

# Simultaneous Measurement of Light Transmission and Heat Flow in a Modified Differential Scanning Calorimeter

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## Synopsis

A commercial DSC cell has been modified to allow simultaneous measurement of heat flow and light transmission. A special fiber optic probe capable of transmitting and receiving light is located immediately above the sample. The sample is held in a reflective aluminum pan during the measurement. Maximum optical signal intensity is recorded when the sample becomes completely transparent. The light from the probe will pass through the sample, reflect off the bottom of the pan, and then pass up through the sample again and back into the probe. The method was developed to augment the normal DSC heat-flow measurement. We find that the additional optical information is useful in elucidating the nature of thermal transitions in polymeric materials. Any transition, physical or chemical, that is accompanied by an appreciable change in optical transmission can be studied by this technique. The probe is useful even in investigations where only the optical signal is desired, because one can make use of the temperature programming and data acquisition capabilities of the DSC instrument. The presence of the probe tip near the sample does not seriously degrade the heat-flow signal. Good calorimetric accuracy is maintained, albeit some baseline curvature is introduced. Several applications of the technique are described. These include melting and crystallization of polymers, solubility behavior of polymer-polymer and polymer-additive blends, and sintering of polymer particles during oxidative degradation.

## INTRODUCTION

Differential scanning calorimetry (DSC) is one of the more versatile methods of solid-state polymer characterization. Both physical transitions (melting, glass transition, crystallization) and chemical transitions (pyrolysis, oxidative degradation, crosslinking) can be conveniently studied by DSC. The technique is especially suited to the determination of compatibility and phase behavior of polymer-polymer and polymer-additive blends. Although many DSC thermograms can be unequivocally interpreted, there are occasions where additional measurements are needed to identify the physical or chemical transition associated with a particular feature of the thermogram. A property of a polymer that can be utilized as a complementary probe is the transmission of light. The analytical technique based upon this approach is commonly referred to as thermal optical analysis, or TOA.

Traditionally, most researchers have chosen to measure heat flow (via DSC) and optical properties (via TOA) for a given material in separate experiments.<sup>1,2</sup> Schultz and Gendron<sup>1</sup> and Barrall and Johnson,<sup>2</sup> for example, developed similar TOA procedures involving the automatic recording of depolarized light intensity of polymer film that was mounted between crossed

polarizers in a hot-stage microscope. The transition temperatures obtained by this method were then compared to those obtained by conventional DSC. However, with the development of fiber optics technology and laboratory data acquisition equipment the combination of DSC and TOA into a single measurement has become feasible. The two major advantages of this approach are the operational simplicity and the confidence inherent in knowing that both the DSC and TOA signals are originating on the same material subjected to identical thermal history.

The system that we chose to develop is unique, to our knowledge, in that it allows simultaneous collection of optical and heat-flow signals on a commercial DSC. Through a relatively simple modification of the cell cover we are able to insert an inexpensive fiber optic probe that can measure the sample transparency without seriously degrading the heat-flow signal. We happen to use the Perkin-Elmer DSC-IV, but the fiber optic probe could be readily adapted to many other standard commercial instruments. Both the DSC and the fiber-optic cell were interfaced to a laboratory computer so that the heat-flow and light transmission signals could be simultaneously recorded and displayed in real time on a terminal. It should be recognized that a commercial instrument is currently available for this combined analysis. The Mettler FP84 is a microscope hot stage that allows heat-flux DSC measurements to be made during the analysis. Our approach, however, allows the TOA capability to be added to existing DSCs for only a modest cost.

In this paper we describe the construction and testing of the cell. Also, applications to polymer thermal analysis are given. These include melting and crystallization of polymers, solubility behavior of polymer-polymer and polymer-additive blends, and sintering of polymer particles during oxidative degradation.

## EXPERIMENTAL

The head cover of a standard Perkin-Elmer DSC cell was modified to allow the insertion of two fiber optic probes. Two holes were drilled through the 4-in. diameter cover, with a hole located above both the platinum sample and reference cups. Fiber optic probes terminating in a brass cylindrical tip 0.125 in. in diameter were inserted into each hole and held in place by means of a set screw.

