

SELF-INITIATION OF PHOTOPOLYMERIZATION REACTIONS BY PENTAHALOGENATED PHENYL METHACRYLATES

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Self-initiation of photopolymerization reactions without the use of a conventional photoinitiator systems can be achieved e.g. by thiol-ene formulations, electron donor/acceptor systems (e.g. maleimide/vinyl ether), certain monomers with self-initiating capability or by direct initiation with short-wavelength UV irradiation in the UV-C or VUV range. Moreover, several halogenated (in particular brominated) acrylic monomers have been demonstrated to be efficient as initiators as well [1-3]. In this contribution, we will show that pentachlorinated phenyl methacrylate (PCPMA) is also able to initiate a photopolymerization reaction. Analytical investigations were carried out by UV/VIS spectroscopy, studies of the reaction kinetics by real-time FTIR spectroscopy, laser flash photolysis and analysis of products and fragments after stationary photolysis using GC/MS. These experimental methods were supported by extensive quantum chemical modelling of possible reaction pathways as well as energetical considerations. All findings for PCPMA were compared with the results for the corresponding brominated monomer (PBPMA). PBPMA was found to release bromine radicals by photolysis of the phenyl-bromine bond with a quantum yield of 0.3 [1]. In contrast, the release of chlorine radicals is much less efficient for energetical reasons. It was found to be possible from the unrelaxed triplet state only. In fact, chlorine radicals were not directly observed (e.g. in LFP studies). Rather, strong indication was found for the formation of radicals by split-off of the chlorine at the ortho position of the phenyl ring and ring closure via the methacrylate group. The probability of the occurrence of various ring structures will be discussed on the basis of further spectroscopic studies. Initiation of a polymerization reaction with PBPMA may occur mainly by addition of the radicals at the polyhalogenated monomers to an acrylic double bond, which is more favorable than that of bromine radicals (reaction enthalpies -40 vs. -10 kcal/mol). In case of PCPMA, initiation is supposed to proceed via the radical at a six-membered ring formed by ring closure via the methacrylate group.

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[3] T. Pelras, W. Knolle, S. Naumov, K. Heymann, O. Daikos, T. Scherzer, *Photochem. Photobiol. Sci.* **16** (2017), 649-662.