

Cure Kinetics of UV-Induced Cationic Polymerization of Tactix123 using CD-1012 as Photoinitiator

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Objective- We have initiated a comprehensive study to investigate the kinetics and mechanism of UV and e-beam induced cationic polymerization of Tactix123 in the presence of CD-1012 as photoinitiator. The objectives of this study is to see whether or not the same reaction conditions and kinetic parameters (e.g. radiation dose, concentration, temperature) control the properties of final polymeric products under both radiation conditions. The ultimate goal of this study is to identify the parameters that give rise to improved thermal and mechanical properties of the final composite prepared by e-beam curing. We have employed fast kinetic spectroscopy to elucidate the mechanism of polymerization and identify the reactive intermediates involved.

Results- Our initial kinetic studies on UV cationic polymerization of Tactix123 using CD-1012 have focused on polymerization rate, the nature of polymeric materials formed, and temperature dependence of polymerization rate. Preliminary data indicate that samples irradiated at 300 nm for a short period of time form both soluble (as evidenced by Gel Permeation Chromatography, GPC) and insoluble polymeric material. The yield of insoluble products (cross-linked polymer) increases as the irradiation time is increased and accounts for up to 70% of the total products (for 64% total Tactix123 loss). At higher conversions, only a small amount of soluble polymeric material is formed (<10%).

The effect of rising temperature on polymerization rate was also studied to obtain Arrhenius parameters for the process. Our data indicates that the polymerization rate at room temperature is $2.8 \times 10^{-3} \text{ s}^{-1}$ and increases to $5.3 \times 10^{-2} \text{ s}^{-1}$ at 80 °C. From the slope of a logarithmic plot of the polymerization rates as a function of inverse temperature (Arrhenius plot) an activation energy of 40.5 kJ/mol is determined for the process.

Solid state NMR has been employed as a tool to obtain structural information on the cross-linked polymer. The room temperature solid state ^{13}C CP/MAS NMR spectrum of Tactix-123 polymer shows ten resolved resonances: nine resonances which map 1 to 1 with resonances of the precursor and one resolved resonance at 51.2 ppm which derives from the low field epoxide resonance of unreacted Tactix123 (solution value 49.9 ppm). The larger line widths seen in solid state ^{13}C NMR spectra (1-2 ppm for homogeneous resonances) obscure the other precursor (Tactix123) resonances. The four aromatic resonances, 157.8, 144.8, 128.8, and 115.5 ppm, and the quaternary and methyl resonances, 42.8 and 32.5 ppm, respectively, are assigned as in the solution spectrum of Tactix123.

The epoxide resonance can be used to estimate the concentration of unreacted epoxide precursor in the polymer. The gross structure of Tactix123 polymer is confirmed by the solid state spectrum. Detailed investigation of the polymer structure (chain length, etc.) may be profitable using high temperature solid state NMR techniques which can greatly improve line width and potentially reveal cross linking sites and secondary reaction channels. Such experiments are currently underway.

Significance of the study- A better understanding of the cure kinetic and mechanism will enable us to identify the parameters that control the properties of the final products. The fundamental knowledge and mechanistic insight gained during this investigation will aid us to improve thermal and mechanical properties of the final polymeric materials.

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