The fiber optic probe consists of an equal number of transmitter and receiver glass fibers arranged in a random pattern. At the detector end, the probe separates into separate bundles for the transmitter and detector fibers. The transmitter fibers are connected to an infrared source (880 nm light-emitting diode) while the receiver fibers are connected to a photodiode detector. The 880 nm wavelength places the probe in the near infrared region of the electromagnetic spectrum. This is only slightly outside the visible range, and in fact if one looks at the probe tip in a darkened room an orange glow is detected. For most applications the TOA data will be identical to that obtained with visible light. One could do the same measurement with visible light, but at a significantly higher cost for the source and detector.

The LED and photodiode are components of an analog electro-optic interface manufactured by EOTec Corporation of West Haven, CT. The specific

probe interface used here was no. ETR-103S. It utilizes a General Electric F5E1 infrared emitter with a wavelength maximum of 880 nm and a 50% band width of 80 nm. The detector is a photodiode manufactured by Optron, no. OP802W.

In these experiments only the sample probe was activated. The fiber optic probe in the reference side is left unconnected and serves to balance the heat losses associated with the sample probe. This heat loss occurs because in order for the fiber optic probe to function the platinum cover lids (that normally cover the sample and reference cells) must be removed.

The fiber optic system functions in the following manner, as shown in Figure 1. A totally transparent sample would allow the infrared light exiting from the fiber optic probe to pass through the sample, be reflected off the bottom of the aluminum sample pan, and again pass up through the sample. This radiation would then be picked up by the receiver glass fibers and channeled to the detector. Any crystallites, impurities, additives, or materials of different refractive index than the matrix would cause the IR radiation to be scattered from the sample and hence the photodiode would register a lower intensity of received light. The probe is placed at a distance from the sample surface such that a maximum intensity of received light is recorded (i.e., for the sample at its maximum level of transparency). This usually corresponds to a probe-to-sample surface distance of 1–3 mm. The output signal is simply a DC voltage that is approximately proportional to the sample transparency. During a temperature scan it is possible to monitor the changes in optical transparency that occur as the polymer undergoes physical or chemical transitions.

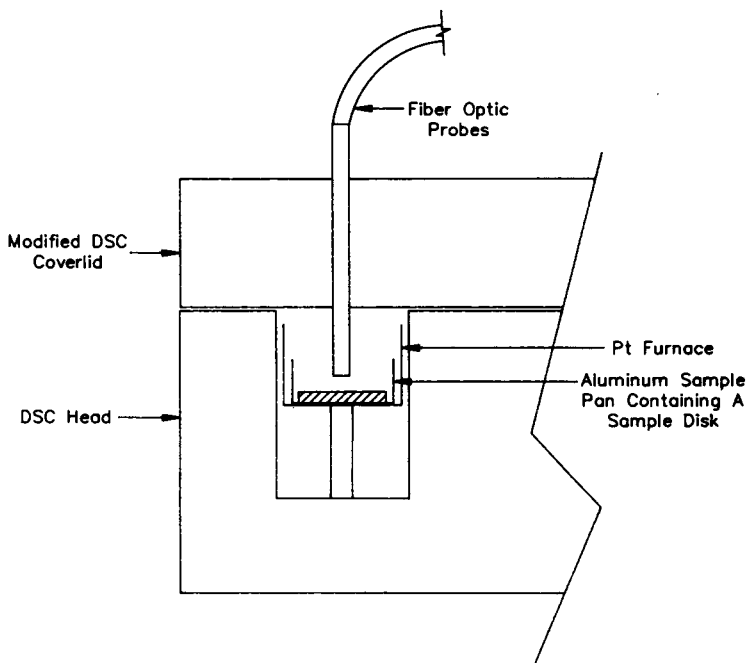


Fig. 1. Diagram of Perkin-Elmer DSC-II cell showing the location of the fiber-optic probe.

Software has been written by Laboratory MicroSystems of Troy, NY, for real time display and collection of the simultaneous DSC and TOA signals on an Ithaca Intersystems laboratory computer system. The software also allows the data to be processed and manipulated in order to produce dual Y-axis (heat flow and optical transmission) plots of the data. At this time the Y-axis units for the optical transmission curves are arbitrary and uncalibrated, and represent a raw DC voltage that is proportional to the intensity of the light at the detector. If absolute quantification is required, then one can calibrate the voltage output against photographic film samples of known optical density. This film is available from photographic supply houses for determining correct exposure times in enlarging.

