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Author(s)	大石，基
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New Synthetic Approach to Optically Active and Stereoregular Poly(siloxane)s

Kawakami Lab. 940006 Motoi Oishi

ABSTRACT

The synthesis and application of optically active and stereoregular polymers are topic currently attracting much attention due to the fascinating properties of naturally occurring polymers. In synthetic polymer chemistry, it seems that one of the most challenging tasks is to construct functional polymeric systems that will be as efficient as those in natural systems, and the optically active and stereoregular synthetic polymers have today great interest and importance in this respect. However, synthesis of optically active and/or stereoregular polymers consisting of heteroatom backbone has not been reported yet different from hydrocarbon polymer systems.

Poly(siloxane)s characterized by a regularly alternating -Si-O- heteroatom backbone have been widely used as various materials by taking advantage of their highly flexible structure and high thermal stability. In some applications based on the architecture of poly(siloxane)s, a great deal of attention will be directed to optically active and stereoregular poly(siloxane)s, which are expected to exhibit significant and unique properties as observed in natural systems. This study was focused on the development of new synthetic approach to optically active and/or stereoregular poly(siloxane)s.

The preparation of highly optically active bifunctional 1,3-dimethyl-1,3-diphenyldisiloxane derivatives containing two asymmetric silicon centers such as 1,3-dimethyl-1,3-diphenyldisiloxanediol [(*S*,*S*):(*R*,*S*):(*R*,*R*)=100:0:0] and 1,3-dihydro-1,3-dimethyl-1,3-diphenyldisiloxane [(*S*,*S*):(*R*,*S*):(*R*,*R*)=84:16:0] was attained by the development of highly stereospecific halogenating cleavage reaction of the silicon-naphthyl bond of (1*S*,3*S*)-1-(4-methoxy-1-naphthyl)-1,3-dimethyl-3-(1-naphthyl)-1,3-diphenyldisiloxane (98% inversion of configuration of silicon atom).

A highly stereoregular (diisotactic) and optically active poly(siloxane)s were prepared by the polycondensation reactions of (*S,S*)-1,3-dimethyl-1,3-diphenyldisiloxanediol with bis(dimethylamino)dimethylsilane or bis(dimethylamino)diphenylsilane. This is the first example of optically active and stereoregular poly(siloxane). In particular, poly(siloxane) prepared from (*S,S*)-1,3-dimethyl-1,3-diphenyldisiloxanediol and bis(dimethylamino)dimethylsilane was proven to be highly diisotactic and optically active as estimated by ^{1}H NMR analysis. Synthesis of poly(methylphenylsiloxane) rich in syndiotacticity (triad tacticity; *S*(*rr*):*H*(*rm*):*I*(*mm*)=60:32:8) was also attained for the first time using the highly stereoselective cross-dehydrocoupling polymerization of optically active (*S,S*)-1,3-dimethyl-1,3-diphenyldisiloxanediol with 1,3-dihydro-1,3-dimethyl-1,3-diphenyldisiloxane (95% retention of configuration of silicon atoms).

The Rh-catalyzed cross-dehydrocoupling polymerization of *meso*-1,3-dimethyl-1,3-diphenylsiloxanediol with methylphenylsilane in the presence of triethylamine or (-)-spartein showed an apparent stereo-recognition feature, affording poly(methylphenylsiloxane) with 75% *mrrm* pentad tacticity. The mechanism for the stereo-recognition feature is considered that silanol (SiOH) *m* diad chain end may preferentially react with hydrosilane (SiH) with *rm* triad chain end.

Novel optically active hyperbranched poly(carbosiloxane) was prepared by the Pt-catalyzed hydrosilylation polymerization reactions with various feed ratios of optically active (*S,S*)-1,5-di(1-naphthyl)-1,5-dphenyl-1,5-diivinyl-3-methyltrisiloxane (>99%ee, AB$_2$-type monomer) and 1,1,3,3-tetramethyl-1-vinyldisiloxane (AB-type monomer). This is the first example of optically active hyperbranched silicon-containing polymers.

In this thesis, new synthetic approach to novel optically active and/or stereoregular poly(siloxane)s was described for the fist time by the polymerization of optically active bifunctional disiloxane derivatives.