Surface-functionalization with novel Germanium-based photoinitiators for surface-mediated, radical and cationic photopolymerization techniques

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During the last decades surface modification based on "grafting from" techniques have received an increasing interest in the industrial as well as in the academic sector. This approach relies on covalently coupled initiating species, that can be triggered either by heat or light, and subsequent (photo)polymerization reactions of functional monomers, which results in a surface-tethered polymer brush system. Typically, those (photo)initiators are coupled to inorganic surfaces via trialkoxysilyl, thiol or diazonium salt anchoring units. In the present work, a novel and visible light sensitive photoinitiator, based on germanium, was prepared and equipped with a halogen coupling unit. This compound was subsequently covalently coupled to spherically shaped SiO_2 nanoparticles and flat substrates. The generated light sensitive surfaces were then employed for surface-initiated free radical photopolymerization of different acrylates and vinyl monomers [1]. Furthermore, and for the first time, we report on surface-mediated cationic photopolymerization [2], also triggered by visible light (450 nm), using the same modified nanoparticles. In that manner, living polymer brushes, derived from vinyl ethers and epoxides were achieved. The surface composition as well as the grafting density were studied using, e.g., TGA, REM, FT-IR and XPS spectroscopy.

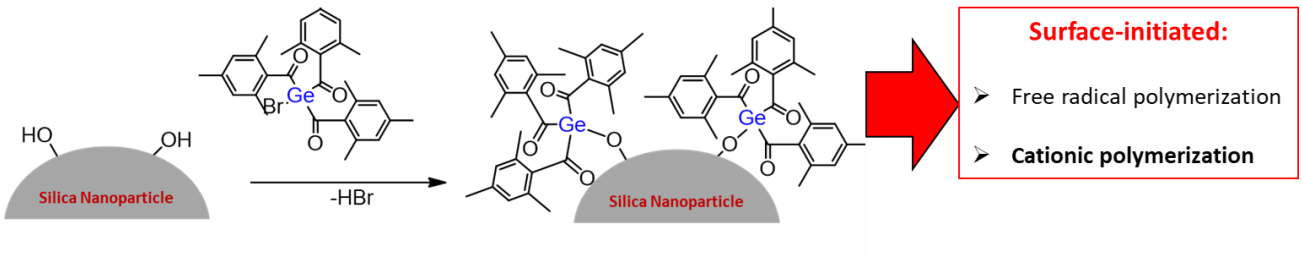

Fig. 1: Photoinitiator immobilization and subsequent grafting-from polymerization

Considering the outstanding advantages of this new and efficient class of photoinitiators, namely the high absorbance in the visible range of the spectrum (up to 485 nm) and low-toxicity, we believe that this technology has a high potential to open up high-end applications, especially in biomedicine.

References

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[2] Durmaz, Y.Y.; Moszner, N.; Yagci, Y. Macromolecules 41, 6714–6718 (2008).