### RESULTS: PERFORMANCE EVALUATION

Three criteria were identified for evaluating the performance of the DSC-TOA instrument, and are listed below:

1. Calorimetric accuracy is maintained through minimum interference with the DSC heat-flow signal.
2. The two signals are truly simultaneous.
3. The light from the probe results in negligible sample heating.

To evaluate the first criterion, we obtained the melting thermogram of indium in both the modified and unmodified DSC cells. The indium was placed in an open aluminum sample pan in the modified cell, and the platinum cover lid for the sample cell was removed. For the unmodified cell the standard procedure of encapsulating the indium in the aluminum pan was used, and the platinum cover lid was placed on the sample and reference cells. The indium analyzed in the unmodified DSC cell gave a melting onset temperature of 156.4°C and a heat of fusion of 6.8 cal/g, which are the accepted values. In the modified cell with the probes inserted and the cover lid

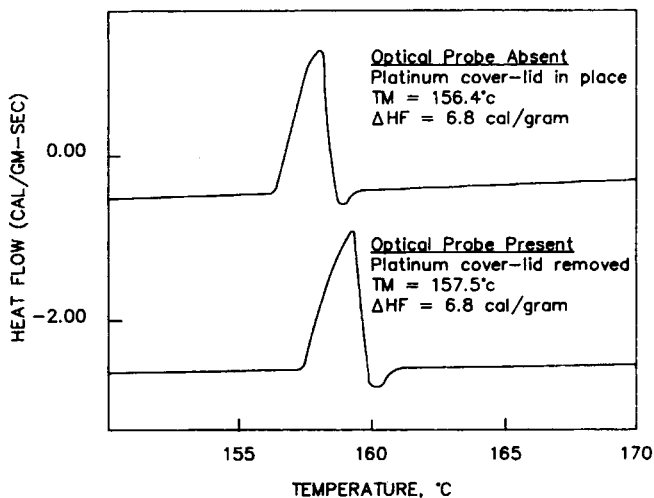


Fig. 2. Melting endotherms of indium in the absence and presence of the fiber-optic probe.

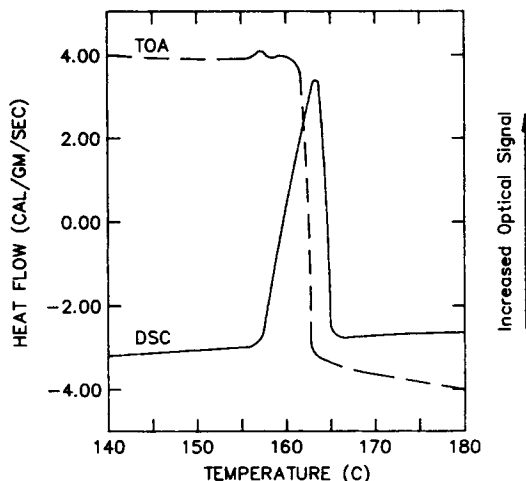


Fig. 3. DSC and TOA curves of indium film obtained simultaneously with the DSC-TOA cell. The decrease in the optical signal results from a change in shape of the film as it melts.

removed, the heat of fusion was unchanged, but the melting point increased by  $1^{\circ}\text{C}$ , which can probably be attributed to the heat loss incurred by removing the platinum cover lid. The two endotherms are compared in Figure 2, and with the exception of the difference in the melting point they are identical.

Evaluation of the relative response times of the two signals was accomplished by monitoring the signals during the melting of a thin film of indium. In this case the signal is reflected off of the top surface of the indium, and the melting changes the shape of the surface, thus inducing a change in the intensity of the optical signal. We know that this change in intensity must be simultaneous with respect to the melting endotherm. This is seen to be the case in Figure 3, where the heat-flow and optical signals are compared.

