

# **THERMAL INITIATORS FOR CATIONIC FRONTAL POLYMERIZATION**

David Wottawa, Moritz Mitterbauer, Patrick Knaack and Robert Liska

Institute of Applied Synthetic Chemistry (IAS), Vienna University of Technology,  
Vienna, Austria

Frontal polymerization is a unique polymerization technique in which only a single stimulus is sufficient to cure bulk samples. In addition to cure large samples in a highly energy-efficient manner, one of the main strengths is that ready-to-use formulations can be premixed and stored. At any desired point in time, these mixtures can be processed and cured. Frontal polymerization is a self-sustaining curing process which can be achieved through the combination of certain ingredients in a formulation. The basic requirements are at least a thermal initiator which triggers polymerization and a monomer that releases heat as it cures. The generated heat in turn decomposes the thermal initiator again to start a chain reaction. This work focuses on the development of formulations which undergo cationic frontal polymerization. The use of thermal acid generators (TAG) as cationic initiators proves to be unfavorable, as TAG-based formulations tend to gel after a short storage time. Therefore, a circuitous route must be taken. It is known that photoacid generators (PAG) used for cationic photopolymerization, especially iodonium- and azonium-based ones, are able to oxidize free radicals to form initiating cations. Therefore, the combination of radical thermal initiators (RTI) and PAG's could be used to promote cationic frontal polymerization. Organic peroxides which are commonly used as RTI's are not appropriate for this type of initiation. Azo compounds would be suitable, but they exhibit a different problem with frontal polymerization. Since nitrogen is released during their decomposition, the resulting polymer is permeated with bubbles which negatively affects the mechanical properties. The aim of this work was to find new systems to generate thermal radicals that undergo a redox reaction with the PAG in order to obtain bubble-free cationic frontal polymerization. Therefore, formulations were prepared and investigated for their ability to perform frontal polymerization. The polymerization experiments were conducted in a PTFE mold equipped with thermocouples and a ruler. The tests were recorded with a camera and the front temperature and the front velocity were evaluated to compare different systems. One system that has proven to be exceptionally appropriate uses 1,1,2,2-Tetraphenyl-1,2-ethandiol (TPED) as RTI. TPED has the peculiarity that it forms carbon radicals during decomposition, without producing any volatile byproducts. But also other very suitable systems have been found to generate thermal radicals which trigger frontal polymerization.