Photoreactivity of Ge-based Initiators for Radical Polymerizations

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Photo-induced radical polymerization plays an essential role in a broad range of industrial processes. For several medical applications such as dental fillings, photoinitiators offering long-wavelength absorption as well as low toxicity are highly desired. Acylgermanes have become successful initiators, meeting these requirements. Recently, we have introduced tetraacylgermanes as a promising class of novel photoinitiators, featuring the potential to outperform current state-of-the-art mono- or bisacylgermane initiators. Generally, photolysis of acylgermanes leads to α -cleavage of a Ge–C(O) bond via the triplet state, yielding a benzoyl-type and a germyl radical (see Scheme 1).

Ar
$$R_2$$
 R_3 R_3 R_4 R_5 R_5 R_5 R_5 R_5 R_5 R_6 R_6 R_7 R_8 R_9 R

Scheme 1. Photocleavage of acylgermanes yielding a benzoyl-type radical **B•** and a germyl radical **G•**. Bond cleavage occurs from the excited triplet state after intersystem crossing (ISC).

In this talk, a comprehensive study on the photoinitiating reactivity of various mono-, bis-, tris- and tetraacylgermanes will be presented, considering the photobleaching behavior of the compounds, quantum yields of cleavage, addition kinetics to monomers and radical reaction mechanisms. This study is accomplished using an array of methodologies, *i.e.* optical spectroscopy, laser-flash photolysis, time-resolved (TR) EPR spectroscopy and chemically induced dynamic nuclear polarization (CIDNP-NMR) spectroscopy.

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References:

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