Thermochimica Acta, 5 (1972) 41–49

A DEPOLARIZED LIGHT INTENSITY APPARATUS FOR USE WITH DIFFERENTIAL THERMAL ANALYSIS

EDWARD M. BARRALL II† and JULIAN F. JOHNSON*
Chevron Research Company, Richmond, California 94802 (U. S. A.)
(Received March 8th, 1972)

ABSTRACT

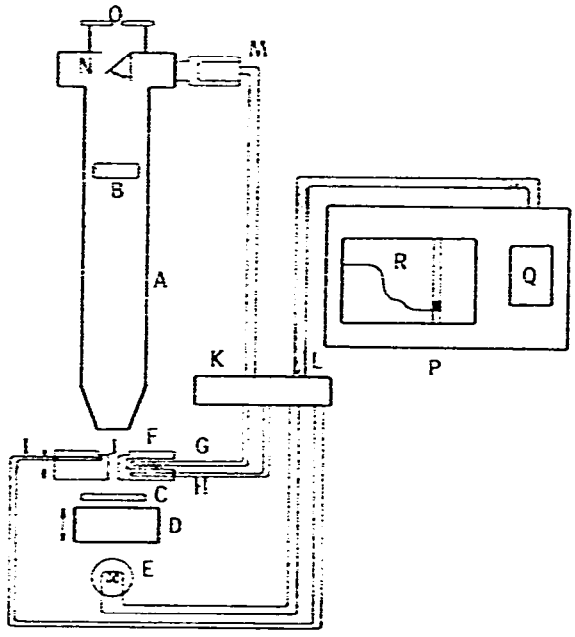
The technique of depolarized light intensity (DLI) measurement yields useful information on polymer melting points, crystallinity, and rate of crystallization. Most of the DLI instruments described to date have been separate, complete units. This paper describes an apparatus to function as an auxiliary module with a differential thermal analyzer. Thus, the differential thermal analyzer provides the necessary temperature programmer, amplifier, and temperature and signal recorder. The necessary auxiliary equipment to obtain DLI measurements is relatively simple and convenient to operate.

INTRODUCTION

The technique of depolarized light intensity (DLI) was introduced by Magill[1]. The basic elements of the apparatus are a light source, polarizer, sample holder, analyzer, and a suitable recording system (see Fig. 1). An isothermal or temperature programmed mode may be employed. Solid crystalline materials, except those in the cubic crystalline region, convert plane polarized light into elliptically polarized light due to differences in refractive index along nonperpendicular and/or unequal crystal axes. At any transition temperature between ordered states, a change in the type of polarized light occurs. Some polymers exhibit form birefringence in addition to crystalline birefringence. This depends on the ratio of the amorphous to crystalline polymer if the refractive indices differ. The amount of translation of the transmitted light is a function of the content of crystalline material, the size of the crystalline regions, and the orientation of these regions. These two processes, as well as scattering, result in a change in light intensity at the photometer. An exact interpretation of the results is complex, see for example the work of Clough, Rhodes, and Stein[2]. Used on an empirical basis alone, DLI measurements have found a number of useful applications[3].

A number of instruments to make DLI measurement have been described[4–10]. These have, in general, been built as separate units for the sole purpose of making

†Present address: IBM Research Laboratory, San Jose, California 95114.
*Present address: The Department of Chemistry, University of Connecticut, Storrs, Connecticut.



A - Unitron MPS Microscope
B - Analyzer Sheet
C - Polarizer Sheet
D - Movable Abbe Condenser
E - Tungsten Lamp
F - Movable Hot Stage
G - Heater
H - Program Thermocouple
I - Sample Temperature Thermocouple
J - Sample Well
K - Pin Plug Terminal Attached to Microscope Stand
L - Shielded Cable to Du Pont Module
M - Photocell
N - Movable Mirror
O - Ocular
P - Du Pont 900 Differential Thermal Analyzer Module
Q - Programmer
R - X-Y Recorder

Fig. 1. Diagram of the depolarized light intensity apparatus.

DLI measurements. It is possible to modify existing differential thermal analysis equipment which contains the temperature programmer, amplifiers, and recording devices to readily accept a separate depolarized light-intensity module, which is thus considerably less complex than a complete instrument. This paper describes the construction, and illustrates the operation of such an auxiliary DLI module for use with a differential thermal analyzer.

