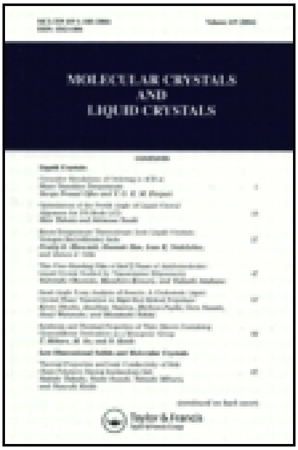
This article was downloaded by: [University of Haifa Library]
On: 20 August 2012, At: 10:50
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Thermally Stimulated Technique Employed to Reactions in Polycrystalline Photochromic Systems

Juliusz Sworakowski [a] , Stanislav Nešpurek [b] & Marcel Bertault [c]

[a] Institute of Physical and Theoretical Chemistry, Technical University of Wroclaw, 50-370, Wroclaw, Poland

[b] Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06, Prague, Czech Republic

[c] Groupe Matiere Condensée et Matériaux, Université de Rennes I, 35042, Rcnnes Cedex, France

Version of record first published: 04 Oct 2006

To cite this article: Juliusz Sworakowski, Stanislav Nešpurek & Marcel Bertault (1998): Thermally Stimulated Technique Employed to Reactions in Polycrystalline Photochromic Systems, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 313:1, 199-204

To link to this article: http://dx.doi.org/10.1080/10587259808044275

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Downloaded by [University of Haifa Library] at 10:50 20 August 2012

Mol. Cryst. Liq. Cryst., 1998, Vol. 313, pp. 199–204
Reprints available directly from the publisher
Photocopying permitted by license only

© 1998 OPA (Overseas Publishers Association)
Amsterdam B.V. Published under license
under the Gordon and Breach Science
Publishers imprint.
Printed in India.

Thermally Stimulated Technique Employed to Reactions in Polycrystalline Photochromic Systems

Juliusz SWORAKOWSKI[a], Stanislav NEŠPUREK[b] and Marcel BERTAULT[c]

[a]Institute of Physical and Theoretical Chemistry, Technical University of Wrocław, 50-370 Wrocław, Poland; [b]Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, 162 06 Prague, Czech Republic; [c]Groupe Matiere Condensée et Matériaux, Université de Rennes I, 35042 Rennes Cedex, France

Downloaded by [University of Haifa Library] at 10:50 20 August 2012

The paper presents preliminary results of measurements of the energetics and kinetics of thermally driven reverse reaction in polycrystalline photochromic systems: substituted dihydropyridines and their thiopyrane analogue. The technique of differential scanning calorimetry (DSC) was employed aiming at obtaining a qualitative information concerning the relative energies of the ground states of the stable and metastable formsof the photochromic systems. Moreover, a DSC experiment can be regarded as a thermally stimulated process and analysed in a way allowing one to extract information about the energy barrier associated with the thermal process. A more detailed study was performed on 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine: two processes were identified, their activation energies amounting to (115 ± 20) and (60 ± 20) kJ/mol. The DSC results were supplemented with those obtained from UV-VIS spectroscopy.

Keywords: photochromic systems; differential scanning calorimetry; thermally stimulated process; dihydropyridine; thiopyran

INTRODUCTION

The photochromic behaviour of molecular materials has been known for a long time (e.g., [1,2]), recently, however, these materials have attracted a growing attention due to their potential use as reversible recording materials [3]. Among several groups of molecules which have been studied to date, derivatives of dihydropyridine, pyrane or thiopyrane have been relatively little known. The formulae of the materials, hitherto studied by the Japanese [4] and Czech

[5-10] groups, are shown in Figure 1. Upon irradiation in the near UV region, they undergo a photoreaction resulting in production of coloured metastable species; the reaction is both thermally and photochemically reversible. The nature of the coloured species has not been unequivocally established; an intramolecular phenyl shift and/or a 3,5-ring closing reaction are likely to be involved (see Figure 1) but the exact reaction path is still uncertain.

