

MECHANISTIC ASPECTS OF SOLID STATE POLYAMIDATION PROCESSES

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INTRODUCTION

Solid state polymerization (SSP) is industrially applied for step-growth polymers, such as polyamides and polyesters; it involves heating the starting material (crystalline monomer or prepolymer) at a temperature below its melting point, permitting the initiation and propagation of typical polymerization reactions. Both chemical and physical steps occur during an SSP process, namely chemical reaction kinetics, reactive chain end movement in the amorphous phase, and condensate removal through convection. These phenomena are herewith discussed and correlated to operational variables, such as starting material nature and additives presence^{1,2}.

In particular, SSP starting from solid polyamide salts was investigated and found to be accompanied, depending on the reaction conditions, by a distinct transition of the process from the solid to the melt state (Solid – Melt Transition, SMT). Considering the hygroscopic nature of the reacting mass, a generalized mechanism for the effect of polycondensation water on reaction behavior was proposed and verified experimentally. It comprises water accumulation–hydration–transition to the melt, predominating in nylon salts of moderate structural organization, such as PA 6.6 salt. Furthermore, the SMT phenomenon was exploited through developing successfully a low-temperature two-stage prepolymerization technique, starting from dry PA 6.6 salt, and scaling up the process, through careful design of the experimental apparatus so as to handle properly the transitions of the reacting mass from solid to melt and solid again³⁻⁶.

Turning to catalytic SSP, the efficiency of phosphorus-containing catalysts, serving also as antioxidants, was evaluated during PA 6.6 prepolymer SSP. The catalytic effect was correlated to the structure of the phosphonates, and, more specifically, to the additive mobility within the solid polymer,

implying the possibility of partial incorporation of the catalyst molecule into the polyamide structure leading thus to reactivity enhancement⁷⁻⁸.

Finally, nanofillers catalytic performance on SSP processes was proved in the current work, in the perspective of promoting their incorporation not only for the modification and/or improvement of materials properties, but also for exploring their performance as SSP “multifunctional” catalyst systems⁹⁻¹⁰.

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