Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Monte Carlo Based Design of Photonic Processes in Azopolymers

A. C. Mitus [a], G. Pawlik [a], B. Sahraoui [b], A. Miniewicz [c] & F. Kajzar [d]

[a] Institute of Physics, Wroclaw University of Technology, Wroclaw, Poland

[b] POMA, Universite d'Angers, Lavoisier, Angers, France

[c] Institute of Theoretical and Physical Chemistry, Wroclaw University of Technology, Wroclaw, Poland

[d] Commissariat a l'Energie Atomique, DRT/LIST/DECS/SE2M/LCOF, Centre d'Etudes de Saclay Gif sur Yvette Cedex, France

Version of record first published: 16 Aug 2006

To cite this article: A. C. Mitus, G. Pawlik, B. Sahraoui, A. Miniewicz & F. Kajzar (2006): Monte Carlo Based Design of Photonic Processes in Azopolymers, Molecular Crystals and Liquid Crystals, 446:1, 47-54

To link to this article: http://dx.doi.org/10.1080/15421400500383113

Mol. Cryst. Liq. Cryst., Vol. 446, pp. 47–54, 2006

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500383113

Monte Carlo Based Design of Photonic Processes in Azopolymers

A. C. Mitus
G. Pawlik
Institute of Physics, Wroclaw University of Technology, Wroclaw, Poland

B. Sahraoui
POMA, Universite d'Angers, Lavoisier, Angers, France

A. Miniewicz
Institute of Theoretical and Physical Chemistry, Wroclaw University of Technology, Wroclaw, Poland

F. Kajzar
Commissariat a l'Energie Atomique, DRT/LIST/DECS/SE2M/LCOF, Centre d'Etudes de Saclay, Gif sur Yvette Cedex, France

Monte Carlo kinetics of diffraction efficiency evolution in a process of a pulsed diffraction grating inscription in a model system consisting of a polymer doped with azo-dye is presented. A comparison between simulations and degenerate two-wave mixing (DTWM) experiment is given. A good qualitative agreement of those results supports the concept of Monte Carlo based analysis and design of temperature-dependent photonic processes in azopolymers.

Keywords: azo-polymers; diffraction efficiency; diffraction grating; information storage and processing; Monte Carlo

OUTLINE

Computer simulations (Monte Carlo, molecular dynamics) offer powerful tools for a study of various systems of many particles in thermal equilibrium [1]. They are helpful in two aspects. The first one is an

Addess correspondence to A. C. Mitus, Institute of Physics, Wroclaw University of Technology, 50-370 Wroclaw, Poland. E-mail: antoni.mitus@pwr.wroc.pl

attempt to understand the nature of unknown physical phenomena underlying observed experimental effects, while the other one is a detailed study of the behaviour of the model system for an arbitrary choice of its parameters. Unlike the experiment, where a change of material constants may be difficult for various reasons, computer simulations offer this possibility practically without any restrictions. This paper deals with Monte Carlo modelling of a process of pulsed diffraction grating inscription in azopolymers.

Writing and erasure of diffraction gratings in azopolymers, doped or functionalized with azobenzenes, is based on the effect of photoinduced anisotropy (birefringence and dichroism) by resonant excitation with a polarised laser beam [2,3]. Theoretical models of time evolution of the photoinduced orientation in azobenzene polymers have been proposed by Dumont *et al.* and Sekkat *et al.* [4–8], by taking into account populations of both the *trans* and *cis* metastable states. Molecular reorientation results because of complex processes taking place in the medium. Angular hole burning reflects the fact that those molecules, which are nearly parallel to the light polarisation direction, are excited to cis^* state and next they relax either to ground *trans* or *cis* state. The angular diffusion takes place both for *trans* and *cis* populations. The dynamics of the grating inscription process depends on the rigidity of the polymer matrix, which can freeze molecular reorientation processes during and after removal of an irradiation, leading to stable gratings. In particular, this scenario can take place in polymers with high glass transition temperatures T_g. On the other hand, mechanisms leading to more complex processes like, e.g., inscription of surface relief gratings [9–11], remain unclear (see, e.g., in Ref. [12]). In such cases computer simulations may be helpful in establishing the physical nature of the process.

The kinetics of diffraction gratings formation and erasure in a polymer matrix doped with azo-dyes can be effectively studied by Monte Carlo approach, using a kinetic model [13] generalised onto the temperature-dependent case [14]. This approach was recently used to model some temperature independent [13] and temperature-dependent phenomena [15,16]. In particular, preliminary Monte Carlo studies of temperature-controlled inscription of gratings in azopolymers, based on an analogy with an opto-thermal writing used in magnetooptic storage [17], were presented in Ref. [18].

