

Title	光学活性シラシクロブテン誘導体の開環重合
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Citation	
Issue Date	2002-03
Type	Thesis or Dissertation
Text version	none
URL	http://hdl.handle.net/10119/2110
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Ring-Opening Polymerization of Optically Active Silacyclobutene Derivatives

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Abstract:

To control the stereoregularity and the molecular weight and its distribution of a polycarbosilane, poly[*methyl(1-naphthyl)silylene(o-phenylene)methylene*], anionic and Pt-catalyzed ring-opening polymerizations (ROPs) of 1-methyl-1-(1-naphthyl)-2,3-benzosilacyclobut-2-ene (**MNBSC**) were attempted.

The Ring opening of **MNBSC** by *n*-butyllithium, benzylolithium, and methyldiphenylsilyllithium proceeded regiospecifically but not stereoselectively. The nucleophilic attack of an alkylolithium and a silyllithium occurs selectively on a silicon atom and a methylene carbon atom of **MNBSC**, respectively, and silicon-methylene carbon bond of the silacyclobutene ring is selectively cleaved in both cases. Enantiomer excess (ee) of the ring-opened products, (-)-1-[(*n*-butyl)methyl(1-naphthyl)silyl]-2-[(methyldiphenylsilyl)methyl]benzene ((-)-**BNDPSB** : $[\alpha]_{\text{D}}^{25} = -0.38$, c 1.06, CHCl_3) and (+)-1-[(benzyl)methyl(1-naphthyl)silyl]-2-[(trimethylsilyl)methyl]benzene ((+)-**BMNTSB** : $[\alpha]_{\text{D}}^{25} = +5.12$, c 1.29, CHCl_3), by *n*-butyllithium and benzylolithium as initiation and model propagation reactions are 33% and 18%, respectively. The ring-opened product, 1-{1,2,2,2-tetramethyl-1-(1-naphthyl)disilyl}-2-[(methyldiphenyl-silyl)methyl]benzene ((-)-**TMNDPSB** : $[\alpha]_{\text{D}}^{25} = -4.79$, c 0.56, CHCl_3), by methyldiphenylsilyllithium is 25%ee. Anionic ROP of optically pure (+)-**MNBSC** ($[\alpha]_{\text{D}}^{28} = +136$, c 1.18, hexane) gave optically active poly[*methyl(1-naphthyl)silylene(o-phenylene)(methylene)*] (*n*-butyllithium : (-)-**P-1a** : $M_n = 25,400$, polydispersity index (PDI) = 2.1, ($[\alpha]_{\text{D}}^{27} = -21.7$, c 1.03, CHCl_3); methyldiphenylsilyllithium : (-)-**P-1b** : $M_n = 9,340$, PDI = 3.0, ($[\alpha]_{\text{D}}^{24} = -22.4$, c 1.07, CHCl_3)). Although the initiator efficiency is not quantitative under the examined conditions, the molecular weights of the formed polymers can be roughly controlled by the monomer and initiator ratio. Triad concentration of (-)-**P-1a** is estimated as $I : H : S = 0.35 : 0.43 : 0.22$ by deconvolution assuming Gaussian distribution.

Reaction of **MNBSC** with platinum-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (PDT) as catalyst (0.1 mol%) gave a polymer, **P-1d**, possibly cyclic, with $M_n = 1,210,000$, PDI = 1.8 and cyclic dimer produced via reductive-elimination. Reaction of **MNBSC** with PDT in the presence of Et_3SiH (**MNBSC** : $\text{Et}_3\text{SiH} = 1 : 1$) gave the following : (1) 1-triethylsilyl-2-[(methyl(1-naphthyl)silylmethyl)benzene (**TEMNSB**) in 54% yield, (2) a dimer, 1-[(methyl(1-naphthyl)(2'-triethylsilylphenylmethyl)silyl)-2-[(methyl(1-naphthyl)silylmethyl)benzene (**MNTEPSB**) in 18% yield, and (3) a trimer, 1-[(methyl(1-naphthyl)(2'-triethylsilylphenylmethyl)silyl)-2-[(methyl(1-naphthyl)[2'-[(methyl(1-naphthyl)silylmethylphenyl]]silyl-methyl)benzene in 11% yield, through regioselective ring-opening reaction, followed by the σ -bond metathesis process. Molecular weight of the formed polymers can be controlled by the amount of Et_3SiH . When optically pure (+)-**MNBSC** was used, (-)-**TEMNSB** ($[\alpha]_{\text{D}}^{25} = -16.3$, c 1.26, CHCl_3) and (+)-**MNTEPSB** ($[\alpha]_{\text{D}}^{25} = +19.8$, c 0.82, CHCl_3) are proved to have enantiomer excess (ee) or optical purity (op) higher than 99%. These products are considered to be formed from the intermediate cyclic Pt complexes, which were formed by a regio- and stereoselective oxidative-addition of silicon-aryl bond of (+)-**MNBSC** to Pt, followed by a

stereoselective σ -bond metathesis process. Pt-catalyzed ROP of optically pure (+)-**MNBSC** provided an isotactic and optically pure (-)-**P-1d** ($M_n = 356,000$, PDI = 1.7, ($[\alpha]_D^{27} = -33.5$, c 1.11, CHCl_3)).