Thermochimica Acta, 59 (1982) 343–359
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

SIMULTANEOUS DIFFERENTIAL SCANNING CALORIMETRY AND REFLECTED LIGHT INTENSITY MEASUREMENT

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(Received 19 May 1982)

ABSTRACT

A simple, cheap modification to a Perkin-Elmer differential scanning calorimeter DSC 1-B is described which enables simultaneous observation and recording of optical changes in the sample during the DSC run. The theoretical background to the reflected light technique is discussed, and the combined technique is shown to have little effect on the operation of the DSC. The need for direct observation of the nature of changes detectable by DSC is demonstrated by a wide variety of applications. Phase changes, liquid crystals, the dehydration and decomposition of inorganic salt hydrates, as well as the study of polymer transitions and decompositions are reported.

INTRODUCTION

The action of heat on materials produces changes in many properties and a useful preliminary test in qualitative analysis is to observe the action of heat on a solid. If these observations can be recorded and additional information obtained about the enthalpy changes involved, improved deductions may be made about the process. It is surprising that few papers have been published which deal with optical methods used simultaneously with another thermal analysis technique.

Wendlandt [1] reviews the use of dynamic reflectance spectroscopy (DRS) and has applied it particularly to inorganic complexes. He points out that "unlike TG or DTA, DRS can be used to monitor a single reaction at a time, thus eliminating the effect of reactions occurring simultaneously." Wendlandt and Bradley [2] coupled a DRS system with gas evolution detection to study changes in $CuSO_4 \cdot 5\ H_2O$ and $[Co(NH_3)_5H_2O]Cl_3$ up to 150°C.

Charsley and Kamp [3] describe a useful hot-stage microscope unit working to 1000°C and have applied it to the study of the oxidation of metal powders, to phase changes and to the decomposition of both inorganic and organic materials.

Transmitted light hot-stage microscopy (HSM) has been described in the

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works of McCrone [4] and the Koflers [5], and Mercer et al. [6] reported in 1965 a simultaneous DTA–HSM system. Barrall et al. [7] and Miller [8] have used the 'depolarized light intensity' (DLI) method, introduced by Magill [9], to detect changes in inorganic, organic and polymeric materials which occur during heating by the effect such changes have on plane polarized light.

Miller [10] comments that this technique can study "a host of other rate phenomena which cannot be measured by DTA or DSC", and Kovacs and Hobbs [11] and Heide [12] have discussed the role of optical constants in this technique.

Perron et al. [13] devised a new apparatus for simultaneous DTA and transmitted light thermomicroscopy up to 300°C which is now available commercially, and has been used for dehydration and phase studies.

We have chosen to use a reflected light method because it requires little modification of the DSC, needs little sample preparation, and enables atmospheric effects to be studied. It may be applied to both transparent and opaque materials and to the detection of surface changes.

The effects observed by DTA or DSC require a fairly rapid rate of change and a detectable change in enthalpy or heat capacity. Changes in reflected light intensity (RLI) may occur at a very slow rate, since the effects are additive, as in thermogravimetry. Subtle phase changes and glass transitions may change reflectance very little while causing large thermal effects. Surface changes may involve little enthalpy change but alter the reflectance greatly. If two or more reactions occur simultaneously, it may be possible to study them separately by RLI. Table 1 summarises some of the effects detected by the separate techniques, all of which should be found from the combined method.

A theoretical approach to reflected light intensity measurements does not seem to be easy for decompositions, but some work has been carried out on aspects of reflectance changes.

Kortüm [14] shows that the regular reflectance R_{Reg} from a non-absorb-

TABLE 1

Phenomena detected by each technique

Differential scanning calorimetry DSC	Reflected light intensity (thermomicroscopy) RLI
Enthalpy change	Colour change
Heat capacity change	Texture and surface change
Rate and extent of reaction	Expansion or contraction
Temperature of event	Nature of event
→ DSC + RLI ←	

ing, isotropic material of refractive index n_1 in a medium of refractive index n_0, when illuminated perpendicularly, is given by

$$R_{\text{Reg}} = \frac{I_{\text{Reflection}}}{I_{\text{Incidence}}} = \left(\frac{n_1 - n_0}{n_1 + n_0} \right)^2 \tag{1}$$

In air, where $n_0 \simeq 1$, this may be simplified. If the sample is transparent and of thickness l_s, the light will pass through the sample, be reflected by the metal pan and come back through the sample again. This will give an additional reflectance R_{Trans}

$$R_{\text{Trans}} = K_{\text{Al}} \exp(-2K_s l_s) \tag{2}$$

where K_{Al} = fractional reflectance of the aluminium pan, approximately 0.90; and K_s = absorptivity of the sample per unit thickness.

