of PEO and functionality of double bond are 50 and 0.9₃, respectively, determined from ¹H NMR spectrum, and the M_w/M_n is 1.10 from size exclusion chromatography (SEC) measurement. The homopolymerization of the macromonomer was carried out in water at 60°C with 4,4'-azobis(4-cyanovaleric acid) (AVA) as the initiator.¹³ The unreacted macromonomers were removed by fractionation with benzene-hexane.⁷ Pyrene partitioning experiments were carried out at 23°C.¹⁴ Steady-state fluorescence spectra were run with Hitachi F4500 and SPEX Fluorog 2 spectrophotometers at 25°C. Excitation wavelengths for pyrene and polystyrene were 338 nm and 225 nm, respectively. The *z*-averaged radius of gyration ($\langle S^2 \rangle_z^{1/2}$) and weight-averaged MW (M_w) were measured at 25°C with SEC (Tosoh Co., Ltd., two Shodex columns, SB-806MHQ) connected to refractive index detector and multiangle laser light scattering instrument (MALLS) (Wyatt Technology Co., Ltd., DAWN-DSP). The Rayleigh ratio $R(90)$ at a scattered angle of 90° was based on the Rayleigh ratio of pure toluene at wavelength of 632.8 nm at 25°C. The scattering volume correction for the detector



Scheme 1.

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at angles other than 90° was performed using the scattering intensities of 0.05 N NaCl solution containing PEO with $M_w = 2.24 \times 10^4$ and $M_w/M_n = 1.15$.¹⁵ The influence of variation of refractive index of the sample solution on the scattering angle and volume was negligibly small in the present study. The precision and reliability of the MALLS-SEC are reported elsewhere.¹⁶ Excess refractive indices of PEO comb-shaped polymers in 0.05 N NaCl were determined to be 0.134₅ at 25°C using the differential refractometer, RM-102 of the Otsuka Electronics Co., Ltd.

Figure 1 presents double logarithmic plots of $\langle S^2 \rangle_z$ (open circles) of poly(C₁-PEO-C₄-S-50) in 0.05 N NaCl solution against M_w . At M_w higher than 3×10^5 , the experimental points can be fitted by a smooth convex curve. The slope of the curve is about 1.5₄ for M_w between 5×10^5 and 1×10^6 and about 1.1₅ for M_w between 3×10^6 and 3×10^7 . This change in the slope implies that the poly(C₁-PEO-C₄-S-50) molecule is rodlike in lower molecular weight and approaches a spherical random coil as M_w increases. This is characteristic of semi-flexible polymers.¹⁷ According to Benoit and Doty,¹⁸ the unperturbed $\langle S^2 \rangle_0$ of a monodisperse wormlike chain is expressed by

$$\langle S^2 \rangle_0 = \frac{qM}{3M_L} - q^2 + \frac{2q^3 M_L}{M} \left[1 - \frac{qM_L}{M} \left(1 - e^{-(M/qM_L)} \right) \right] \quad (1)$$

with the molecular weight M , the persistence length q , and shift factor $M_L = M/L$, where L is the contour length of a wormlike chain. Murakami *et al.*¹⁹ showed that when $M/(2qM_L) > 2$, eq 1 can be approximated by

$$\left(\frac{M}{\langle S^2 \rangle_0} \right)^{1/2} = \left(\frac{3M_L}{q} \right)^{1/2} \left(1 + \frac{3qM_L}{2M} \right) \quad (2)$$

Zhang *et al.*²⁰ showed that for $M/(2qM_L) < 2$ eq 1 may be replaced by

$$\left(\frac{M^2}{12\langle S^2 \rangle_0} \right)^{2/3} = M_L^{4/3} + \frac{2M_L^{1/3}}{15q} M \quad (3)$$

When the Murakami and Zhang plots are applied to the present data for $M_w > 7 \times 10^5$ and $5 \times 10^5 < M_w < 7 \times 10^5$, respectively, both plots afford straight lines to give $q = 17 \pm 1$ nm and $M_L = (1.03 \pm 0.1) \times 10^4$ nm⁻¹, within experimental error. The value of M_L is in good agreement with that ($M_L = 1.05 \times 10^5$) calculated from molecular structure, with the main chain assuming a trans zigzag conformation. The theoretical curve (broken line) in Figure 1 was computed from eq 1 with $q = 17$ nm and $M_L = 1.03 \times 10^4$ nm⁻¹. The theoretical curve describes the chain length dependence of the dimension of poly-macromonomers for $M_w < 1.5 \times 10^6$ but above it deviates from the experimental data. This is most likely due to excluded-volume effects.