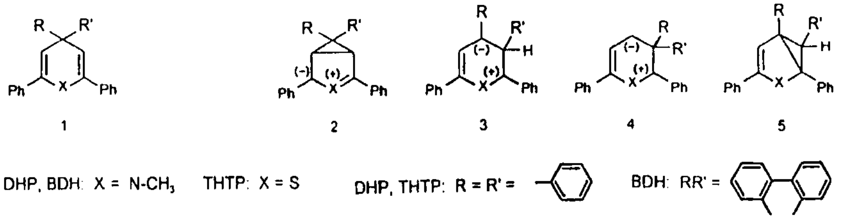


FIGURE 1. Chemical formulae of the stable form (1) and some postulated coloured forms (2-5) of the photochromic compounds under investigation [4-7].

The aim of the present contribution is to put forward preliminary results of the measurements of the energetics and kinetics of the reverse reaction in three representatives of the family: 1-methyl-2,4,4,6-tetraphenyl-1,4-dihydropyridine (hereafter referred to as DHP), 4,4-(biphenyl-2,2'-diyl)-2,6-diphenyl-1-methyl-1,4-dihydropyridine (BDH) and 2,4,4,6-tetraphenyl-4*H*-thiopyran (THTP). We have employed the technique of differential scanning calorimetry (DSC) aiming at obtaining at least a qualitative information concerning the relative energies of the ground states of the stable and metastable forms. Basing on a simple thermodynamic argument , one may show that the energy difference between the ground states of the stable and metastable forms of a photochromic system should be equal to the enthalpy of the reverse reaction. Moreover, the reactions studied in DSC experiments can be regarded as thermally stimulated processes [11] and analysed in a way allowing one to extract information about the kinetics of the reverse reaction, and hence the energy barrier associated with the thermal process. These DSC results can be compared with those obtained from isothermal kinetic measurements employing the UV-VIS spectroscopy.

EXPERIMENTAL

The measurements reported in this paper were carried out on polycrystalline samples supplied by Prof. J. Kuthan and Dr S. Böhm (Prague Institute of Chemical Technology). Details of synthesis, purification and characterization of

Downloaded by [University of Haifa Library] at 10:50 20 August 2012

Downloaded by [University of Haifa Library] at 10:50 20 August 2012

the materials were described elsewhere [6-8]. The polycrystalline samples were irradiated with a UV lamp supplied with a bandpass filter shining into the UV absorption bands of the materials. As comes from earlier experiments [7,8], thermally driven reverse reactions in the materials under study are quite slow at ambient temperature thus allowing for a safe manipulation with the irradiated samples. UV-VIS spectra and the kinetics of isothermal bleaching were determined from measurements of the diffuse reflection of mixtures of polycrystalline materials powdered with MgO, using a Perkin-Elmer-Hitachi 340 spectrophotometer. The DSC measurements were carried out employing a Perkin-Elmer DSC7 scanning calorimeter, between 250 K and a temperature ca. 5 K below the respective melting point.

RESULTS AND DISCUSSION

Irradiation of the polycrystalline materials results in appearance of coloured forms, their absorption maxima located between ca. 550 nm and 640 nm depending on the material. The absorption spectra of the materials under study in their stable and coloured forms are shown in Fig. 2.

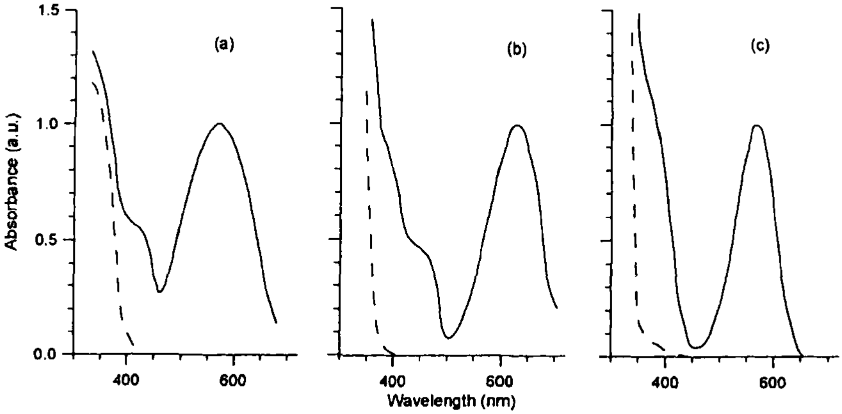


FIGURE 2. Absorption spectra of stable (broken lines) and coloured (full lines) forms of polycrystalline DHP (a), BDH (b) and THTP (c). The spectra are normalized at the maxima of the absorption peaks of their coloured forms