Kortüm considers very extensively the diffuse reflectance R_∞ from powders and the dependence of this on the absorption coefficient K and scattering coefficient S of the powder. Each of these will depend upon particle size, composition in the case of mixtures, and the wavelength and polarization of light used. The Kubelka–Munk theory [14] of multiple scattering by powders, papers and crystals gives a basis for quantitative measurements. The theory shows that the diffuse reflectance may be written

$$R_\infty = 1 + \frac{K}{S} - \left(\frac{K^2}{S^2} + \frac{2K}{S} \right)^{1/2} \tag{3}$$

or, the Kubelka–Munk function, $\mathrm{F}(R_\infty)$ may be written

$$\mathrm{F}(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} \tag{4}$$

For a series of mixtures in a common diluent, S is determined by the diluent so that, from a Lambert–Beer Law on the surfaces

$$\mathrm{F}(R_\infty) = \text{Constant} \times C \tag{5}$$

where C is the molar concentration of the surface species. This has been used by Kealey [15] and others in quantitative reflectometry studies.

Batsanov [16] discusses the effect of temperature on refractive index and molar refraction R_{L}

$$R_{\text{L}} = V_{\text{m}} \left(\frac{n_1^2 - 1}{n_1^2 + 2} \right) \tag{6}$$

where V_{m} is the molar volume, and n_1 is the refractive index. Although the molar volume may change greatly in heating through a phase change, the molar refraction changes much less, e.g., Table 2 [16]. This seems to indicate that the refractive index changes, and hence the regular reflectance R_{Reg} and the scattering coefficient respond to density changes during phase transitions.

TABLE 2

Molar refractivity of different phases

Substance	Phase (Temp.)	V_m(cm^3 mole^{-1})	n_D[a]	R_L(cm^3 mole^{-1})
H_2O	Ice (0°C)	19.57	1.310	3.77
H_2O	Water (20°C)	18.00	1.333	3.70
SiO_2	Quartz	22.66	1.545	7.16
	Cristobalite	25.78	1.485	7.39
	Tridymite	26.46	1.472	7.41

[a] Averaged.

TABLE 3

Molar refractivity of $CuSO_4$–H_2O systems

Substance	V_m(cm^3 mole^{-1})	n_D	R_L(cm^3 mole^{-1})
$CuSO_4 \cdot 5\ H_2O$ (s)	109.5	1.514	33.0
$CuSO_4 \cdot 3\ H_2O$ (s)	80.4	1.554	25.8
$CuSO_4 \cdot H_2O$ (s)	54.1	1.626	19.2
$CuSO_4$ (s)	44.4	1.724	17.6

Additionally, Batsanov has examined systems where water of crystallisation is present, and shows that the loss of such water involves considerable changes in optical properties, density and molar refraction, and that this would affect the reflectance of such powders.

Data are given in Table 3 for the loss of water of crystallisation from copper sulphate pentahydrate. These changes in refractive index, together with particle size and absorbance changes, may explain the RLI trace of Fig. 7.

EXPERIMENTAL

A Perkin-Elmer DSC 1-B differential scanning calorimeter was modified by making a larger cover and fitting a rigid support for a Beck Binomax stereo microscope giving a magnification of ×25. This microscope has a built-in light source which was powered by a stable, adjustable 0–12 V DC power supply. The cover was used as a stray light trap, and to allow a flowing gas stream to sweep over the 'Perspex' window to reduce condensation of volatiles to a minimum.

Various detectors were tried but the most satisfactory stability and sensi-

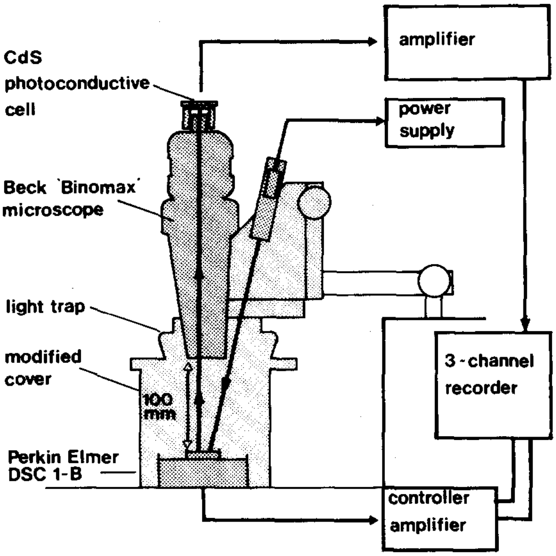


Fig. 1. Arrangement of DSC–RLI apparatus.

tivity was achieved with a Vickers CdS photoconductive cell which has a large light sensitive area and a maximum response at 545 nm. The signal from this detector was amplified by a simple operational amplifier. The experimental arrangement and amplifier circuit are shown in Figs. 1 and 2, respectively.