EXPERIMENTAL

Description of apparatus

Fig. 1 shows a schematic design of the DLI apparatus, and Fig. 2 is a photograph of the instrument. A microscope of the type used for chemical analysis is a satisfactory optical system. The field of view can be restricted to particular areas, but the light loss is not great. The Du Pont Model 900 Differential Thermal Analyzer was used in this work. Fig. 3 shows a wiring diagram for the DLI module. At 110V,

60-Hz regulated power output can be obtained between pins 6 and 24, as shown in Fig. 3. The temperature program heater voltage is obtained between pins 5 and 25. This is sufficient to operate a 60-W cartridge heater. The chromel—alumel thermocouples for the regulation of the program output are introduced at pins 13 and 30. A separate ice junction for the program is supplied at the microscope platform. The stage temperature is measured by a second chromel—alumel thermocouple at the microscope platform. The output of this pair is introduced through pins 33 and 34.

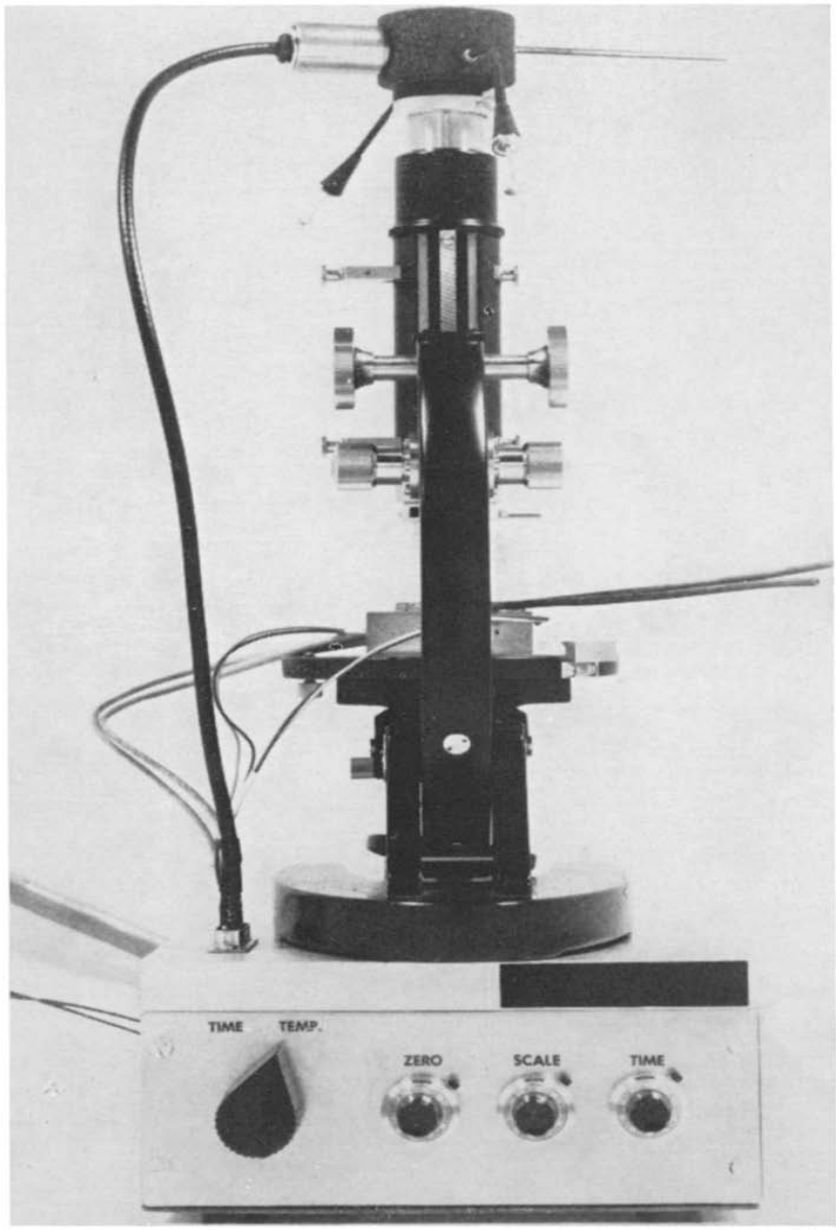


Fig. 2. Photograph of the depolarized light intensity module.