The Yamakawa–Stockmayer–Shimada (YSS) theory^{21–23} predicts that the radius expansion factor α_s [$= (\langle S^2 \rangle / \langle S^2 \rangle_0)^{1/2}$] is a universal function of the scaled excluded-volume parameter \tilde{z} defined by

$$\tilde{z} = \left(\frac{3}{4} \right) K(\lambda L) z \quad (4)$$

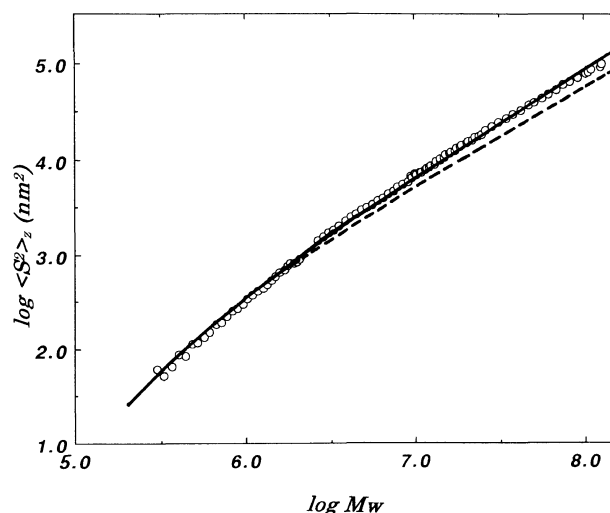


Figure 1. Double logarithmic plots of $\langle S^2 \rangle_z$ of poly(C₁-PEO-C₄-S-45) in 0.05 N NaCl solution against M_w at 25°C. The solid line is for theoretical values calculated for the perturbed Kratky Porod chain with $q = 17$ nm, $M_L = 1.03 \times 10^4$ nm⁻¹, and $B = 5.78$ nm; dashed line, theoretical values for the unperturbed KP chain with $q = 17$ nm, $M_L = 1.03 \times 10^4$, and $B = 0$ nm.

with

$$z = \left(\frac{3}{2\pi} \right)^{3/2} (\lambda B)(\lambda L)^{1/2} \quad (5)$$

and

$$K(\lambda L) = \frac{4}{3} - 2.711(\lambda L)^{-1/2} + \frac{7}{6}(\lambda L)^{-1} \quad \text{for } \lambda L > 6 \quad (6)$$

or

$$K(\lambda L) = (\lambda L)^{-1/2} \exp[-6.611(\lambda L)^{-1} + 0.9198 + 0.03516(\lambda L)] \quad \text{for } \lambda L \leq 6 \quad (7)$$

where λ^{-1} is the Kuhn segment length ($= 2q$) and z is the conventional excluded-volume parameter for the Kratky–Porod (KP) chain and B is the excluded-volume strength ($= \beta/a^2$) for the KP chain with a as the bead spacing and β , the binary cluster integral. The YSS theory with the Domb–Barrett function²⁴ for the α_s^2 is applied to the experimental data of $\langle S^2 \rangle_z$ and M_w in Figure 1. The experimental values in $3 \times 10^5 < M_w < 1 \times 10^8$ are quantitatively described in terms of the YSS theory (solid line) with $B = 5.78$ nm, $q = 17$ nm, and $M_L = 1.03 \times 10^4$ nm⁻¹ within experimental error. The Kuhn segment number, $n_K (= M_w/(2qM_L))$, $M_w = 1.5 \times 10^6$ at which onset of excluded-volume effects appears is calculated to be 4.3, in agreement with the YSS theory.²¹ The poly-macromonomer, poly(C₁-PEO-C₄-S-50) thus behaves in water as an unperturbed semi-flexible polymer in the region of $n_K < 4.3$ and as a perturbed semi-flexible polymer when $n_K > 4.3$.

Preliminary experiments on other comb-shaped polymers with different PEO chain lengths suggest that the persistence length increases with PEO chain length. The steric hindrance of the concentrated long PEO chain around a main chain appears responsible for the increase in stiffness of the comb-shaped polymers.