The signals from the RLI detector, and from the DSC and temperature event marker, were recorded on a Smiths Servoscribe 2 Type RE 520

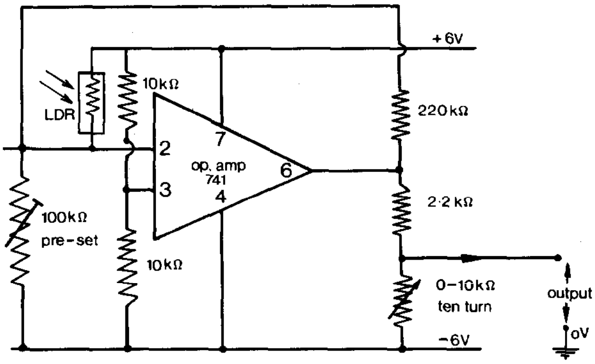


Fig. 2. Circuit of RLI amplifier used.

recorder. A sensitivity of 1 V gave full-scale deflection between white (Al_2O_3 powder) and black (carbon black powder) on the RLI trace.

A permanent record of the actual appearance of the sample at any temperature could be obtained by photographing with a single-lens reflex camera through the second eyepiece not used for the detector. We obtained good results with Kodak High Speed Tungsten Ektachrome (ASA 160) with exposures of about 2 s.

Samples slightly larger than those normally employed in DSC were found to be satisfactory and usually 5–10 mg of powdered material were used with the DSC sensitivity set at 16 or 32 ("mcal s^{-1} full scale"). The samples were prepared in the same way as for normal DSC [17,18] except that either open pans were used or instead of aluminium discs, transparent discs of mica were crimped on to maintain a flat sample. The mica used exhibited no thermal effects below 500°C.

Solid film samples of polymers and papers were cut with a sharp 6 mm hole punch on a clean block, and loaded with tweezers. Occasionally better results were obtained by depositing from solution and allowing the solvent to evaporate. Solid block samples of crystals or polymers were cut with a scalpel to give suitable fragments. Fibres can be retained using a pre-heated washer.

The DSC was calibrated in accordance with the manufacturers' instructions using the high purity metal samples for temperature calibration and an indium sample of known mass for power calibration. Additionally, Reichert hot-stage microscope standards were also used for temperature checking, and other reference materials to confirm the power calibration.

The effects of changes in the emissivity of the samples on the DSC baseline have been reported [19]. Since open pans with no covers were used, this was expected to cause trouble and to give a very poor baseline. In fact, below 300°C, there was only a very small effect of transitions of the baseline at the sensitivity used. At higher temperatures and with sample shrinkage rather larger effects were encountered. The "slope" control was adjusted to compensate as far as possible for the differences between samples and reference.

Since no apparatus which combines two techniques is acceptable if one adversely affects the other or if there is interference, the system was checked with and without the RLI section in operation. There was no detectable effect on the indicated temperatures of the transitions, and the calorimetric sensitivity was the same for both types of operation within experimental error.

Similarly, the effect of DSC operation on reflected light intensity was checked by running calibration materials covered with aluminium discs. An absolutely flat RLI baseline was obtained.

Peak areas were measured with a planimeter whose accuracy and reproducibility and those of the calorimeter give an error of about ±5% on most measurements.

Runs were usually conducted in air. Flow rates and other gases are indicated in the figures.

APPLICATIONS

A variety of applications is given to show the wide range of materials and transitions which may be observed with this combined method. Many other materials have also been studied.

Phase changes

Melting and recrystallisation of benzanilide

Samples of benzanilide, $C_6H_5 \cdot NHCO \cdot C_6H_5$ (Reichert Test Substance), were encapsulated using the mica disc method described above. This was found to give reproducible peak shapes on the DSC and reproducible changes in RLI on melting and, in reverse, on recrystallisation. Slight sublimation onto the Perspex disc of the cover caused the small decrease in RLI, shown in the lower trace of Fig. 3. The enthalpy change on fusion of benzanilide was estimated to be 159 ± 3 J g^{-1}.