The isothermal kinetics of the reverse reactions can be followed as a decrease of the intensities of the bands in the visible region; earlier experiments (e.g., [7,8]) showed that the decays are reasonably described by „stretched exponential" functions, with temperature-dependent exponents and the average

Downloaded by [University of Haifa Library] at 10:50 20 August 2012

activation energies amounting to ca. 37 kJ/mol for all materials.

The calorimetric measurements were performed on both unirradiated samples (containing crystallites of stable forms only), and on the samples irradiated with UV. In the former case, the temperature dependences of the specific heat exhibited no anomalies over the entire temperature range covered by our experiments. The behaviour of the irradiated materials was qualitatively different: in all of them, we observed the appearance of exothermic anomalies at elevated temperatures. The effect could be observed only once after each irradiation: to within experimental accuracy, subsequent runs performed on the same samples were essentially identical with those obtained on unirradiated samples. This difference can be attributed to the heat evolved during thermally driven reverse reactions occurring between the metastable and stable forms of the photochromic systems.

The largest value of the enthalpy determined from the experiments amounted to -22 kJ/mol. Our results demonstrate, however, that the temperature dependence of the excess heat flow (the difference of the heat flows measured during the first and the second run) is a function of the conditions of irradiation. A detailed study was performed on DHP: depending on the irradiation conditions, we could observe the presence of *two* peaks with different build-up times, and apparently associated with two different processes (cf. Figure 3a).

To get an insight into the kinetics of the processes, we used the technique of partial heating. The technique, often employed in studies of distributions of dipolar relaxations in dielectrics [12,13] and allowing one to separate the

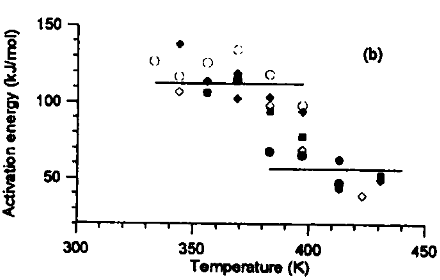


FIGURE 3. (*a*) The excess heat flow measured on DHP samples irradiated during 60 minutes (triangles), 120 minutes (diamonds) and 180 minutes (circles). (*b*) Activation energies obtained from the partial heating experiments (cf. Fig. 4). Different symbols refer to series of experiments performed on different samples.

Downloaded by [University of Haifa Library] at 10:50 20 August 2012

activation energies associated with these processes, consists of a sequence of heating runs terminating at increasing temperatures. An example of such an experiment is shown in Figure 4. Analysis of the DSC partial heating curves seems to reveal the presence of two processes, their activation energies amounting to (115 ± 20) and (60 ± 20) kJ/mol (see Figure 3b). Such a large spread of the activation energies is due to several factors, mainly to a strong dependence of the reaction kinetics on the sample history (size of the crystallites, concentration of defects, conditions of irradiation etc.). It should also be noted that the values determined from DSC significantly exceed those obtained from isothermal measurements [7,8]. One may speculate that the differences are due to different conditions of experiment: time of irradiation, morphology of samples etc. Additional experiments are carried out, at present, however, we are unable to offer any final explanation of the discrepancies.