The third criterion is to have minimal sample heating by radiation from the probe. We were able to show that sample heating is negligible. This was done by placing a thin layer of carbon black in an aluminum sample pan and turning the probe on and off. The carbon black should absorb the light and begin to heat, and the DSC will sense this and compensate by decreasing the heat flow to the sample cell so that the temperature remains constant. The response of the DSC heat-flow signal is seen in Figure 4, and, as expected, when the probe is emitting radiation the DSC responds by withdrawing heat. From the magnitude of the heat-flow shift we calculated that the effective power of the probe was 0.15 mW at the sample. The magnitude of the transition in Figure 4 is approximately 0.005 cal/g s. This is approximately 1/6 of the heat-flow signal generated by an amorphous polymer undergoing a glass transition, and the latter transition is very weak in comparison to melting, crystallization, and oxidation events. Therefore, we can conclude that the effect of sample heating can be ignored in most cases.

The DSC-TOA is shown to have performed well against the three performance criteria. We will now describe some examples of applications to polymers.

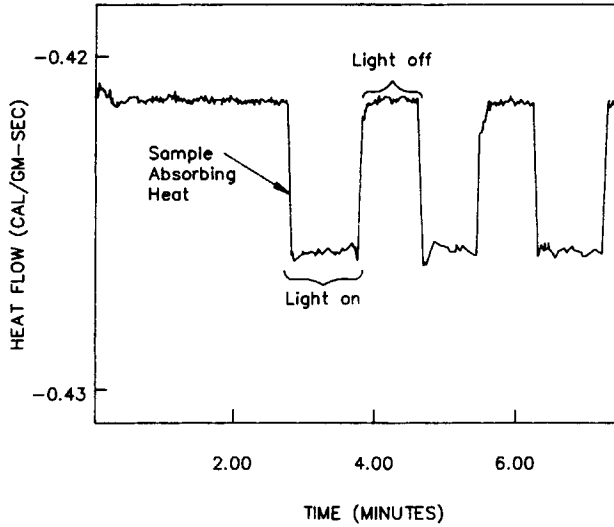


Fig. 4. Response of the heat-flow signal to switching the light source off and on.

### APPLICATIONS TO POLYMERS

The first polymer we analyzed using the simultaneous DSC-TOA technique was medium-density linear polyethylene (PE). A thin disk of polymer (about 0.5 mm) was heated at a rate of  $5^{\circ}\text{C}/\text{min}$ . The combined DSC-TOA curves are shown in Figure 5. The resulting DSC curve shows a melting onset temperature of about  $114^{\circ}\text{C}$ , a peak maxima at about  $122^{\circ}\text{C}$ , and completion of melting by  $124^{\circ}\text{C}$ . The TOA curve follows the transition of the PE sample from an opaque to transparent material as it passes through this melting endotherm. The curve shows a gradual increase toward greater light transmission beginning at about the same temperature as the onset of the melting

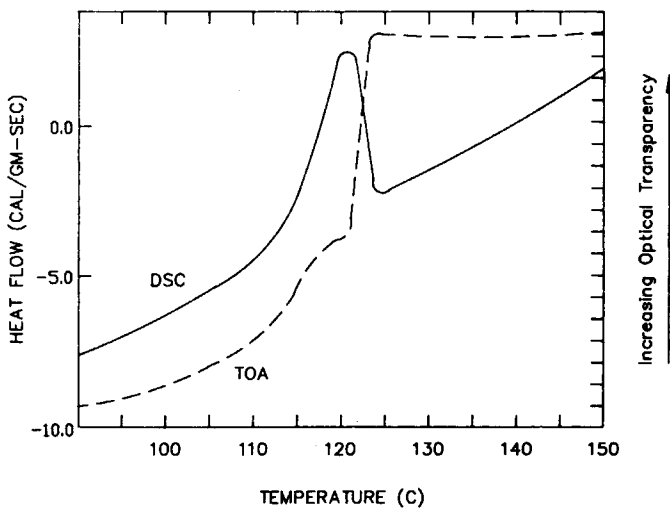


Fig. 5. Simultaneous DSC and TOA curves of medium-density polyethylene.

endotherm. At 122°C the TOA curve displays an inflection and then rapidly progresses toward a state of essentially 100% transmission at 124°C. We believe that the inflexion at 122°C arises from the maximum in light scattering that occurs with crystalline polymers when the crystalline volume fraction passes through 0.50.<sup>3</sup>

The baseline of the thermogram in Figure 5 has a high degree of curvature in the endothermic direction, which is attributable to heat loss from the sample to the probe. The DSC cell is unbalanced in the sense that the reference side of the cell does not contain any polymer. In the sample side the probe is located very close to the sample surface. The heat loss due to radiation transfer to the probe will be greater on the sample side, and this imbalance will increase at higher temperatures because the radiation loss is proportional to the fourth power of absolute temperature.<sup>4</sup> We are currently investigating approaches to minimize the baseline curvature. These include a computer correction, which would work by subtracting out a curved baseline of opposite slope, and repositioning both the sample and reference probes to balance out the heat loss.