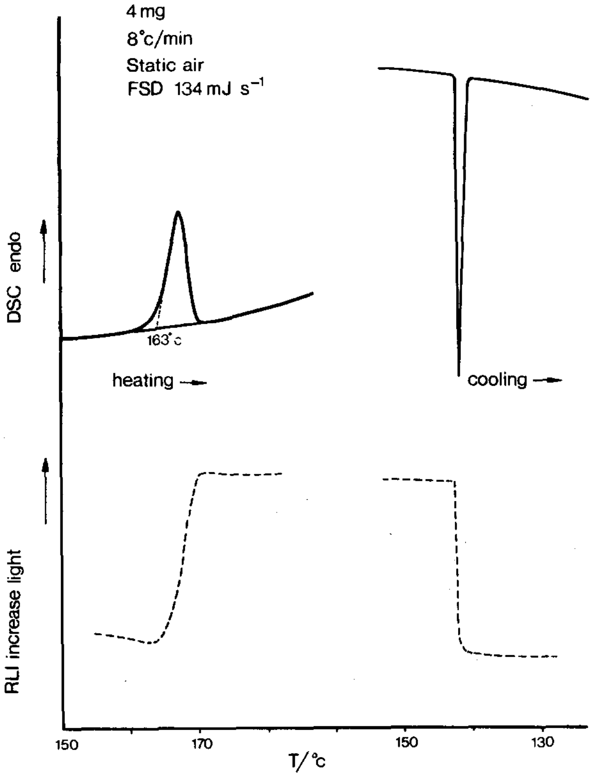


Fig. 3. DSC–RLI of benzanilide.

Potassium nitrate

This material has been recommended as an ICTA standard but the particular sample used (Hopkin & Williams "Educhem" Grade) was not a reference material. The phase behaviour is reported to be quite complex [20] and to depend upon the thermal history. Samples were run as crystalline powder through the melting temperature, cooled to room temperature and re-run. Both traces are shown in Fig. 4 for DSC and RLI. The small transition below 100°C has been reported and the main crystal phase transition from rhombic phase II to tetragonal phase I was observed at 128°C with an enthalpy change of 49 ± 2 J g^{-1}. The RLI change was much more noticeable on the pre-melted sample.

A slight change in RLI almost invariably occurred as the temperature was raised towards the melting point of 334°C, when the fusion endotherm and an increase in RLI were observed, and the enthalpy change was measured as 106 ± 7 J g^{-1}. These ΔH values differ slightly from those given in references [20].

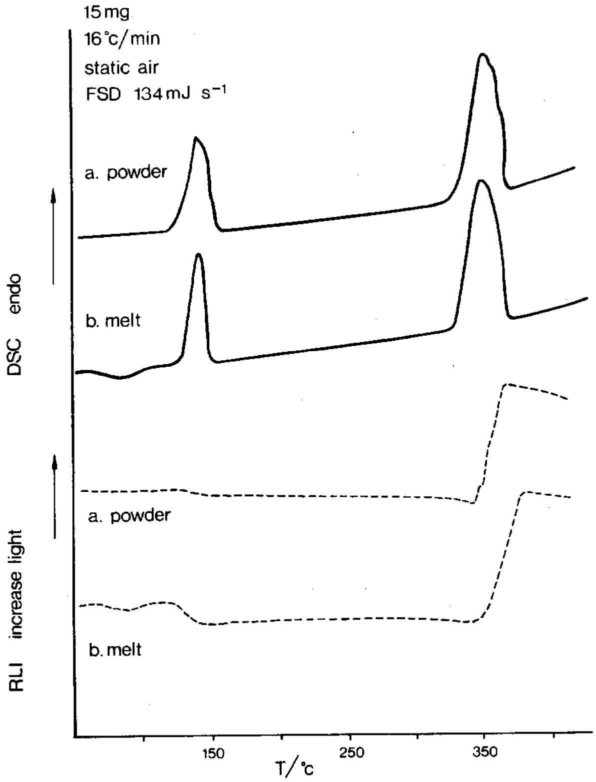
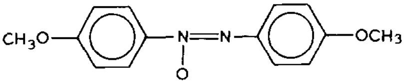


Fig. 4. DSC–RLI of potassium nitrate.

Liquid crystals

p-Azoxyanisole



This material (Hopkin & Williams) shows in Fig. 5 a large DSC peak at 119°C corresponding to the crystal → nematic liquid crystal transition with an enthalpy change around 100 ± 20 J g^{-1}. The preliminary melting always gave a higher value of ΔH, subsequent meltings were much lower. This transition shows a small, marked RLI change. Further heating to 135°C gave an exceedingly small DSC peak (3.0 ± 0.2 J g^{-1}) but a large change in RLI.

The enthalpy changes and temperatures are in reasonable agreement with those reported by Barrall et al. [21] on very pure material. Observations and photography clearly reveal the nature of each transition, and the use of polarisers in the incident and reflected beams has been investigated.

Cholesteryl myristate

This material is difficult to obtain in high purity and our sample (Merck "Li crystal" Grade) gave evidence of some impurity, but the temperatures and enthalpy changes noted in Fig. 6 are in fair agreement with the values of Barrall et al. [22] of 78.5, 2.1 and 1.7 J g^{-1} for the crystal → smectic, smectic → cholesteric, and cholesteric → isotropic transitions, respectively.

