Backbone Stiffness of Cylindrical Brushes Consisting of Rodlike Side Chains. Influence of Side Chain Length on Main Chain Stiffness
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Introduction
A macromonomer is any polymer or an oligomer with a polymerizable functionality as an end group. Formally, the macromonomer homopolymerizes to afford a star- or comb-shaped polymer and copolymerizes with the conventional monomer to give graft copolymer. Recently, some interesting properties of poly(macromonomers) have been explored as a simple model of brush polymers. However, most of macromonomer used in these studies is limited to that consisting from the flexible chains.[1,2]

In the present study, we report conformational properties of the polymacromonomers, consisting of a flexible polystyrene chain backbone and rod-like poly(n-hexyl isocyanate)(PHIC) side chains by SAXS, light scattering, [η] and AFM measurements in THF.[3-5]

Experimental
SAXS Measurements. SAXS measurements of polymacromonomers were carried out in THF at 25 °C, using BL-10C with a synchrotron orbital radiation as an X-ray source set up in the Photon Factory of the High Energy Accelerator Organization at Tsukuba, Ibaraki, Japan. The wavelength of the X-ray was 1.488 Å. The scattered intensity was recorded by a position-sensitive proportional counter (PSPC) with 512 channels over a scattering vector range from 0.02 to 0.30 Å⁻¹. The scattered vector was calibrated using a sixth peak of dry collagen.

Results and Discussion
Figure 1 shows a double logarithmic plot of cross-sectional radius of gyration, <Rc>o₁/₂ of poly(VB-HIC-nw) determined by SAXS in THF with weight averaged degree of polymerization of the side chain (nw). The solid curve is a theoretical one given by the equation,

\[ <Rc^2>_o = <Rc^2>_m + \frac{(2L_w)^2}{12} \]

where \(<Rc^2>_o\) is that of the main chain and \(L_w\) is the weight-averaged contour length of a rod. The solid curve quantitatively describes the experimental data, implying the brush-like conformation consisting of the rods as a side chain.

Figure 2 shows a plot of main chain stiffness parameter (λ⁻¹) with contour length of side chain. It is clearly seen that the main chain stiffness linearly increases with increasing side chain length.

References
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