RADICAL INDUCED CATIONIC FRONTAL POLYMERIZATION OF EPOXIDES USING BISMUTHONIUM-AND PYRYLIUM-SALTS

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Cationic polymerization is a powerful tool when it comes to adhesive, coating, composite and bulk material production. A variety of monomers is suitable for cationic polymerization, however epoxy-based systems are used in many applications, due to their high reactivity and versatility. With the introduction of the radical induced cationic frontal polymerization (RICFP), an even more efficient pathway to cure epoxides and with it a variety of new applications was obtained. [1] The prevailing initiator class for RICFP applications is the iodonium salt, which can be cleaved by light as well as radicals. [2] A lot of research and fine-tuning of the formulations lead to a highly effective and versatile initiator system. With the introduction of bismuth- and oxygen-based onium salts for frontal polymerization, the well-known iodonium salt is challenged. Bismuthonium hexafluoro-antimonates (Figure 1) show fast frontal velocities of 6.2 cm min⁻¹, a high polymerization rate and conversions of 84% in an epoxy system.



Figure 1: Commercially used iodonium salt I-Sb and the new initiators based on the bismuthonium salt Bi-Sb and the pyrylium salt O-Sb

The advantage of bismuthonium-based systems is the excellent pot life of the formulations, which can be cured at the press of a button. In this study, iodonium salts last around three days before a significant viscosity increase is measured, while the bismuthonium initiator lasts over 10 times as long with no significant drop in reactivity or frontal velocity.

^[1] Bomze, D.; Knaack, P.; Koch, T.; Jin, H. F.; Liska, R., Radical Induced Cationic Frontal Polymerization as a Versatile Tool for Epoxy Curing and Composite Production. J Polym Sci Pol Chem 2016, 54 (23), 3751-3759.

^[2] Dadashi-Silab, S.; Doran, S.; Yagci, Y., Photoinduced Electron Transfer Reactions for Macromolecular Syntheses. *Chem Rev* 2016, 116 (17), 10212-10275.