The RLI was rather variable in this case, and probably shows the effect of previous thermal history on the sample. Each transition gave a change in reflected light until the maximum reflectance was reached for the clear isotropic liquid.

TABLE 4

Applications of DSC–RLI

Phase changes

Melting, solid phase transitions and crystallisation of polymers, inorganic complexes, liquid crystals and minerals

Chemical changes

Decomposition of compelxes, hydrates, minerals and polymers
Metal oxidation (Cu, Fe, Mg)
High alumina cements
Polymer fire-retardance and ignition studies

Physical changes

Swelling and shrinkage (e.g., papers)
Surface melting, surface area changes and cracking
Colour changes due to chemical or physical causes

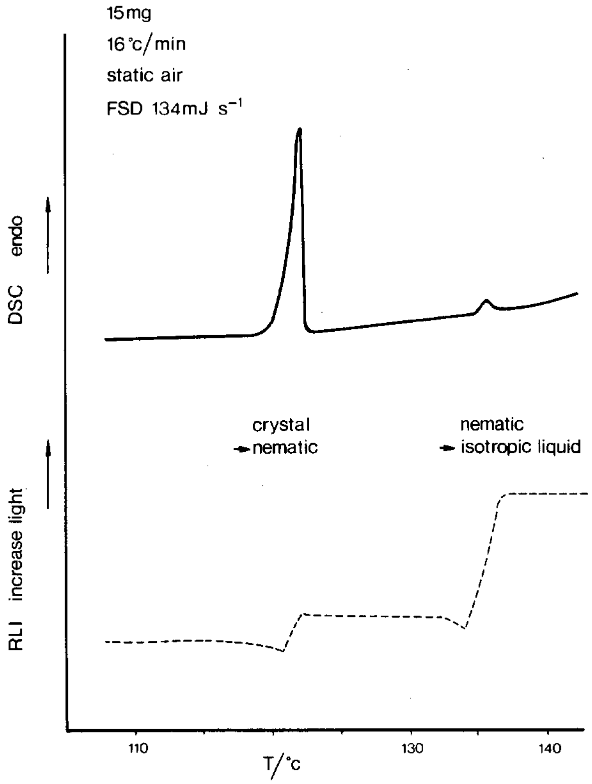


Fig. 5. DSC–RLI of *p*-azoxyanisole.

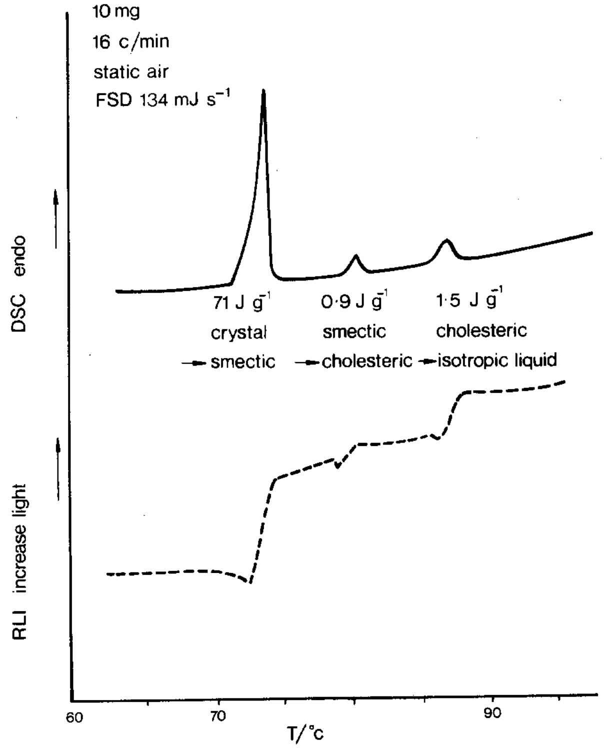


Fig. 6. DSC–RLI of cholesteryl myristate.

Wendlandt [1] has shown the applicability of these types of technique to complexes, and colour changes due to chemical reactions can easily be recorded. No attempt was made at 'diffuse reflectance spectroscopy', but the RLI curves do correspond pretty well to an isolambdic curve at $\lambda = 550$ nm.

Copper sulphate pentahydrate, $CuSO_4 \cdot 5\ H_2O$

A sample of small (> 100 mesh) crystals (Hopkin & Williams, recrystallised) was used and gave the usual DSC trace with no liquid water phase. The RLI trace (Fig. 7) shows an increase in reflectance for the initial loss of 2 H_2O, and a further increase for the formation of the monohydrate. These could be due to colour changes and to particle size changes.

The slight decrease in RLI below 240°C seems to be due to surface browning from traces of basic sulphate present. The decrease as the last water is lost also corresponds to further brown colouration. The enthalpy changes noted on the graph are comparable with those found by Beech et al. [23].

