CHAPTER 1

Polymerization of Si-Containing Vinyl Monomers and Acetylenes

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1.1 Si-Containing Styrenes

Almost all silicon-containing styrenes and the polymers derived from them possess one functional group in the para position relative to the vinyl group. The silicon in this functional group may exclusively form Si—C bonds but it may also involve Si—O, Si—S and Si—N bonds. All these Si-bonds are more or less sensitive to reactive cations, and thus, reports on cationic polymerizations of Si-containing styrenes are scarce. Albeit, Si—C and Si—O bonds do not poison Ziegler-Natta (ZN) catalysts, even reports on ZN-catalysed polymerizations of Si-containing styrenes are rare to the best of our knowledge. Therefore, this review will mainly deal with the synthesis of monomers and their polymerization by free radical mechanisms (discussed first)[1 – 27] or by anionic mechanisms (discussed second).

The interest in Si-containing vinyl monomers and their polymers has rapidly increased since 1980 for several reasons. Some of these polymers may serve as compatibilizers or “coupling agents” in polymer blends and composites. Polymers with a high content of silyl and siloxane groups may be useful as membranes with high permeability to oxygen. Blockcopolymers with well-defined morphology allow a controlled preparation of micro porous membranes. Furthermore, silyl groups (particularly trimethylsilyl and tert-butyldimethylsilyl) were used as protecting groups for OH, SH and NH functions during the polymerization process and removed afterwards (see Appendix B). The removal of these silyl groups usually occurs under mild hydrolytic conditions (these and other chemical modifications will be discussed in chapter 7). Another important application of Si-containing styrenes and other vinyl monomers concerns the fabrication of resist materials for any kind of microlithography and semiconductor devices. The problems of a high-resolution, high-aspect ratio imaging technology are apparently best solved by bilayer or multilayer resists [4, 28]. In the simplest case, the bilayer system consists of a thin radiation-sensitive “imaging layer” on top of a oxidation sensitive thick “planarizing layer”. The top layer receives the image in the standard fashion by UV- or X-ray radiation through a mask. After fixation the image of the thin top layer is then transferred to the lower “planarizing layer” by rapid oxidation with an O₂-plasma in a vacuum. Therefore, the lower layer must be an oxidation sensitive polymer with a relatively low carbon content [29, 30]. In contrast, the imaging layer needs to be
stable against complete oxidation. This property is imparted by silicon (or tin and other metal atoms), because the initial oxidation with the $O_2$-plasma produces a non-volatile layer of $SiO_2$ which protects the lower layer against oxidation. Therefore, the material of a typical imaging layer consists of a copolymer or a blend of polymers containing silyl groups, on the one hand, and a radiation-sensitive group, on the other hand.

1.1.1 Radical Polymerizations

The syntheses of most Si-containing styrenes are based on the reaction pathways outlined in Eqs. (1-7). The Si—C bonds are typically formed via a Grignard