

Synthesis and conformational properties of polymacromonomers consisting of rod-like poly(*n*-hexyl isocyanate) macromonomers

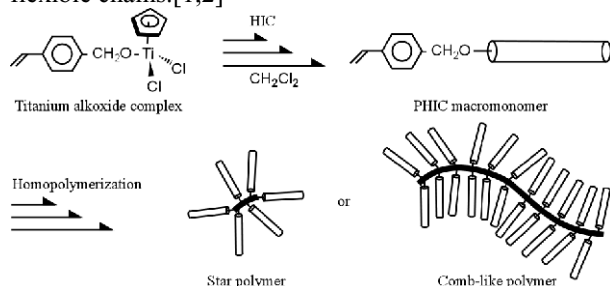
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Introduction

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]



Scheme. Reaction schemes of rod-like macromonomers and polymacromonomers.

In the present study, we report synthesis and conformational properties of the polymacromonomers, consisting of a flexible polystyrene chain backbone and rod-like PHIC side chains by SAXS, light scattering, $[\eta]$ and AFM measurements in THF.

Experimental

Syntheses of polymacromonomers

The macromonomers (VB-HIC-*n*) were prepared by living coordination polymerization of HIC in CH_2Cl_2 at room temperature using titanium alkoxide complex as an initiator, as shown in the scheme.[3] The homopolymer, poly(VB-HIC-*n*)s were prepared by radical homopolymerization of VB-HIC-*n* using dimethyl 2, 2'-azobis(2-methyl propionate) (V-601) as an initiator in *n*-hexane at 60 °C and fractionated by repeating fractional precipitation.

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 double logarithmic plot of radius of gyration, R_g of poly(VB-HIC-*n*) determined by SEC-MALS in THF with weight averaged degree of polymerization of the main-chain N_w . The R_g data for linear polystyrene are plotted in the figure for comparison. It can be seen clearly that R_g at fixed N_w increases with increasing side chain length, most likely due to the increase of chain stiffness.

The experimental data for poly(VB-HIC-*n*) could be quantitatively described in terms of the wormlike chain model with the thickness and end effects. It is concluded that the chain stiffness of the polymer is increased by the presence of the rod-like side chains.

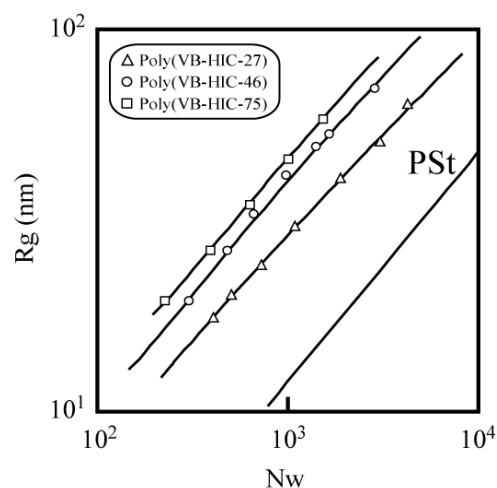


Figure 1. Dependence of the measured R_g on main-chain length (expressed in terms of the degree of polymerization) for poly(VB-HIC-*n*) (*n* = 27, 46 and 75) in THF. The solid lines show the theoretical values calculated from unperturbed cylinder worm-like chain model.

References

- [1] K. Ito et al. *Adv. Polym. Sci.* 142, 129(1999).
- [2] S. Kawaguchi et al. *Adv. Polym. Sci.*, **175**, 317(2005).
- [3] M. Kikuchi, et al. *Des. Monom. Polym.*, **7**, 603 (2004).

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