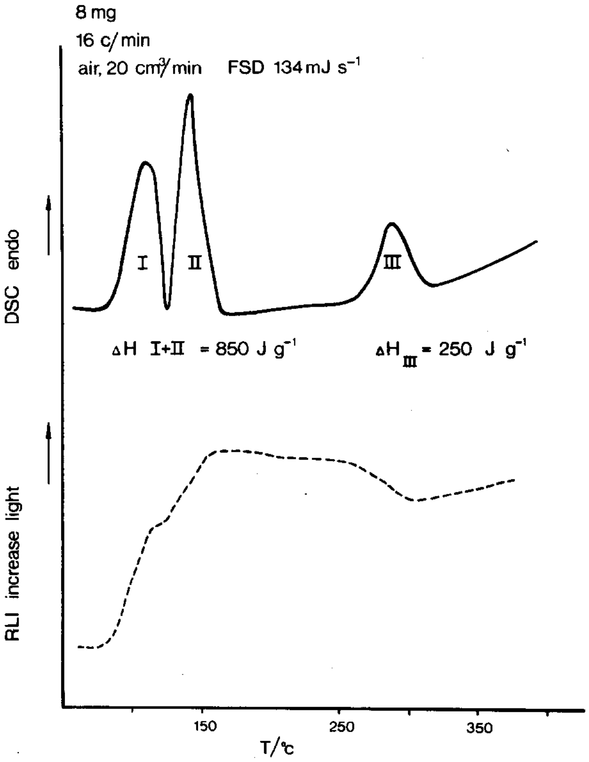


Fig. 7. DSC–RLI of copper sulphate pentahydrate.

Manganese formate dihydrate, $Mn(O_2C \cdot H)_2 \cdot 2\ H_2O$

We were interested in studying this compound because the dehydration has been studied kinetically [24,25] by DSC and by microscopy.

The commercial material (Harringtons) was carefully recrystallised from distilled water to give well-formed pink translucent crystals. These were run, both as a few separate crystals and as ~ 100 mesh powder. The DSC and RLI traces were similar and a typical run is shown in Fig. 8.

The first endothermic peak is due to loss of hydrate water with $\Delta H = 600 \pm 15$ J g^{-1}, and the exothermic peak at about 290°C corresponds to decomposition to manganese oxides, mostly MnO, and $\Delta H = -1250 \pm 50$ J g^{-1}.

The RLI increases considerably during the loss of hydrate water at 130°C and observations show a change from translucent pink to opaque, white crystals, but no change of crystal shape. An extra change appears in the RLI trace around 200°C. This decrease in reflection is clearly observable, and produces slightly shiny, browner crystals. Scanning electron microscopy of these samples reveals that the crystal shape is retained, but the sample begins to crack and disintegrate around 200°C. The final product at 500°C appears

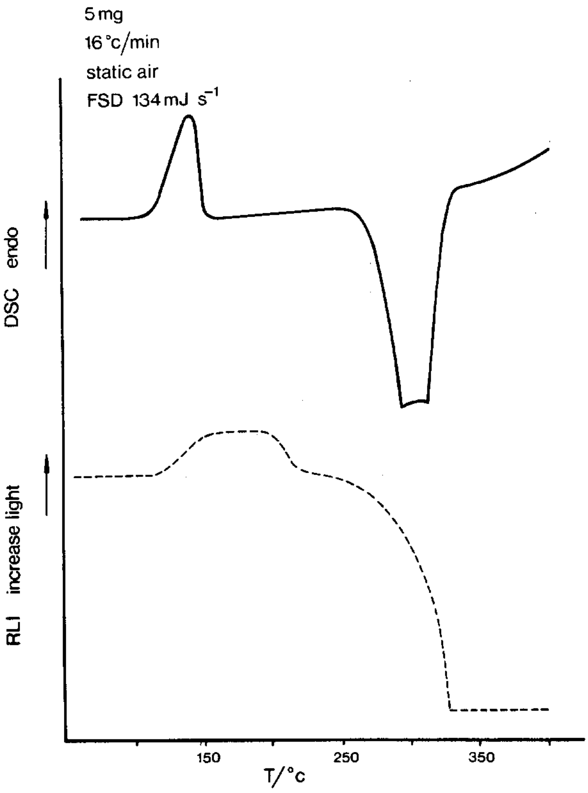


Fig. 8. DSC–RLI of manganese formate dihydrate.

