

142e The Influence of N-Vinyl Pyrrolidinone on the Photopolymerization Kinetics and Mechanical Properties in Copolymerization with Acrylates with Increasing Functionality

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Initiating polymerization by radiation curing is beneficial as it reduces the need for volatile organic solvents, allows spatial and temporal control of initiation and is more rapid than thermal polymerization. Unfortunately, it is sometimes difficult or expensive to undertake large-scale photopolymerization in an environment free of molecular oxygen, a well-known inhibitor of free radical polymerization. To this end, polymer scientists have often included the molecule n-vinyl pyrrolidinone (NVP) in photopolymer formulations as it has been shown to dramatically reduce oxygen inhibition. In addition, NVP markedly increases the rate of polymerization in copolymerization with acrylate regardless of the presence of oxygen. This research examines the copolymerization of NVP and a number of acrylate monomers to determine the influence of crosslink density on the reactivity of NVP and acrylate. The relative polymerization rate enhancement due to the addition of NVP increases with monomer functionality. At low double bond conversion for high functionality acrylate systems, NVP decreases the overall crosslink density and reacts in a semi-alternating manner. Furthermore, as a small molecule with preferential reactivity with acrylate, initiated NVP seeks out unreacted acrylate double bonds prevalent in the polymer matrix facilitating additional acrylate double bond conversion. These behaviors can be ascribed to the reaction diffusion termination mechanism (RDT). Data indicates that NVP delays the onset and extends the predominance of RDT into higher double bond conversion. Results from these photopolymerization kinetics also correspond well with modulus and T_g observations in NVP/acrylate systems.