The next example is amorphous PET, a polymer which gives rise to three distinct physical transitions during a single heating run. The combined DSC-TOA signals are compared in Figure 6. From the DSC thermogram one can see a glass transition at about 73°C, a crystallization exotherm beginning at about 140°C, and a melting endotherm at about 220°C. Again, significant curvature is apparent in the heat-flow trace at the higher temperatures. The optical curve very clearly follows all of the mentioned transitions. The sample begins as an amorphous transparent glass at room temperature. At the glass transition temperature, the optical trace registers a very small inflection that may be associated with the rapid change in volume at the glass transition temperature. Slightly before the crystallization exotherm maxima the optical

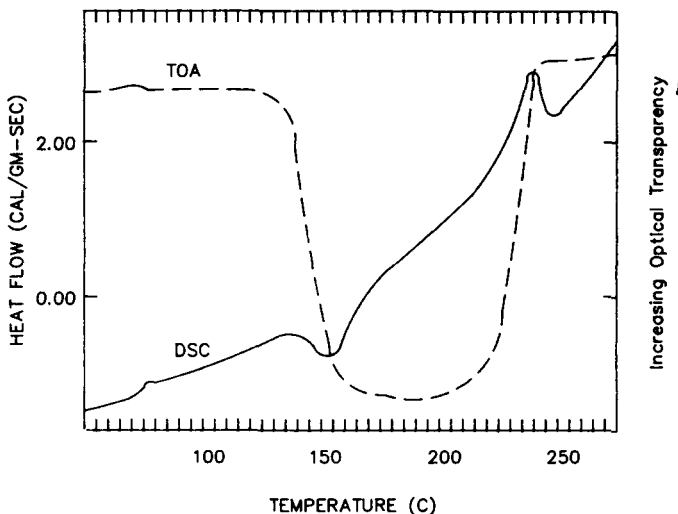


Fig. 6. Simultaneous DSC and TOA heating curves of amorphous polyethylene terephthalate (PET). This material undergoes three transitions during heating: glass transition, crystallization, and melting.

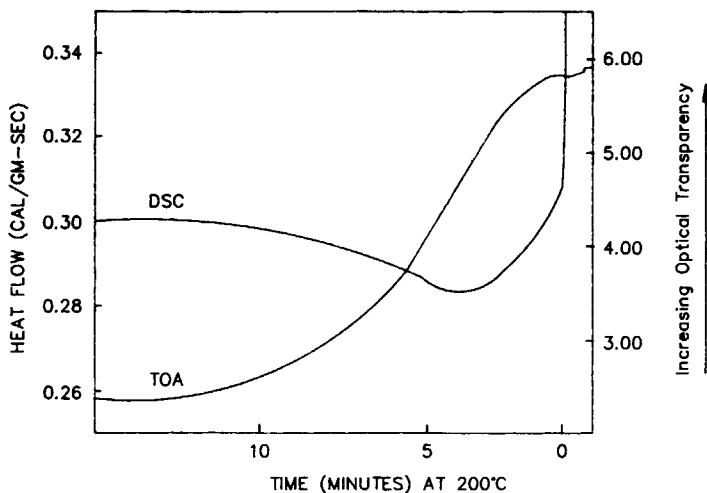


Fig. 7. Isothermal crystallization of PET at 200°C. The polymer was first melted and then cooled from 285 to 200°C at 85°C/min.

curve records a rapid change in sample opacity. As the heating progresses, the crystallites begin to melt and the optical curve records the increase in sample transparency.