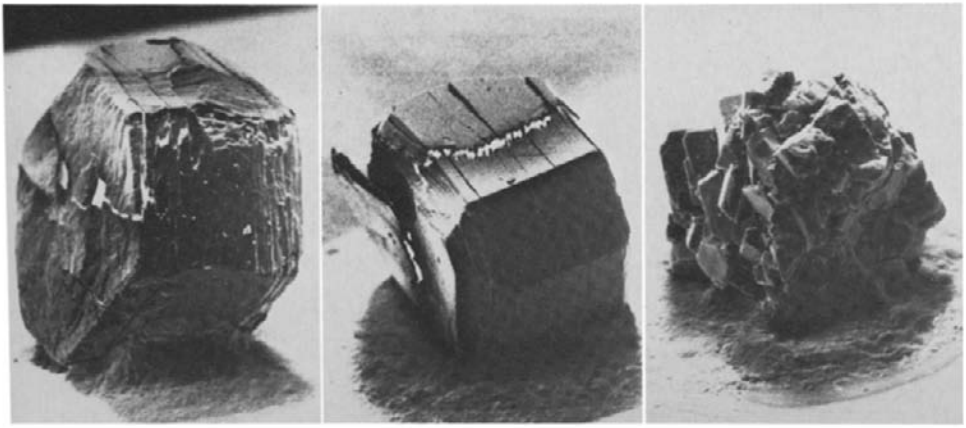


Fig. 9. Electron microscope photographs of manganese formate after heating to various temperatures: (a) 200°C; (b) 250°C; (c) 500°C. Magnification ×50.

to be a conglomerate of small crystals (Fig. 9).

The final decomposition is probably complex but may clearly be followed by RLI since the crystals change from white, through shades of brown to black.

Polymers and papers

Miller [10] has reviewed optical techniques applied to polymers and we hope that the combined technique will lead to a better understanding of fire retardant systems in polymers.

Poly(ethylene terephthalate)

A sample of woven polyethylene terephthalate fibres was cut to a 6 mm disc shape and heated to above the melting point. The melt was then rapidly cooled and re-run to give the traces shown in Fig. 10. The glass transition does not show in the original run, but may be detected by the change in reflectance at T_g at 80°C as the stress surface relaxes during subsequent heatings.

The cold crystallisation of the amorphous polymer produces a decrease in RLI and an exotherm ($\Delta H \approx -34$ J g^{-1}) at 150°C. Melting of the polymer at 250°C gives an increase in RLI corresponding to clearing of the polymer, and an endotherm ($\Delta H \approx +40$ J g^{-1}). These are more regular for the pre-melted sample. These temperatures correspond to those of the literature [26,27].

Poly(acrylonitrile)

A sample of fibres ['Dralon', Bayer (U.K.) Ltd.] was crimped into the pan and held by a metal washer which had been heated previously. This avoided

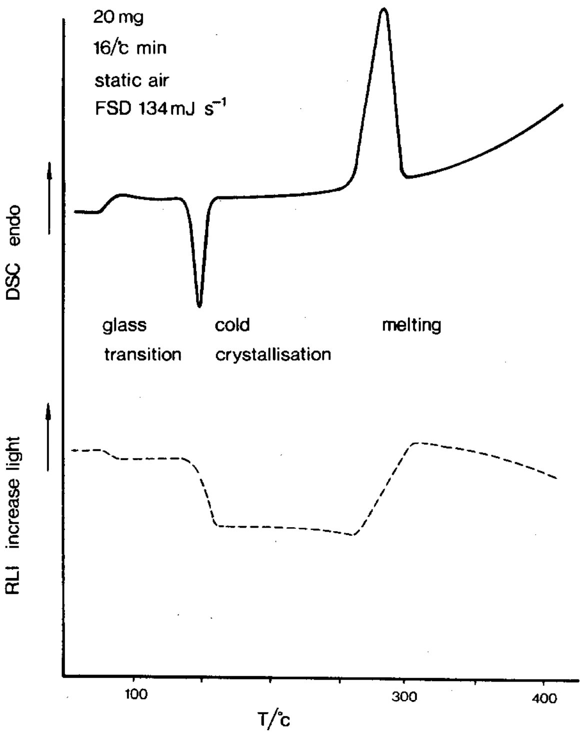


Fig. 10. DSC–RLI of poly(ethylene terephthalate).

the effects of the fibres curling up or moving during the run.

Dunn and Ennis [28] report that at heating rates of 100°C min^{-1} the melting point (~300°C) may be resolved from the exothermic decomposition. We were unable to observe any melting at the heating rates used, but the initial shrinkage of fibres at 230–250°C may indicate surface melting. No observable T_g, reported at 87–104°C [26] was found (Fig. 11).

The large exothermic decomposition with $\Delta H \approx -365 \pm 5$ J g^{-1} was observed and the decrease in RLI was accompanied by sharp jumps as the fibres moved. The colour changes reported by Madorsky [29] were observed and recorded.

