

A variation of DSC is the modulated DSC (MDSC), wherein heat is applied sinusoidally, such that any thermal events are resolved into reversing and nonreversing components to allow complex and even overlapping processes to be deconvoluted. The heat flow signal in conventional DSC is a combination of “kinetic” and heat capacity responses, and Fourier transform (FT) techniques are used to separate the heat flow component from the underlying heat flow signal. The cyclic heat flow part of the signal (heat capacity, $C_p \times$ heating rate) is termed the reversing heat flow component. The nonreversing part is obtained by subtracting this value from the total heat flow curve. It is important to note that all these noises appear in the nonreversing signal. The limitations of the MDSC studies include the requirement of a sufficient number of cycles to cover thermal events. In cases where the samples do not follow the signal or where there is fluctuation in temperature during the sinusoidal ramp, these compounds may not be suitable for this study.

6.9.3 Hot-Stage Microscopy

Hot-stage microscopy is a thermal analytical technique, whereby a few milligrams of the material is spread on a microscope slide, which is then placed in the hot stage and heated at various rates and under different atmospheric environments, including very low temperatures. The events can be recorded using video systems. Hot-stage microscopy is routinely used in conjunction with other methods. Although many newer automated methods to observe the melting behavior of crystals are available, to a trained eye, this classic method remains one of the most powerful tools.

6.9.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) is used to detect the amount of weight lost on heating a sample. It is based on a sensitive balance that records the weight of the sample (generally 5–10 mg), as it is heated under nitrogen. Thermogravimetric analysis experiments can detect the presence of water or solvent in different locations in the crystal lattice. This technique has an advantage over a Karl Fischer titration or a loss on drying experiment that can only detect the total amount of moisture present. In addition, TGA requires smaller quantities of the compounds than the other two techniques. However, the use of very little sample in TGA can yield erroneous results because of buoyancy and convection current effects. The total amount of moisture lost in TGA experiments is not affected by the heating rate; however, the temperature at which it occurs may vary. It is noteworthy that the dehydration mechanism and activation of the reaction may be dependent on the practice size and sample weight. The TGA is calibrated using magnetic standards.

6.9.5 Solution Calorimetry

Solution calorimetry involves the measurement of heat flow when a compound dissolves in a solvent. There are two types of solution calorimeters, that is, isoperibol and isothermal. In the isoperibol technique, the heat change caused by the dissolution of the solute gives rise to a change in the temperature of the solution. This results in a temperature–time plot from which the heat of the solution is calculated. In contrast, in isothermal solution calorimetry (where, by definition, the temperature is maintained constant),