To characterize the environment of the polystyrene

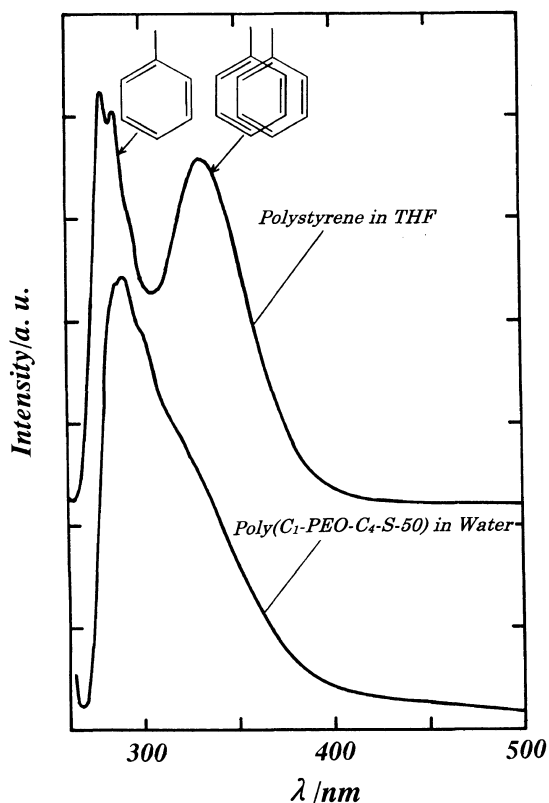


Figure 2. Fluorescence spectra of poly(C_1 -PEO- C_4 -S-50) in water and polystyrene ($M_w = 3.79 \times 10^4$, $M_w/M_n = 1.05$) in THF: $\lambda_{ex} = 255$ nm and concentration is 0.10 wt%.

backbone, we carried out two experiments using fluorescence spectroscopy. We first examined the intrinsic fluorescence of the polystyrene main chain. In Figure 2 ($\lambda_{ex} = 255$ nm) we compared the dilute solution fluorescence of (2) in water with that of polystyrene itself in tetrahydrofuran (THF). In the poly(macromonomer) the excimer intensity at 335 nm is very much reduced compared to polystyrene in THF. This indicates that the conformational mobility of the hydrophobic polystyrene backbone of the bottlebrush is much restricted so that the phenyl groups are relatively isolated from one another. This effect parallels the increase in chain stiffness of the bottlebrush polymer in water.

Another way to characterize the "hydrophobicity" of the polystyrene backbone in aqueous solutions of (2) is to examine the effects of the polymer for enhancing the solubility of non-polar substances in water. We made fluorescence measurements to follow the solubilization of pyrene in water in the presence of (2). These experiments show that a limiting pyrene solubility increases linearly with the concentration of (2), with only about one pyrene dissolved per 50 backbone repeat units. In Figure 3, the vibronic fine structure of the pyrene fluorescence (I_1/I_3) is plotted against polymer concentration. I_1/I_3 is 1.5 ± 0.1 and almost constant at all polymer concentrations. This is consistent with the pyrene solubilized in a rather hydrophilic environment, such as on a backbone-PEO interface. A semiflexible polymer is thus demonstrated in which strong repulsion between adjacent PEO chains leads to significant stretching and conformational distortion of the polystyrene main chain, so that even in aqueous solution it

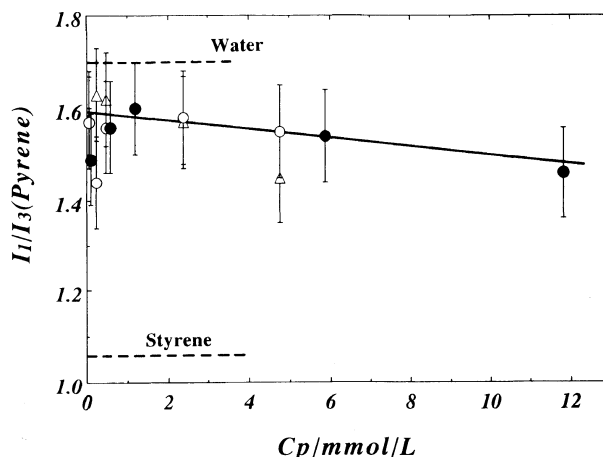


Figure 3. Intensity ratio (I_1/I_3) of the vibrational bands of pyrene-saturated solutions against polymer concentration: (Δ) poly(C_1 -PEO- C_4 -S-50); (\circ) poly(C_1 -PEO- C_1 -S-50); (\bullet) poly(C_1 -PEO- C_1 -S-17).

is unable to form hydrophobic microdomains.

The present results seem different from the previous intrinsic viscosity; we recently fractionated samples and observed that in high M_w region, $[\eta]$ increases steeply with M_w .²⁵ Theoretical treatment is now in progress. We hope to examine a broader variety of polymers and carry out NMR relaxation, dynamic light scattering, intrinsic viscosity, fluorescence spectroscopy, and cloud point measurements.

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