An advantage of having the TOA signal available is that one can "observe" the sample under instrumental conditions where the DSC heat-flow signal is inaccessible. One of the undesirable characteristics of scanning calorimeters in general is the large transient signal that is generated when the temperature program undergoes a change from isothermal to scanning mode, or vice versa. One typically studies isothermal crystallization of polymers by cooling the polymer from the melt in the DSC to some isothermal crystallization temperature. The crystallization of PET, for example, is typically studied by first melting the polymer at 285°C and then rapidly scanning down to the desired isothermal crystallization temperature, which may be about 200°C. The abrupt termination of the scanning mode generates a large transient signal that may require up to 30 s to decay to the point where the heat-flow signal can be seen. If the polymer begins to crystallize during this time, then the analysis of the crystallization exotherm becomes difficult, if not impossible.

Having the TOA signal can be very helpful in this type of measurement because one can tell if the polymer has started to crystallize before the heat-flow signal settles down. In Figure 7 we show the DSC-TOA signal for the crystallization of PET at 200°C. Notice that the TOA signal is flat for the first minute, indicating no crystallization for that period of time. At zero time the heat-flow signal is off-scale and does not settle down until approximately 30 s into the isothermal period. Then one sees the beginning of the crystallization exotherm, which mirrors the TOA signal for the remainder of the crystallization. When the experiment is repeated using an isothermal temperature of 150°C, the crystallization begins immediately, and much of the exotherm is lost as the signal transient decays.

TOA analysis is especially valuable in studying the solubility behavior of polymers. The components of the system can be either two miscible polymers



or a polymer and a low-molecular weight additive. If the two components are soluble and the polymer is noncrystalline, then the solution will be transparent. In many of these systems the solubility will be temperature-dependent and lower and upper critical solubility points will occur without measurable transitions in heat flow. Nevertheless, the combined DSC-TOA instrument is still useful because of the ease with which the sample temperature can be changed, and the capability of utilizing both scanning and isothermal temperature control. Also, a lack of a thermal transition accompanying a phase transition at elevated temperature assures the investigator that interfering artifacts such as polymer decomposition and additive volatilization are absent. If one or both of the components are crystalline then miscibility may be dependent on the phase state of one or both components, and the presence of the DSC heat-flow signal will then be useful.

The first application example of phase behavior concerns the solubility of a flame retardant, decabromodiphenyl oxide, in high-impact polystyrene. The system was previously studied by Sprenkle and Southern<sup>5</sup> using a simple TOA apparatus, but no DSC signal was recorded. At the 30% additive loading level a two-phase mixture is formed at temperatures below about 290°C. Above this temperature, the additive dissolves in the polymer giving a single-phase material. It is possible to supercool this solution to obtain a one-phase system in the glassy state. Then, when the glass is reheated above the polystyrene glass transition temperature, which is 100°C, phase separation occurs, and it reverts to a two-phase system again. Examination of the TOA curve for a supercooled sample in Figure 8 shows this behavior. Reproducible fine detail is seen in the TOA curve at the glass transition temperature of this sample, and during phase separation and additive solubilization. Our results correspond very well to those reported by Sprenkle and Southern.<sup>5</sup>

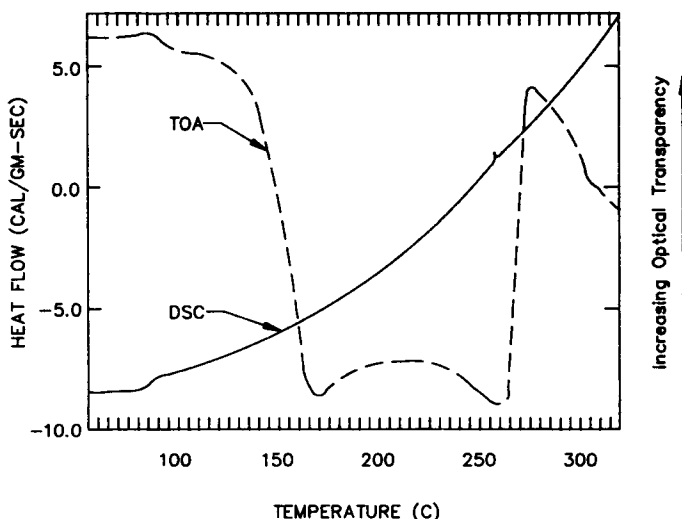


Fig. 8. DSC and TOA curves of a blend of high-impact polystyrene and the flame retardant decabromodiphenyl oxide. The TOA behavior of this system was previously studied by Sprenkle and Southern.<sup>5</sup>