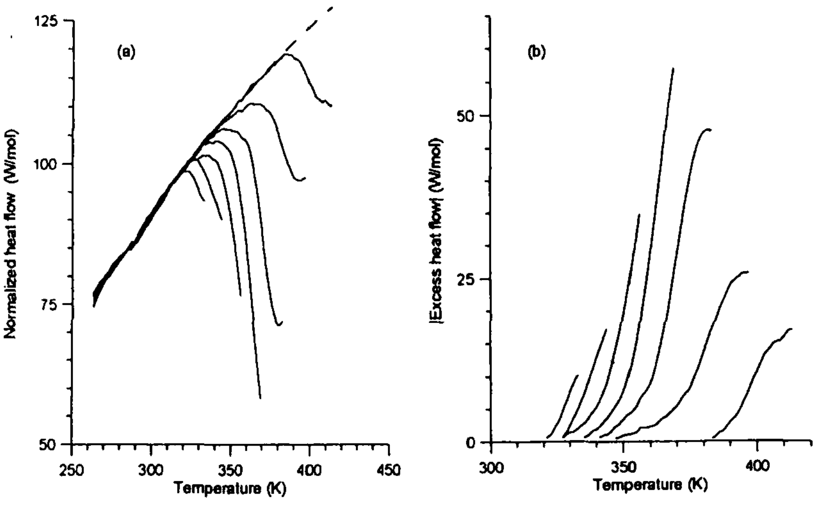


FIGURE 4. (*a*) DSC partial heating experiment measured on a DHP sample. (*b*) Excess heat flow calculated by substracting the baseline (broken line in (*a*))

Experiments performed on BDH yield similar results, indicating that the processes leading to the photochromic behaviour should be of similar nature. It is, however, interesting to note that the experiments performed to date seem to reveal the presence of one peak only. Irradiated polycrystalline THTP behaves qualitatively in the same way; the exothermic anomaly appears, however, at markedly higher temperatures (only ca. 20 K below the melting point), partly overlapping with a pre-melting endotherm. Any quantitative interpretation of the results is in this case much more difficult.

Downloaded by [University of Haifa Library] at 10:50 20 August 2012

Acknowledgements

This work was partly supported by the Polish State Committee for Scientific Research within the grant No 3T9A4812. Some experiments were carried out using equipment purchased by the Foundation for Polish Science. The authors thank Prof. J. Kuthan and Dr S. Böhm for the gift of the photochromic materials used in this study.

References

[1] *Photochromism,* edited by G.H. Brown, (J. Wiley-Interscience, New York 1971).

[2] *Photochromism. Molecules and Systems,* edited by H. Dürr and H. Bouas-Laurent (Elsevier, Amsterdam 1990).

[3] *Photo-Reactive Materials for Ultrahigh Density Optical Memory,* edited by M. Irie (Elsevier, Amsterdam 1994).

[4] *Reactivity in Molecular Crystals,* edited by Y. Ohashi (Kodansha, VCH, Tokyo and Weinheim, 1994), Chap. 5 and references therein.

[5] S. Nešpůrek and W. Schnabel, *J. Photochem. Photobiol.* **A 60**, 151 (1991).

[6] S. Nešpůrek, M. Schwartz, S. Böhm and J. Kuthan, *J. Photochem. Photobiol.* **A 60**, 345 (1991).

[7] P. Šebek, S. Nešpůrek, R. Hrabal, M. Adamec and J. Kuthan, *J. Chem. Soc. Perkin Trans. 2,* 262 (1992).

[8] S. Böhm, M. Hocek, S. Nešpůrek and J. Kuthan, *Coll. Czech. Chem. Commun.* **59**, 262 (1994).

[9] S. Böhm, P. Šebek, S. Nešpůrek and J. Kuthan, *Coll. Czech. Chem. Commun.* **59**, 1115 (1994).

[10] S. Nešpůrek, S. Böhm and J. Kuthan, *Mol. Cryst. Liq. Cryst.* **246,** 139 (1994).

[11] R. Chen and Y. Kirsh, *Analysis of Thermally Stimulated Processes* (Pergamon, Oxford 1981).

[12] J. van Turnhout, *Thermally Stimulated Discharge of Polymer Electrets* (Elsevier, Amsterdam 1975).

[13] J. Vanderschueren and J. Gassiot, in *Thermally Stimulated Relaxation in Solids,* edited by P. Bräunlich (Springer, Heidelberg 1975), Chap. 4.