Model-free Kinetic Analysis: Getting the Most from your DSC Data
James J. Christensen Award Lecture

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Model-free kinetic analysis is based on an isoconversional method of evaluating the effective activation energy as a function of the extent of conversion. The analysis has found its most exciting applications in combination with DSC measurements of the processes of polymerization, crystallization, and relaxation. It has allowed one to use calorimetry for obtaining information that had not been accessible by means of calorimetry. Curing kinetics. While analyzing the heat release kinetics in epoxy-amine copolymerization, we established that calorimetric data can be used for detecting the process of vitrification via detecting a decrease in the activation energy measured as a function of conversion. This finding has been confirmed by using a variety of other techniques, including temperature modulated DSC. Further applications of this analysis have demonstrated that calorimetry is suitable for untangling complex curing mechanisms that include multiple chemical or diffusion steps. Crystallization kinetics. In this area, we pioneered a combination of model-free analysis with DSC measurements of the crystallization kinetics in the polymer melts. This combination has provided an unparalleled opportunity for extracting the Hoffman-Lauritzen parameters from simple calorimetric measurements as opposed to the traditional approach that is based on laborious microscopic experiments. The approach has been successfully used for several polymer melts, and most recently expanded to include crystallization of polymer glasses. Relaxation kinetics. We have proposed to apply model-free kinetic analysis to DSC data in order to detect variations in the effective activation energy throughout the glass transition (α-relaxation). Such information had been traditionally extracted from relaxation techniques such as dielectric or mechanical spectroscopy. Relaxation kinetics derived from calorimetric measurements had been typically described via simplified models that assume the constancy of the activation energy. By performing calorimetric measurements on the glass transition in various glassy systems we have determined that the variation in the activation energy correlates with the dynamic fragility of the glass forming liquids, being especially great for polymers.