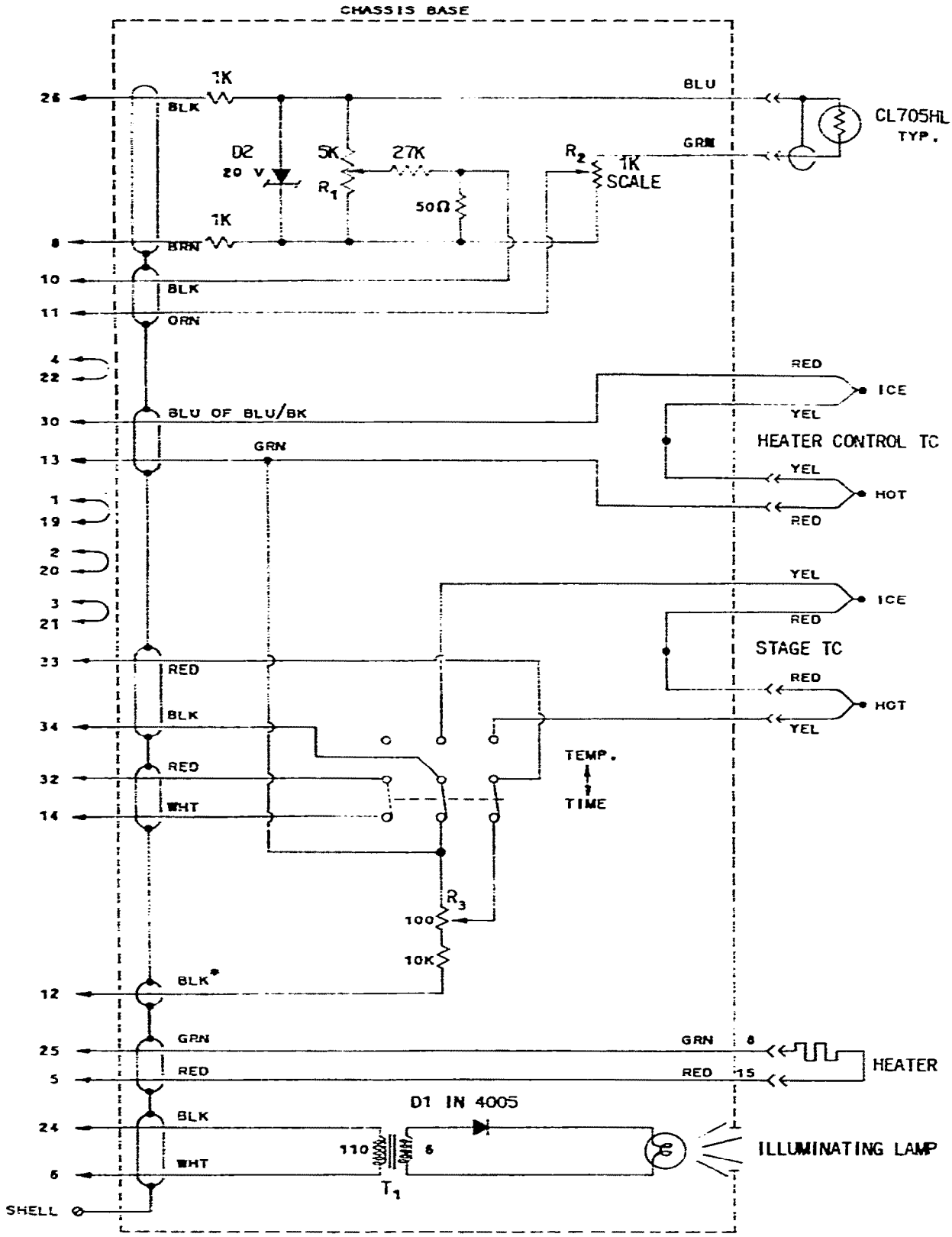


Fig. 3. Schematic diagram of the depolarized light intensity module.

