

NOVEL PHOTOACID GENERATOR FOR CATIONIC PHOTOPOLYMERIZATION

Nicolas Klikovits^a, Patrick Knaack^a, Daniel Bomze^a, Ingo Krossing^b, and Robert Liska^a

^a Institute of Applied Synthetic Chemistry, Technische Universität Wien,
Getreidemarkt 9/163 MC, 1060 Vienna, Austria

^b Institute of Inorganic and Analytic Chemistry, University Freiburg, Albertstrasse 21,
79104 Freiburg, Germany

Cationic photopolymerization is a powerful method for light-induced curing of heterocyclic and vinyl monomers such as epoxides, oxetanes and vinyl ethers. High reaction rates, insensitivity towards oxygen, as well as the unique post-curing behavior make it highly useful for the production of coatings, adhesives and inks. Many of these benefits cannot be reached by predominant free radical photopolymerization and give rise to the further interest in cationic UV-curing.

Still the lack of suitable and efficient photoinitiators limits its potential. Photoacid generators (PAGs), which liberate protons and carbocations upon irradiation, are used to initiate the reaction. However, only little progress has been achieved since the development of onium salt PAGs in the 1970s. [1] Efficiently photodecomposing diaryliodonium and triarylsulfonium cations were combined with low nucleophilic, perfluorinated anions, such as BF_4^- , PF_6^- , AsF_6^- , SbF_6^- and $\text{B}(\text{Ar}^{\text{F}})_4^-$. [2,3] The major problems of these anions are low hydrolysis stability, severe heavy metal toxicity or difficult synthesis procedures, respectively.

We present a novel class of cationic photoinitiators by introducing tetrakis(perfluoro-*t*-butyloxy)aluminate as acid-forming anion for onium salt PAGs. This weakly coordinating anion (WCA) is characterized by its outstandingly low nucleophilicity, inherent stability, absence of heavy metals, as well as straight-forward and up-scalable synthesis procedures. [4] Following the facile preparation of the diphenyliodonium and triarylsulfonium salt of the named WCA, photo-DSC studies revealed the superior reactivity in different cationically polymerizable monomers. Their beneficial properties for cationic photopolymerization were investigated and enable the use in a broad spectrum of UV-curing applications.

[1] Crivello, J.V. and J.H.W. Lam, *Diaryliodonium Salts. A New Class of Photoinitiators for Cationic Polymerization*. Macromolecules, 1977. **10**(6): p. 1307-1315.

[2] Crivello, J.V., *The discovery and development of onium salt cationic photoinitiators*. Journal of Polymer Science Part A: Polymer Chemistry, 1999. **37**(23): p. 4241-4254.

[3] Castellanos, F., et al., *Synthesis, reactivity, and properties of new diaryliodonium salts as photoinitiators for the cationic polymerization of epoxy silicones*. Journal of Applied Polymer Science, 1996. **60**(5): p. 705-713.

[4] Krossing, I., 1.23 - *Weakly Coordinating Anions: Fluorinated Alkoxyaluminates A2* - Reedijk, Jan, in *Comprehensive Inorganic Chemistry II (Second Edition)*, K. Poeppelemeier, Editor. 2013, Elsevier: Amsterdam. p. 681-705.