Very few polymer pairs are mutually soluble when blended together. An exothermic heat of mixing is required to achieve solubility, since the increase in entropy that is gained upon mixing two polymers is quite small (in comparison to the mixing of low molecular weight materials). One pair of polymers that exhibits mutual solubility is poly(methyl methacrylate) (PMMA) and styrene and acrylonitrile copolymer (SAN). This pair is also interesting in that a lower critical solubility temperature is observed between the glass transition of the blend and the decomposition temperature of the PMMA.<sup>6</sup> This is also known as the cloud point because the sample undergoes a sharp transition from clear to white and opaque. The DSC-TOA probe can be extremely useful in studying the cloud point behavior of these miscible polymer pairs.

A miscible blend of PMMA and SAN was prepared by dissolving equal amounts of the two polymers in methylene chloride and casting a film. The residual solvent in the film was removed by heating the film in a vacuum oven at 120°C for several days. The weight and mole fractions of AN in the SAN were 0.261 and 0.409, respectively.

The DSC-TOA curve for the PMMA:SAN blend is seen in Figure 9. A large decrease in light transmission occurs at 255°C, and this arises from the phase separation, or cloud point. Optical photographs of the blend before and after the phase separation are compared in Figure 10. The speckled appearance comes about from the scattering off of the separated phases. The large holes are bubbles resulting from vaporization of trace amounts of solvent. The small decrease in transmission at approximately 125°C can also be attributed to bubble formation, in this case directly under the probe tip. It has been our experience that removal of residual solvent by heating in a vacuum oven is very difficult. It is better to prepare the blends by melt blending whenever possible.

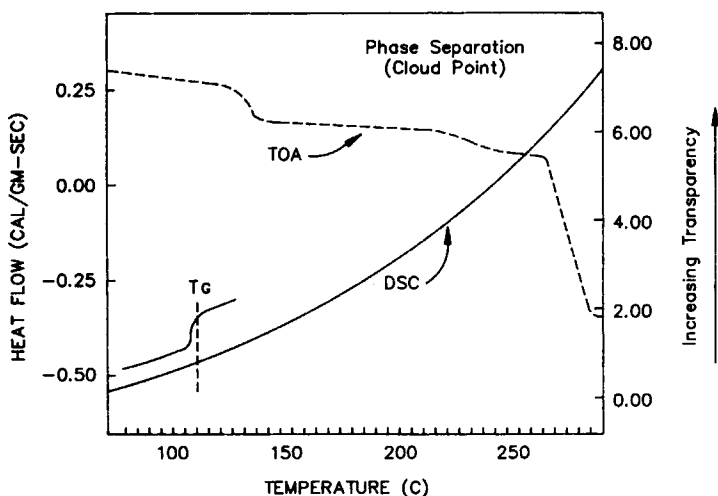


Fig. 9. Use of DSC-TOA probe to detect the cloud point of a miscible blend of two polymers. The blend contains equal weight fractions of SAN and PMMA.



Fig. 10. Optical micrographs of the SAN and PMMA miscible blend before and after heating above the cloud point.

The corresponding DSC curve shows no significant thermal activity at the cloud point. This type of phase separation is not expected to be accompanied by a strong thermal transition. Despite this lack of thermal activity, this cell is still very useful for the study of polymer miscibility, since the investigator can make use of the flexible temperature programming capability of the DSC. For example, we can now proceed to study the kinetics of phase separation by carrying out isothermal measurements.

The DSC-TOA technique can also be used to study chemical reactions of polymers. A case in point is the oxidative thermal degradation of poly(vinyl butyral). In Figure 11 we show the isothermal DSC-TOA curve for this polymer in oxygen at 200°C. The polymer is initially heated to 200°C in a nitrogen atmosphere, and then, after the signal transient decays, the atmosphere is switched over to oxygen. This leads to the evolution of an exothermic peak characteristic of the oxidation. The TOA curve shows that the polymer undergoes a change from opaque to transparent during the oxidation process. This observation, along with molecular weight measurements on the degraded polymer, led us to conclude that the primary mechanism of the