Paper

A filter paper (Whatman No. 1) was cut into 6 mm discs by using a sharp metal hole punch. The discs, weighing about 3 mg, were run in the aluminium pans. Samples showed clearly the stages of decomposition reported for cellulose samples [29,30].

Initial loss of adsorbed water showed very small peaks on DSC and negligible change in RLI. Loss of the combined water crosslinking gave little DSC effect but large decrease in RLI corresponding to the browning of the sample. Oxidative degradation above produced a large exothermic peak and

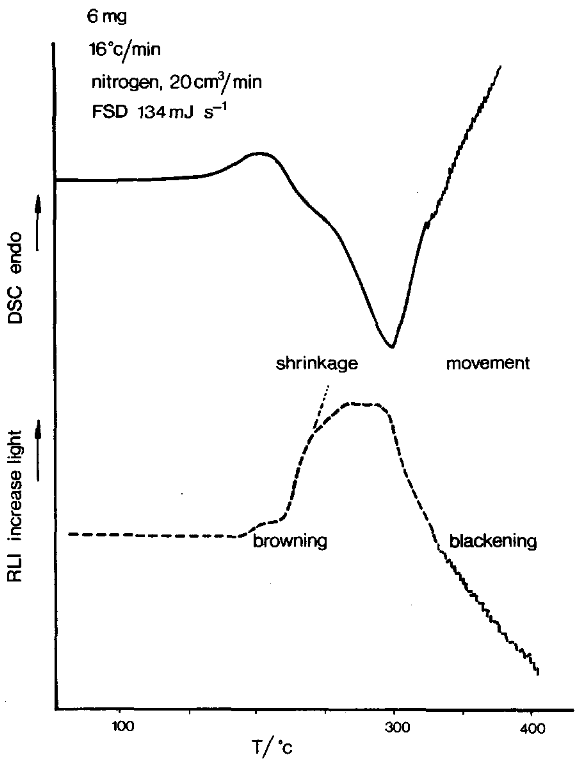


Fig. 11. DSC–RLI of poly(acrylonitrile).

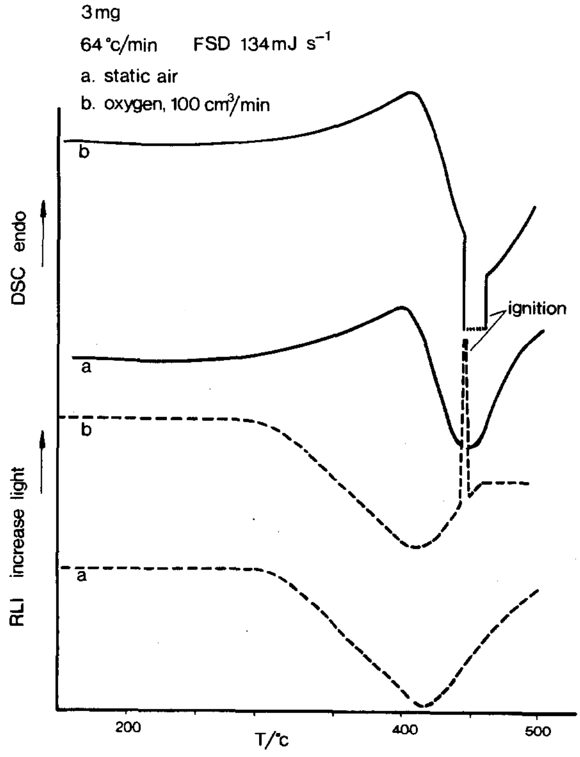


Fig. 12. DSC–RLI of paper samples: (a) in static air; (b) in flowing oxygen.

an increase in RLI because the sample shrank in the pan to a much smaller disc (Fig. 12a). Complications on the DSC trace must be expected in this instance because of the large changes in emissivity and the high temperatures involved.

One additional advantage of using this combined method is shown in Fig. 12b where the sample was run in flowing oxygen, and using a high heating rate. At 440 ± 5°C ignition of the sample occurred and it burned completely. This produced a brilliant flash on the RLI and a wild exothermic spike on the DSC. The effect of fire retardants on ignition might be studied using this.

CONCLUSIONS

The addition of a relatively simple microscope system to the DSC has given substantially more information about the nature of the events which occur, and enabled simultaneous recording and photography of thermal changes to be added to the DSC study, with no loss of facilities, little modification and little loss of calorimetric accuracy. Table 4 shows some of the applications in which the system has already been of value.

ACKNOWLEDGEMENTS

The authors gladly acknowledge the contributions made to this work by their students, particularly A.J. Dolan and A.H. Warner, and the invaluable skills of the workshop of Kingston Polytechnic in constructing parts of the apparatus.

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