A time axis generator for isothermal studies, important in the measurement of nucleation rates, is also provided by 100 and 10K ohm resistors with power and signal injection at pins 33, 34, 32, 14, and 12. These connections will furnish either a temperature or time base for the Du Pont 900 Module x-axis, depending on the switch position (see Fig. 2 and 3). The 100-ohm variable potentiometer controls the rate of pen advance in the time axis mode. After initial setting, its use is restricted to fine calibration of the rate of pen advance.

The intensity of the depolarized light is measured with a photoconductive cell (CL705HL) and a modified wheatstone bridge. Power for operating the bridge is

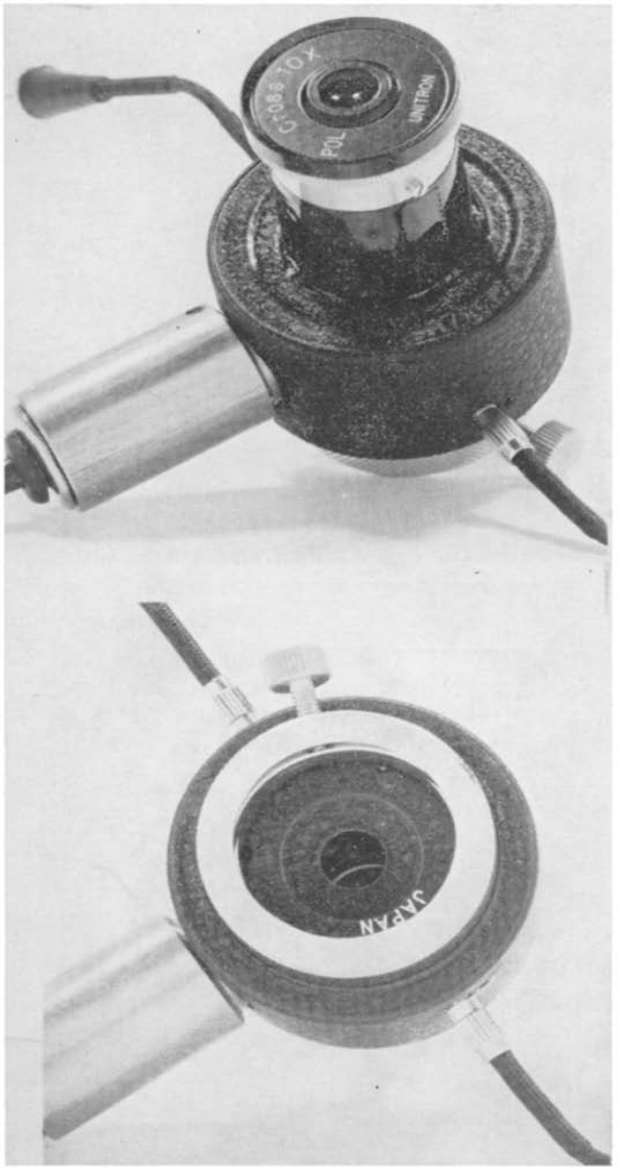


Fig. 4. Photograph of the photocell housing.

