

THE COMBINATION OF UV/VIS/IR SPECTROSCOPY WITH ISOTHERMAL FLUXMETRY AND ISOPERIBOLIC CALORIMETRY TO PERFORM AND MONITOR POLYMERIZATION IN ORGANIC MEDIA

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Anionic polymerization of lactams in nonpolar solvents occurs through the "activated monomer" mechanism featuring a particular two-step propagation mechanism and leads to semi-crystalline microscopic polyamide powders. Combining two different physico-chemical approaches like UV/VIS/IR spectroscopy and calorimetry allows, in taking advantage of both techniques, to better understand the whole process and eventually to properly monitor such type of polymerization.

Two types of differential calorimeters designed and built by Setaram, the Calvet type C80 calorimeter and the DRC reaction calorimeter, working both in isothermal conditions, were used. The *in situ* simultaneous spectroscopic detection was possible through the use of several optical fibers connected to miniaturized spectrophotometers. As a matter of fact, the calorimeters were used as instrumented reactors, in which active species, like chain initiator and catalyst, could be fed under well controlled fashion either in one shot or by computer-controlled injection. In the C80 calorimeter the one-shot addition is easily feasible to observe the initial "zero" moment of polymerization and the propagation step, preceded by an initiation step, can be perfectly documented. The DRC reaction calorimeter was equipped with a dosing system and the thermal and spectral responses of the successive or continuous injections of the active species could be analyzed in detail. Thus, in the stepwise manner of adding the catalytic system after each addition, the two above-mentioned distinct parts of the calorimetric signal observed in the case of one shot mode could be clearly distinguished. The intensity of the calorimetric signal was proportional to the delivered volume from the dosing device. In the case of continuous adding of catalytic species a steady state of the calorimetric signal was achieved after a certain period suggesting an expected regularity in the advance of the involved phenomena.

In all cases the thermal response is accompanied by the associated spectroscopic signature. In this way the two complementary techniques yield a very versatile set-up, in which recorded heat flux provides the information concerning the overall rate of the process while spectroscopic information is obtained on phase separation, nucleation and growing of separated polymer particles.

Illustration of such spectro-calorimetry technique is made on some selected examples where the influence of the reaction parameters on the advance of the process as well as the competition between the chemical reactions and concomitant physical phenomena are highlighted through the corroborated *on line* recorded pertinent data.