Chapter 8
Organosilicon – Organic Hybrid Polymers and Materials

Abstract Hybrid organic-organosilicon materials, obtained by the combination of molecular organic and organosilicon components, have been considered potentially attractive for the purpose of development of new materials with distinct and specific properties, if compared to single organic and organosilicon constituents. One of the most useful methods for the synthesis of such materials is based on hydrosilylation processes. In this chapter, hydrosilylation is discussed in the aspects of its use for organic polymer modification and syntheses of multiblock and segment polymers. Another part of this chapter is devoted to the manufacture of nanocomposite, via hydrosilylation by using functionalised silsesquioxanes as fillers. Finally, the application of hydrosilylation processes to functionalisation of surfaces of materials as well as silicon single crystals and porous silicon is presented.

8.1 Functionalisation of Unsaturated Organic Polymers by Silicon Compounds

The hydrosilylation reaction of unsaturated polymers offers a useful and convenient method for preparing silane-modified polymers which may find potential applications as rubber materials, adhesives and drug delivery agents [1]. The hydrosilylation of vinyl- or allyl-containing organic monomers or macromonomers by hydrosilanes or hydrosiloxanes can lead to block or graft copolymers and hybrid materials. The hydrosilylation of unsaturated polymers (e.g. polybutadiene, polyisoprene, polyesters, other polyenes, polycarbonates) with silane having hydrolysable substituents at silicon atoms leads to the formation of polymeric systems with enhanced activity toward mineral fillers [2]. Both > C≡C< as well as >C=O bonds are capable of hydrosilylation. This modification is connected with a reversed use of the silane (siloxane) coupling agents. Trialkoxysilyl groups are commonly incorporated into the polymers by Pt-catalysed hydrosilylation of internal or terminal olefinic bond.
The hydrosilylation of polyisobutylene telomers by various chlorohydrosilanes proceeds after the substitution of chlorine atom by living polystyrene anions $\text{Pst}^-$ to a variety of glassy rubber block co-polymers [3]:

\[
\text{CH}_2=\text{CH-CH}_2 + \text{HSiCl} \xrightarrow{\text{cat.}} \text{ClSiCH}_2\text{CH}_2 \text{SiCl}_2
\]  

(8.2)

The hydrosilylation has been investigated as a possible method for polymer functionalisation in the solution [4–6] but also in the melt-phase. For example, the melt-phase hydrosilylation of polypropylene was performed by both noncatalytic free radical method [7–10]:

\[
\text{RO'} + \text{SiO}_3^- \xrightarrow{\text{cat.}} \text{SiO}_3^- \text{SiH}_3
\]  

(8.3)

and also in the presence of platinum (Karstedt’s) catalyst [7, 11]. In this case, a peroxide cocatalyst, such as $\text{t}$-butylhydroperoxide, is necessary to maintain the catalytic activity.

Polybutadiene is one of the most popular and commonly modified unsaturated polymers. Its availability at various molecular weight ranges and well-defined microstructures make it a practical choice for catalytic modification [2]. Hydrosilylation of polybutadiene by tri(alkyl, aryl)silane (HSiEt$_3$, HSiBu$_3$, HSiPhMe$_2$) in the presence of Wilkinson catalyst $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ leads to the formation of a mainly anti-Markovnikov product [12]. Similarly, the hydrosilylation of butadiene copolymers with styrene (SBR) and nitrile (NBR) was also examined and the influence of functional groups was studied [13]. In the case of SBR, the reaction occurred via a typical anti-Markovnikov addition contrary to the reaction of NBR, in which Markovnikov addition was observed.