

OSCILLATING TEMPERATURE REACTION CALORIMETRY AND MODULATED TEMPERATURE DSC FOR POLYMER SYNTHESIS AND CHARACTERIZATION

Florin DAN

Department of Macromolecular Chemistry, "Gh. Asachi" Technical University Iasi, 700050 Iasi, Romania.

Jean-Pierre E. GROlier

Laboratory of Thermodynamics of Solutions and Polymers, Blaise Pascal University, 63177 Aubière, France.

Progress in the understanding of polymer synthesis, including the crucial step of initiation and undesired side reactions, and in characterization of polymers, especially their thermal behavior, is directly related to noticeable advances in calorimetric technologies. Foremost developments in associated instruments and techniques were possible through the evolution of electronic hardware which made the control of heat flow on a (non micro) laboratory scale easy.

Reaction calorimetry (RC) is an appropriate technique for on-line process monitoring, since polymerization reactions are highly exothermic. Measurements are noninvasive, rapid, and straightforward. Nowadays RC is the technique recognized as the most powerful way to study such process in near-to-the-industrial conditions. The science of calorimetry is based on only two laws, *i.e.* energy conservation and heat transfer. Viscosity increase and fouling at the reactor wall are typical features of many polymerizations. The overall heat transfer coefficient also changes drastically when viscosity increases and affects the accuracy of calorimetric measurements. Our approach was focused on two recently developed methods for concomitant determination of heat of reaction ΔH_R and heat transfer coefficient k , namely intermediate jacket method and temperature oscillating calorimetry (TOC). Reactions were performed with two different reaction calorimeters, *i.e.* a power compensation calorimeter with Peltier elements for controlling the temperature of intermediate thermostat and a Calvet type high sensitivity differential calorimeter, respectively. Comparison was made with data obtained using a classic isoperibolic RC. A special attention was paid to the interpretation of the measured signals in order to obtain reliable calorimetric data. The evolution of heat transfer coefficient was followed by performing two Joule effect calibration experiments, before and after the reaction, and the two values have been interpolated to obtain the desired profile of k . A differentiation method based on the convolution of the measured heat flow by the generated one was used for determining the time constants and deconvoluting the measured heat flow. In addition the combination of RC and simultaneous *in situ* Vis-spectroscopy for controlling the particles size and shape through the fine tuning of reaction parameters was advantageously realized.

Differential scanning calorimetry DSC has been used to successfully characterize structures and transitions (changes in structures) in polymeric materials for almost half a century. Commonly called "plastics", *i.e.* materials made from polymers, are becoming more complex in order to meet the demand for lower-cost materials and improved physical properties, including possible complete recycling. Consequently, it is becoming more difficult to characterize the structures and resulting physical properties of plastics that are often polymer blends and composites. Of particular

importance is the investigation and detection of the glass transition of such materials, since this region of temperature conditions processing operations and target utilization of these materials. The result is that new approaches to using DSC and new techniques like Modulated Temperature DSC (MTDSC) are required. MTDSC employs a modulated or sinusoidal change in heating rate in order to automatically separate the total heat flow signal into two differential signals, the heat capacity-reversing contribution and the non reversing kinetic contribution. Apart from conventional DSC, with MTDSC, the two signals are generated in a single experiment so that each component to the total heat flow signal can be shown and analyzed independently. Undoubtedly, MTDSC is now a well established technique which allows asserting non ambiguously the glass transition temperature T_g since this transition and its characteristic temperature selectively appear, from other transitions only on the reversing component.

Bibliography

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