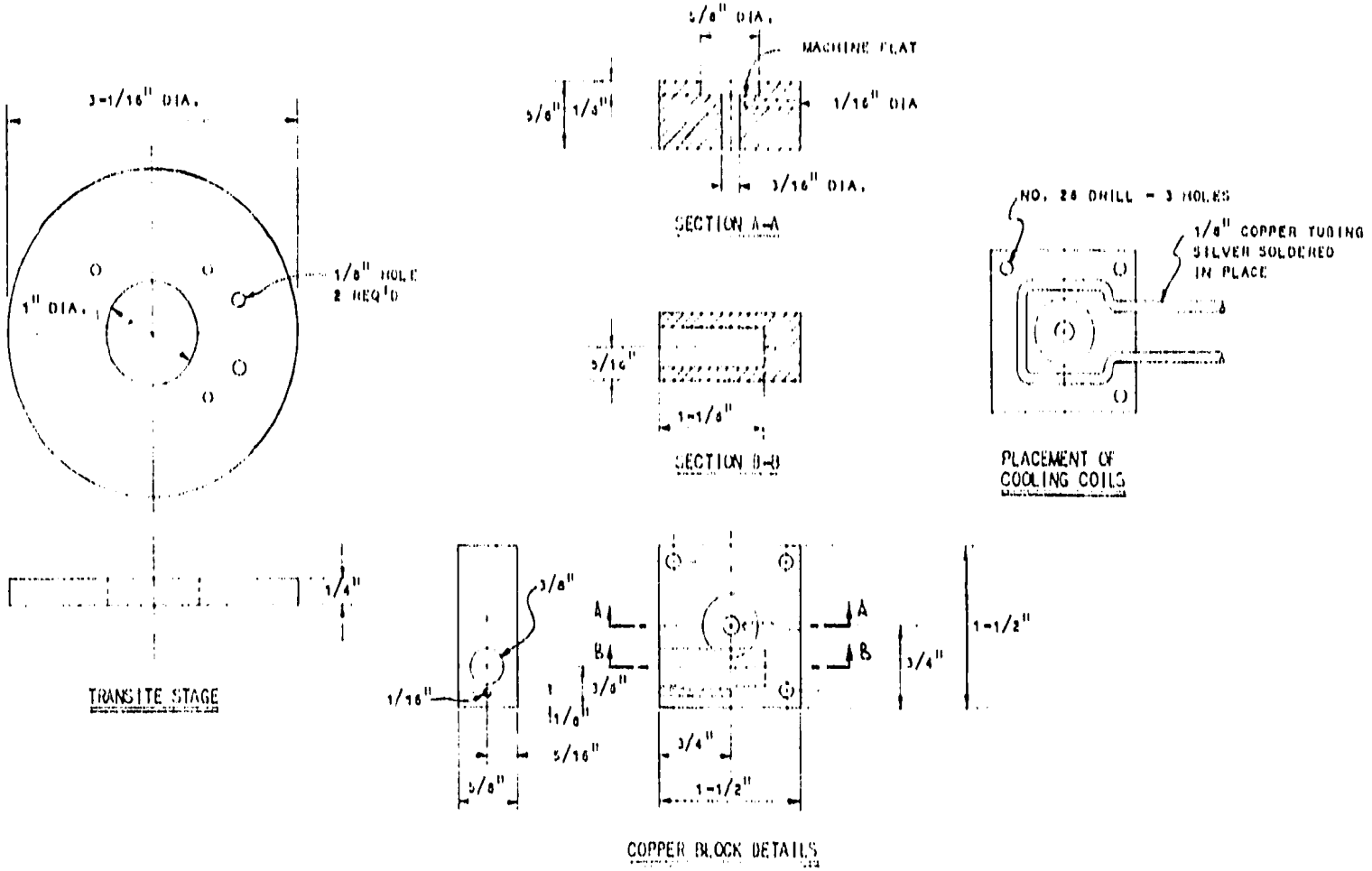


Fig. 5. Diagram of the copper block hot stage.

obtained at pins 8 and 26. The degree of null departure is measured at pins 10 and 11. The 1K ohm control provides an effective means of regulating the "sensitivity" of the bridge outside the instrument module. At the thermal analyzer, the controls for the temperature programming work are described in the Du Pont Manual[11]. In the time axis mode, the instructions given[12] for isothermal thermobalance operation applies. The *y*-axis or differential axis control now regulates the sensitivity of the apparatus to the bridge output. The units of this axis are purely arbitrary and relative.

