Formation and Reactions of Bromo- and Iodosilane Intermediates

(プロモおよびヨードシラン中間体の生成と反応)

氏名 呂洲 (Zhou Lu)

Bromo- and iodosilanes are versatile reagents for the preparation of various organosilicon compounds. In this thesis, the formation of diiodo- and dibromosilanes from bis(dimethylamino)dimethylsilane, and iodo- and bromopolysiloxanes from two types of hydrosiloxanes, \( \alpha,\omega \)-dihydopoly(dimethylsiloxane) and cyclotetra(hydromethylsiloxane) in the presence of a catalytic amount of PdCl\(_2\), and their reactions are described.

In Chapter 1, ring-opening halosilation of cyclic ethers with reagents of (Me\(_2\)N\(_2\))\(_2\)SiMe\(_2\)/4Mel (1a) and (Me\(_2\)N\(_2\))\(_2\)SiMe\(_2\)/4allylBr (1b) was studied. Tetrahydrofuran and cyclohexene oxide reacted with 1a and 1b to give ring-opened di(haloalkoxy)dimethylsilanes in good yield. With less strained tetrahydropyran, however, only reagent 1a gave the ring-opened product. Reactions of reagents 1a and 1b with propylene oxide also proceeded smoothly, although the regioselectivity was rather low. When similar reactions were carried out with (Me\(_2\)N\(_2\))\(_2\)SiMe\(_2\)/2Mel (2a) and (Me\(_2\)N\(_2\))\(_2\)SiMe\(_2\)/2allylBr (2b) in a ratio of cyclic ethers/2a or 2b = 1/1, the corresponding 1:1 adducts were obtained.

In Chapter 2, palladium-catalyzed formation of iodo- and bromopolysiloxanes from two types hydrosiloxanes, \( \alpha,\omega \)-dihydopoly(dimethylsiloxane) (3) and cyclotetra(hydromethylsiloxane) (4), and their reactions were studied. Treatment of 3 with mixtures of cyclic ethers or lactones and Mel or allylBr in the presence of a catalytic amount of PdCl\(_2\) gave the corresponding \( \alpha,\omega \)-bis(haloalkoxy or haloalkanoyloxy)poly(dimethylsiloxane)s in good yields, via iodo- or bromopoly(dimethylsiloxane)s intermediates. Similar palladium-catalyzed reactions of 4 with THF/Mel, THF/allylBr, and \( \delta \)-valerolactone/allylBr afforded cyclo(halobutoxy- and bromobutanoyloxy)methylsiloxane)s in moderate yields. The reaction of \( \alpha,\omega \)-dibromopoly(dimethylsiloxane) with 2,5-dilithiothiophene gave a
polymethylsiloxane-thiophene alternating polymer in 83% yield.

In Chapter 3, the reactions of dilithiooligothiophene with \( \alpha, \omega \)-dibromooligo(dimethylsiloxane) prepared by Pd-catalyzed dehydrobromination of \( \alpha, \omega \)-dihydrooligo(dimethylsiloxane) with \( i \)-PrBr were studied. The reactions proceeded smoothly to give polymers composed of alternately arranged oligo(dimethylsiloxane) and oligothiophene units, \([\text{Me}_2\text{SiO}]_x\text{SiMe}_2(\text{C}_3\text{H}_2\text{S})_y\text{]}_n\) (\( x = \text{ca. } 8, y = 2-5 \)). Poly[dimethyl(siloxanylene)heptathiophenylene] (PDMS-7T) was obtained by the Stille-coupling reaction of \( \alpha, \omega \)-bis(5-bromo-2-thienyl)oligo(dimethylsiloxane) with bis(tributylstannyl)dibutylquinquethiophene in moderate yield. Spin-coated film of PDMS-7T polymer showed semi-conducting properties in the thin film transistor system, after annealing at 60 °C.

In Chapter 4, alternate polymers composed of pyrene-containing \( \pi \)-conjugated systems and oligosiloxane chains were prepared. Polymer–SWNT hybrids were prepared as brownish black solids by the ball-milling, which are the first example of siloxane-based SWNT-solubilising reagents. Film morphology of PDMS-TAPAT was also explored, showing the microphase separated structure, which could be controlled by annealing the film.

On the basis of the studies summarized above, it can be concluded that iodo- and bromosilane equivalents are of importance not only as halosilation reagents with cyclic ethers and lactones, but also as useful building units of organosilicon polymers.