

Solution Properties of Cylindrical Poly(*n*-hexyl isocyanate) Brushes

Seigou KAWAGUCHI^{1*}, Moriya KIKUCHI¹, Yuji Jinbo²,
Yoshinobu Izumi², and Katsutoshi Nagai¹

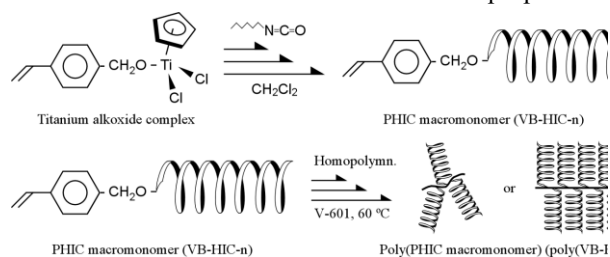
¹Department of Polymer Science and Engineering, Faculty of Engineering,
Yamagata University, Yonezawa 992-8510, Japan

²Graduate Program of Human Sensing and Functional Sensor Engineering,
Graduate School of Science and Engineering, Yamagata University, Yonezawa 992-8510, Japan

Introduction

A macromonomer is any polymer or an oligomer with a polymerizable functional group at 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. Some interesting properties of poly(macromonomers) have also been explored very recently as a simple model of brush polymers which are of increasing interest. However, most of the macromonomer which has so far been prepared is the macromonomer with a flexible chain [1,2].

In the present study, we report preparation of novel rod-like poly(*n*-hexyl isocyanate) (VB-HIC-*n*) macromonomers with a *p*-vinylbenzyl polymerizable functional group by a coordination living polymerization of *n*-hexyl isocyanate (HIC) with titanium alkoxide complex as an initiator, as shown in scheme. The radical homopolymerization behavior of the PHIC macromonomers and their dilute solution properties of



Scheme. Reaction scheme of rodlike macromonomer and poly(VB-HIC-*n*) using their macromonomer.

novel comb-shaped poly(PHIC macromonomer) have been studied by SAXS, SEC-MALS, [η] and AFM.

Experimental

Initiator, titanium alkoxide complex was synthesized by reaction of sodium *p*-vinylbenzyl alcoxide with trichloro(cyclopentadienyl) titanium (IV) in benzene under argon atmosphere with 70-90% in yield [3]. PHIC macromonomers were prepared by living coordination

polymerization of HIC in CH₂Cl₂ at room temperature using the titanium alkoxide complex as an initiator [4]. Homopolymerization behavior of the rod-like macromonomers was investigated at 60 °C in *n*-hexane using dimethyl 2,2'-azobis (2-methyl propionate) (V-601) as an initiator. The mean square radius of gyration of poly(VB-HIC-*n*)s were determined by small-angle X-ray scattering (SAXS) and size exclusion chromatography equipped with a multi-angle laser light scattering detector (SEC-MALS) measurement in THF.

Results and Discussion

Macromonomers (VB-HIC-*n*, *n* is a degree of polymerization and 27, 46, 75) with high degree of conversion (80~90 %) and high double bond functionality were found to be successfully prepared. The polymerization was found to proceed in a manner of living polymerization to afford PHIC macromonomer with narrow molecular weight distribution ($M_w/M_n \leq 1.20$). Figure shows double logarithmic plot of radius of gyration, R_g of poly(VB-HIC-46) determined by SAXS (\square) and SEC-MALS (\circ) in THF with M_w . The present data may be described by wormlike chain model (solid line) with a persistence length $q = 22$ nm and shift factor $M_L = 2.35 \times 10^4$ nm⁻¹. The result implies that the polymacromonomer behaves as a semi-flexible polymer. Solution properties of polymacromonomers with different side chain are currently under study.

References

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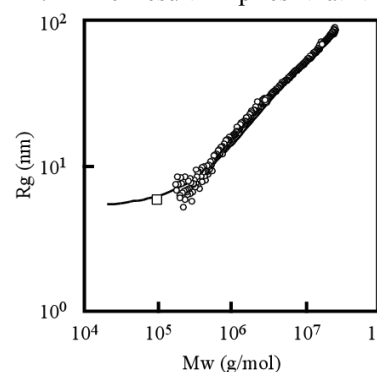


Figure. Comparison of the measured R_g with the theoretical values (solid line) calculated from unperturbed KP chain model equation.