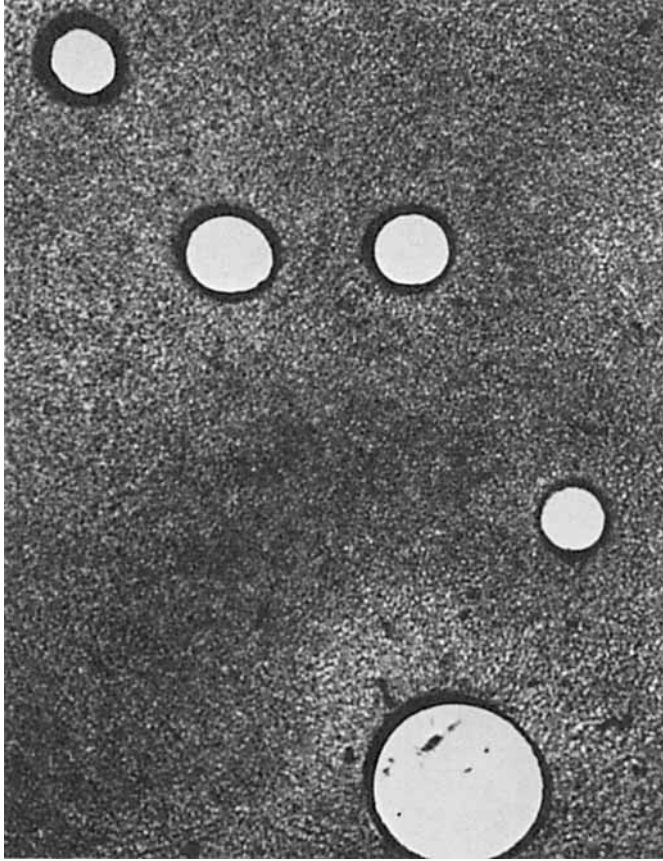


Fig. 10. (Continued from the previous page.)

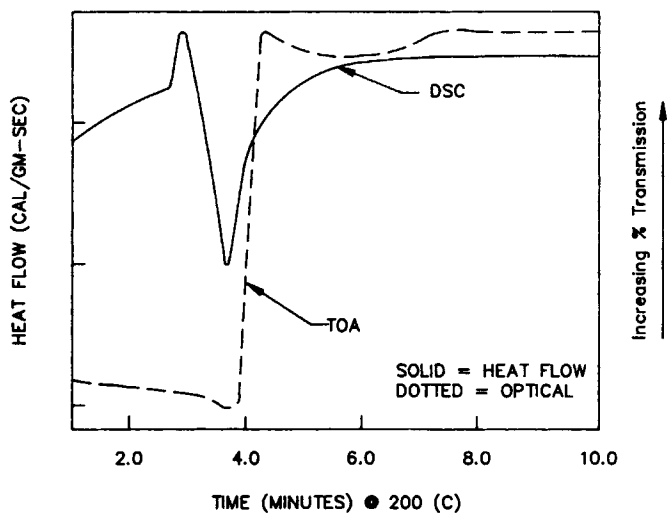


Fig. 11. The use of simultaneous DSC and TOA to study the oxidative degradation of polyvinyl butvar.

oxidation was simple chain scission.<sup>7</sup> The change in transparency comes about from sintering of the initial white opaque polymer particles into a liquid. The rate of polymer sintering increases very rapidly as the molecular weight is decreased.<sup>8</sup> When the same polymer is held at 200°C in nitrogen only partially sintering is observed even for times as long as 1 h, and no thermal activity is seen in the DSC signal.

## DISCUSSION

The simultaneous DSC-TOA probe we have developed does not appear to compromise the accuracy and resolution of the DSC heat flow measurements to any appreciable extent. The excess curvature seen in all thermograms is attributable to sample-optical probe interaction and possibly can be eliminated by careful attention to reference balancing.

The quality and resolution of the optical data is excellent. The optical probe appears to be extremely sensitive to minute changes in a sample's optical characteristics. One area that does need improvement is probe placement in relation to the sample surface. At present this is done on an empirical basis, but we plan to develop a calibrated probe height adjustment apparatus. Also in the future it will be necessary to calibrate the photodiode's output voltage in terms of a percent transmittance scale. This will allow optical curves to be easily compared on a quantitative basis.

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