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Preparation and dimensional properties of poly(*n*-hexyl isocyanate) rod-like macromonomers in hexane

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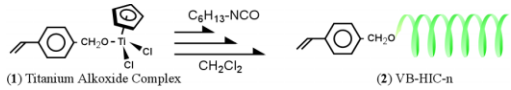
Introduction

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 a conventional monomer to give a graft copolymer. Thus the macromonomer serves as a convenient building block to constitute arms or branches of known structure in the resulting polymer. A large number of macromonomers, differing in the type of the repeating monomer and the end-group have so far been prepared, thereby offering the possibility of construction of an enormous number of branched polymers in a variety of architectures, combinations, and compositions. Polymerization and copolymerization of macromonomers have also been studied in great detail in order to understand their unique behavior in comparison with that of conventional monomers.Their useful application in design of polymeric microspheres has also been appreciated recently. Some interesting properties of poly(macromonomers) have also been explored very recently as a simple model of brush polymers which are of increasing interest [1,2].

In the present paper, we report preparation of novel rod-like macromonomers of poly(*n*-hexyl isocyanate) (**2**) (VB-HIC-n) with a *p*-vinylbenzyl polymerizable functional group by a coordination living polymerization of *n*-hexyl isocyanate (HIC) with titanium alkoxide complex (**1**) as an initiator, as shown in below. The dimensional characterizations of the VB-HIC-n macromonomers in hexane at 25 °C have been carried out by SAXS measurements.



(**1**) Titanium Alkoxide Complex (**2**) VB-HIC-n

Experimental

Synthesis. Initiator (**1**), 4-vinylbenzyloxy-dichloro(cyclopentadienyl) titanium (IV) was synthesized by reaction of sodium *p*-vinylbenzyl alcoxide with trichloro(cyclopentadienyl) titanium (IV) in toluene under argon atmosphere with 70-90% in yield [3]. The rod-like macromonomers (2) (VB-HIC-n, n is a degree of polymerization and 9, 13, 19, 26, 57, 75, 88) with narrow molecular weight distribution and high double bond functionality were successfully synthesized by coordination living polymerization of HIC in CH_2Cl_2 at room temperature.

SAXS Measurements. SAXS measurements of VB-HIC-n in hexane were carried out 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 shows double logarithmic plot of radius of gyration, $\langle S^2 \rangle_z^{1/2}$ of VB-HIC-n macromonomers determined by SAXS (○) in hexane at 25 °C with M_w, together with reference values (□) [4]. The present data may be perfectly described by wormlike chain model (solid line) with persistence length q = 42 nm and shift factor M_L=715 nm^{-1}. The result implies that the macromonomers are considered as a stiff rod.

References

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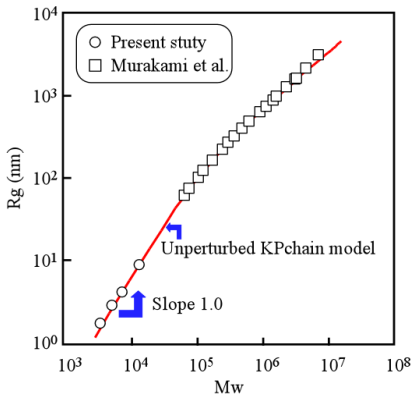

Figure. Comparison of the observed Rg with the theoretical values (solid line) calulated from unperturbed KP chain model equation.

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