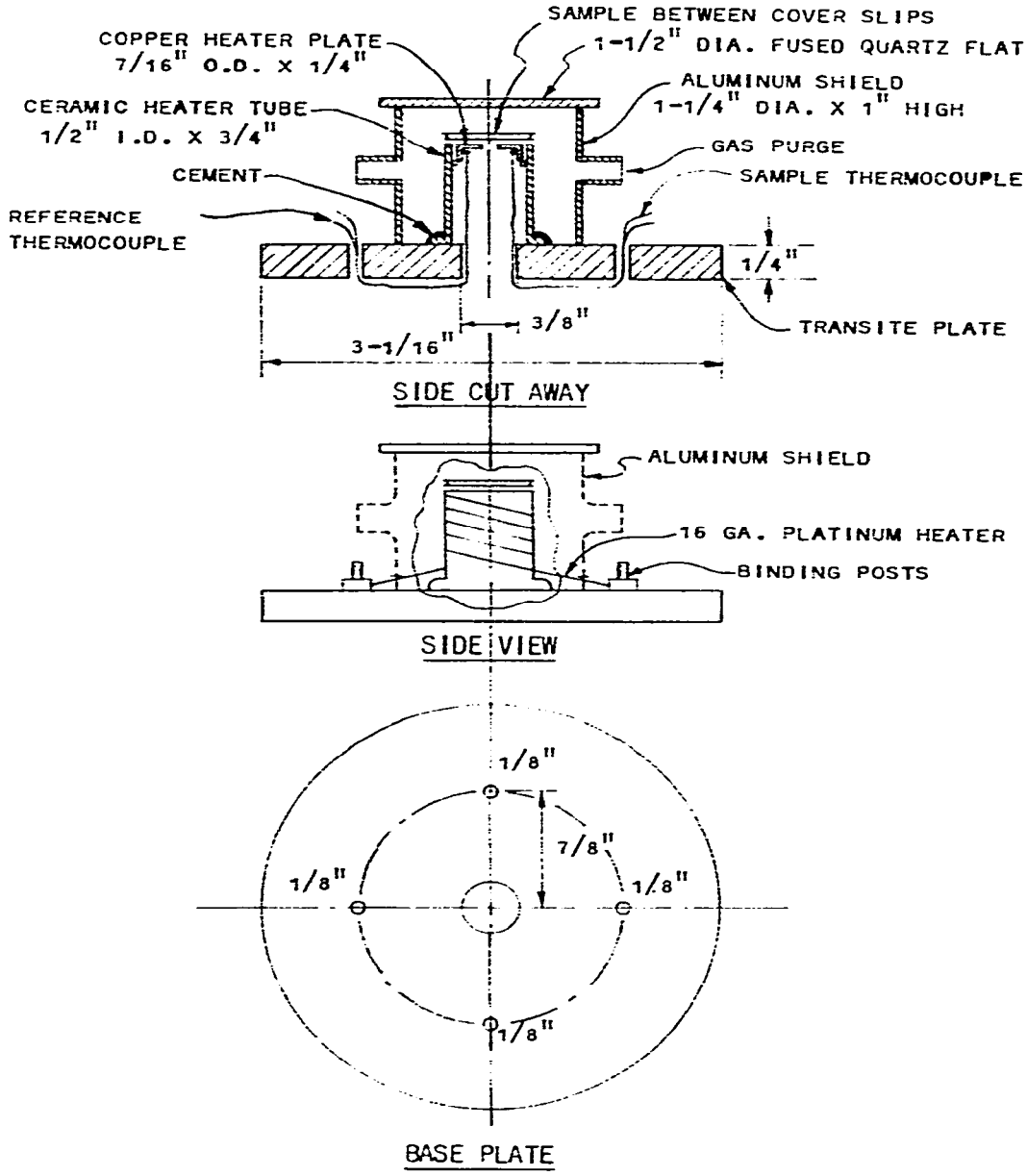


Fig. 6. Diagram of the low-mass hot stage for depolarized light intensity measurement.

The microscope is a Unitron MPS chemical microscope equipped with an abbé condenser; rotatable polarizer; fixed analyzer; quartz red plate; 4×, 10× objectives; 5× and 10× oculars; and a 35-mm camera attachment. The camera attachment permits convenient addition of the photocell (Fig. 4). The side focusing objective lens was removed and the photocell housing threaded in. In the opening normally reserved for the camera objective, the conventional 10× microscope ocular has been cemented. By depressing one or the other of the cable buttons, the image form the objective passes vertically up the microscope to the ocular for observation or is deflected by a mirror for measurement by the photocell.

The stage shown in Fig. 5 is a copper block with the necessary holes for the light path, control thermocouple, measuring thermocouple heater cartridge, and sample mounting. Dry nitrogen, previously chilled in a heat exchange coil at dry ice temperature, is carried in a copper tube braised to the top of the stage. In operation, the sample well is covered by a flat vitreous quartz plate to reduce cooling by draft. Temperatures from −40 °C to 600 °C can be covered by this stage at heating rates under 5 °C/min or for isothermal operation.

