Journal of Thermal Analysis, Vol. 33 (1988) 1167–1169

INVESTIGATIONS OF PHOTOPOLYMERIZATION BY MEANS OF INTERMITTENT ILLUMINATION

W. Trautsch, H.–J. Flammersheim and *G. Rudakoff*

DEPT. OF CHEMISTRY, FRIEDRICH SCHILLER UNIVERSITY, LESSINGSTR. 10, JENA, 6900 G.D.R.

An apparatus is described for intermittent illumination of the sample in a DSC–2C (Perkin-Elmer) modified with some additional optical equipment. A slotted disk is used as a light chopper. This is driven by a computer-controlled stepping motor. The various frequencies needed for investigations of this kind are derived from a computer quartz-controlled clock frequency by means of software. The operator dialogue is achieved through the Perkin-Elmer Data Station to simplify the use of the equipment.

Polymerization reactions induced by either UV or visible light are used in several branches of industry. The polymers are utilized as coating materials, as photocurable surface layers, or as adhesives in optical systems. The reactions are not only of commercial importance, but also of great theoretical interest. For optimization of the reaction parameters, it is desirable to know the details of the kinetics of this kind of reaction.

There are various ways to determine the kinetic constants of these reactions. One of them is through investigations involving intermittent illumination. A typical way to perform this technique is to cut a steady light beam by means of a rotating wheel with dark and light sectors (the "rotating sector method").

A summary of this method and its theory, including a computer program which is able to display the radical concentration of vinyl polymerization as a function of time for selected initial conditions, is given in [1].

The principle of the method is as follows:

If the speed of the rotating sector is low, the concentration of radicals reaches the steady-state value during illumination of the sample, and falls to zero when the illumination is stopped. The average rate of reaction scarcely depends on the speed of the slotted disk if the time of illumination is clearly different from the average lifetime of the radicals. In the case of a high sector speed, new radicals are generated before the active centers from the last flash have been used up. Here the average concentration of radicals is somewhat lower than its steady-state value.

If the time of a light flash is similar to the lifetime of the radicals, the average rate of reaction evidently varies with the frequency of the light-

John Wiley & Sons, Limited, Chichester
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dark cycles. Therefore, the lifetime of the chain carriers can be determined from a plot of the ratio of the average and steady-state values of the reaction rate *vs.* the cycle time of illumination. Through use of the lifetime obtained and the rate of initiation, which can be determined separately, the constants for chain propagation and termination can be computed.

To use this technique, it is necessary to acquire information about the reaction rate at any moment. Differential scanning calorimetry is a good method of obtaining the rate through the heat of reaction produced.

As calorimeter, a Perkin-Elmer DSC-2C was used, which was modified to allow the illumination of the sample holder. The DSC was complemented with some optical equipment: A high-pressure HBO 200 mercury lamp serves as a light source. This lamp is connected to a special stabilization circuit to permit control of the light intensity. For the absorption of the IR radiation of the light source, a water filter is used.

The light beam itself is focused on the slotted disk by means of some quartz lenses. At the end of the optical bench, a mirror reflects the light into the DSC. In the sample holder cover of the DSC, two holes are drilled, both closed with quartz disks to let the light fall onto the sample and/or the reference. The glove box of the DSC was modified in a similar way. Inside the box, a quartz lens is installed to increase the light intensity inside the sample holder. This lens may be adjusted from outside the box.

The main part of the entire apparatus is the "rotating sector" itself. Because of the high requirements as concerns frequency range and stability, a slotted disk driven by a stepping motor is used. The motor is connected to a single board computer. This computer controls the speed of the disk in a wide range and makes it possible to change the light-dark ratio in an uncomplicated way. The time base is quartz-controlled, and therefore very good reproducibility of the illumination times is guaranteed. A further advantage in using a stepping motor is the relatively sharp change from light to dark, even if the cycle time is long.

All the information necessary for the single board computer comes from a Perkin-Elmer 3600 Data Station. A short program on this computer is used to make up a dialogue with the operator, to simplify the operation of the apparatus for intermittent illumination. Software for analysis of the obtained data on the 3600 Data Station will produced shortly.

References

1 S. J. Moss, Free-Radical Polymerization Using the Rotating-Sector Method, J. Chem. Educ., 59 (1982) 1021–1024.

Zusammenfassung – Mit Hilfe einiger optischer Ergänzungsausrüstungen wurde ein DSC-2C (Perkin-Elmer) Gerät modifiziert, um Proben unterbrochen belichten zu können. Als Lichtunterbrecher diente eine Lochscheibe, die von einem computerkontrollierten Schrittmotor getrieben wurde. Die verschiedenen Frequenzen, die zu Untersuchungen dieser Art notwendig sind, werden softwaregestützt aus der quarzgesteuerten Uhrenfrequenz des Computers gewonnen. Zur Vereinfachung der Kommunikation mit dem System geschieht diese über die Perkin-Elmer Data Station.

РЕЗЮМЕ — Описана аппаратура для прерывистого освещения образца в приборе ДСК—2С фирмы Перкин-Эльмер, дополненного соответствующим оптическим оборудованием. В качестве прерывателя света был использован секторный диск, управляемый шаговым мотором. Необходимые световые частоты устанавливались на основе частоты кварцевых часов, программно-управляемых с помощью ЭВМ. Для более простого управления аппаратурой введен диалог оператора посредством базовых данных фирмы Перкин-Эльмер.