Conformational Properties of Cylindrical Rod Brushes

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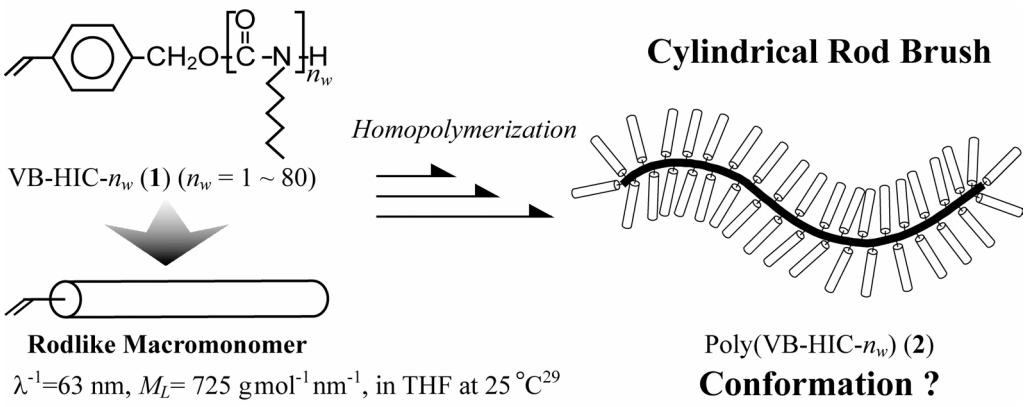
Since an initial report by Schmidt and Tsukahara et al.[1] in 1994, poly(macromonomer)s, bottle brush macromolecules, or cylindrical polymer brushes, which have one of the best defined comb-branching architecture, have attracted considerable attention. A number of brush polymers consisting of flexible polymer main and side chains have so far been prepared[2]. One interesting and very valuable finding in conformational properties of the brushes with the regular comb-branching structure is that the main chain remarkably stiffens in a dilute solution and solid state, despite being originally composed of flexible chains. The main chain stiffness parameter (λ^{-1}) in the wormlike cylinder model increases with increasing side chain length and solvent power. Cylindrical brushes, however, are limited to those consisting of flexible main and side polymer chains in solution. Little experimental work is known about brushes consisting of semi-flexible, or rodlike polymer side chains[3].

In the present paper, we report many details of the experimental works of the conformational properties of poly(*n*-hexyl isocyanate) PHIC rod brushes in THF at 25 °C by small-angle X-ray scattering (SAXS) and SEC-MALS, as shown in Scheme 1.



Scheme. Reaction scheme for cylindrical rod brush using PHIC rodlike macromonomer.

The mean-square cross-sectional radius of gyration ($\langle R_c^2 \rangle_o$) of the brush at an infinite dilution is determined by SAXS measurements and rationalized as a function of n_w. The experimental value of $\langle R_c^2 \rangle_o$ gradually increases with n_w but above n_w higher than 20 increases to follow the scaling law of $\langle R_c^2 \rangle_o \propto n_w^{0.87}$. The experimental n_w-dependence of $\langle R_c^2 \rangle_o$ may be explained by the wormlike comb model whose main and side chains have different stiffness parameters. The molecular weight dependence of z-averaged mean-square radius of gyration ($\langle Rg^2 \rangle_z$) of the brush is determined and analyzed in terms of the wormlike cylinder model taking into account the end effects. The parameters characteristic of the rod brush in THF solution, such as the main chain stiffness parameter (λ^{-1}), the molecular weight per unit contour length (M_L), the excluded-volume strength (B) are determined and rationalized as a function of the contour length of the side rod (L_s). The polystyrene main chain stiffness of the rod brush λ^{-1} remarkably increases by the densely located rod side chains, to follow the scaling law of $\lambda^{-1} \propto L_s^{1}$. The backbone stiffness of the rod brush is found to be much higher than that of the flexible brush consisting of flexible polystyrene side chains with the corresponding L_s.

References

1) M. Wintermantel, M. Schmidt, Y. Tsukahara, K. Kajiwara, S. Kohjiya, *Macromol. Rapid Commun.*, **15**, 249(1994). 2) K. Ito, S. Kawaguchi, *Adv. Polym. Sci.*, **142**, 129 (1999). 3) M. Kikuchi et al., *Macromolecules*, **41**, 6564 (2008).