To obtain heating rates of 5 °C/min or faster, a cell design which has a relatively low mass and uses a 10-ohm platinum heater is shown in Fig. 6. The upper temperature of this design is 800 °C.

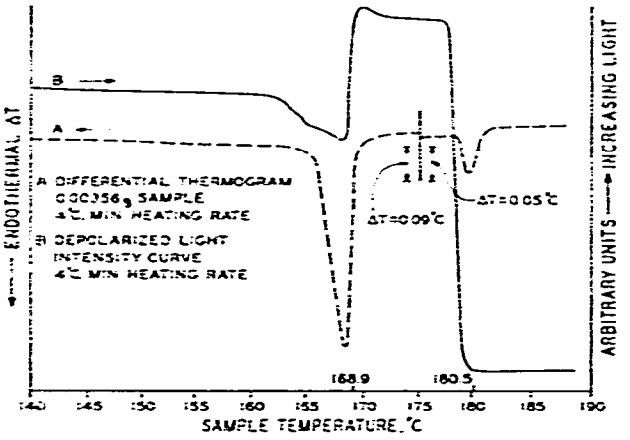


Fig. 7. DLI trace for anisaldazine.

Applications

The DLI is particularly useful for following small changes in solid structure. Transitions requiring only a few hundredths of a cal/g are recorded as easily as much more energetic processes (Fig. 7). Recrystallization of polymers during heating can be observed with great sensitivity (Fig. 8). Other applications are covered in references previously cited.

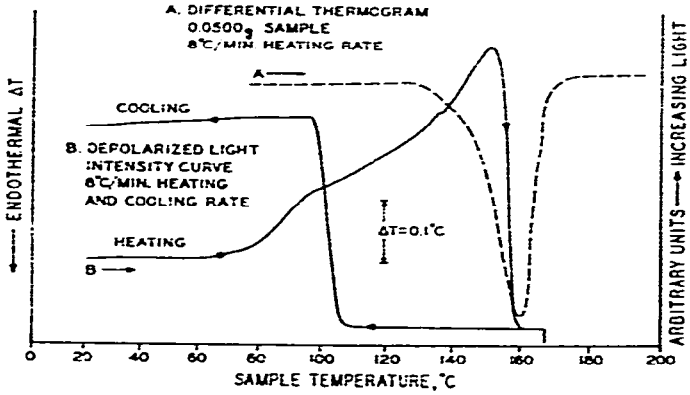


Fig. 8. DLI trace for cast polypropylene.

CONCLUSIONS

A simple module-type construction provides a depolarized light intensity apparatus that utilizes existing differential thermal analysis equipment.

REFERENCES

1 J. H. Magill, *Nature*, 187 (1960) 770.
2 S. Clough, M. B. Rhodes, and R. S. Stein, *J. Polym. Sci. Part C*, 18 (1967) 1.
3 E. M. Barrall II, R. S. Porter, and J. F. Johnson, *Appl. Polym. Symp.*, 8 (1969) 191.
4 E. M. Barrall II and E. J. Gallegos, *J. Polym. Sci. Part A*, 5 (1967) 113.
5 E. J. Gallegos, *J. Polym. Sci. Part A*, 3 (1965) 3982.
6 C. W. Hock and J. F. Arbogast, *Anal. Chem.*, 33 (1961) 462.
7 S. Hoshino, E. Meinecke, J. Powers, and R. S. Stein, *J. Polym. Sci. Part A*, 3 (1965) 3041.
8 N. S. Ivanov, T. N. Sal'nikova, and D. V. Fil'bert, *Sov. Plast.*, 11 (1965) 54.
9 A. K. Kolb, C. L. Lee, and R. M. Trail, *Anal. Chem.*, 39 (1967) 1206.
10 J. H. Magill, *Polymer*, 2 (1961) 221.
11 *Du Pont 900 Differential Thermal Analyzer Instruction Manual*, pp. 6–7.
12 *Du Pont 950 Thermogravimetric Analyzer Instruction Manual*, pp. 3–17.