The aim of the paper is to model, using Monte Carlo simulations, the main features of diffraction efficiency evolution during pulsed diffraction grating recording and erasure reported in a DTWM experiment.

PULSED GRATING RECORDING: DTWM

The kinetics of grating recording using pulsed laser is presented in Figure 1 [18]. The thin 2 μm films of the photochromic polymer were confined between two glass plates and illuminated by spatially and temporally coherent two 532 nm beams from pulsed laser working at 10 Hz repetition rate and supplying pulses of 16 ps duration. The pulse energy was 1.3 mJ. The *s-s* polarisation was set thus producing interference pattern in the sample volume with periodicity $\Lambda = 0.98\,\mu m$. The light of 532 nm wavelength is partially absorbed in the sample and causes both *trans-cis-trans* isomerisation of azo-benzene derivatives and periodic local temperature increase due to radiativeless processes. The reading of arising diffraction grating was monitored by recording the first diffraction order of cw He-Ne laser beam ($\lambda = 632.8\,nm$) directed at the intersection area of the 532 nm beams. The light from He-Ne laser was negligibly absorbed by the polymer film. Each shot of pulsed laser produced a measurable increase of diffraction efficiency. The studied polymer E-28 (N,N-diglicidylaniline (DGA) cured with 2,4-diamino-4′-methylazobenzene) displays fast dynamics of grating recording and equally fast spontaneous erasure.

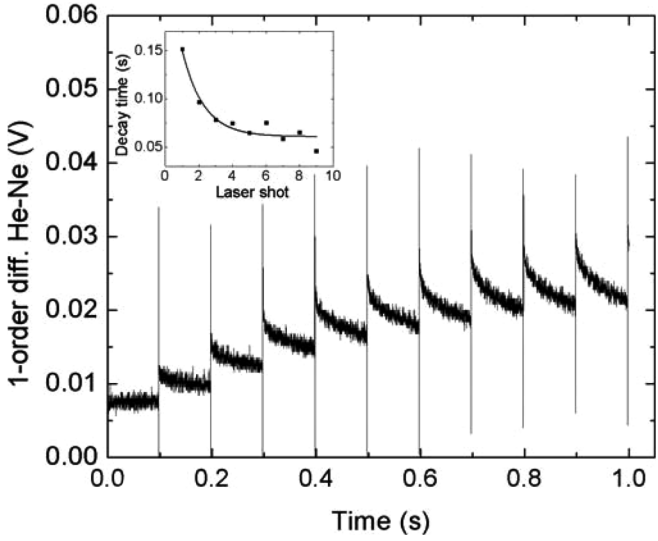

FIGURE 1 Pulsed grating recording in E-28 polymer by two 532 nm and 16 ps light pulses of the same *s-s* polarisation (10 Hz laser pulse repetition rate). Inset: time constants of spontaneous grating erasure calculated from exponential fit between consecutive laser pulses.

It was found [18] that the speed of erasure of diffraction efficiency after successive pulses was becoming faster, finally reaching a saturation. The plot of decay time constant, obtained from an exponential fit, against time or laser shots, is shown as Inset in Figure 1. The observed process was linked with a total temperature increase of the polymer within illuminated region. The accumulated heat dissipated after each laser shot gradually increased the sample temperature, leading to greater polymer chain mobility and faster spontaneous grating erasure. More details can be found in Ref. [18].

KINETIC MONTE CARLO MODELING

The Monte Carlo simulations were done using the temperature-dependent kinetic model of diffraction grating formation, described in details in Refs. [14–16], which is a generalisation of an athermal model [13]. The model which describes the polymer matrix with doped azodyes, has three parameters related to physical processes enumerated in the Introduction: $p_{c\to t}, p_{t\to c}, p_{diff}$. The first two parameters are the probabilities of the photoisomerization transitions in a single act of interaction of a photon with a dye: *trans* $\to$ *cis* and *cis* $\to$ *trans*; their ratio is denoted by R. Parameter p_{diff} tunes the strength of an orientational diffusion of long axis of a *trans* particle. The simulations were done on a two-dimensional lattice [13] of size 120×400, using the standard bond-fluctuating method [19]. To increase the statistics, 10 independent replicas of the systems were used. The geometry of the simulated system corresponds to a DTWM experimental setup [13]. During pulsed inscription of the grating the light field intensity varies along the x axis in the following way:

$$\mathrm{I(x)} = I_0(1 + \sin(qx)), \tag{1}$$

where q stands for the grating wave-vector, and the light with intensity $I_0 = 10$ (in arbitrary units) is linearly polarized along the z axis. In previous simulations [13–16,18] the light intensity was lower ($I_0 = 1$). The diffraction efficiency η in Raman-Nath regime was calculated using the method proposed in [13]. It requires the calculation of a nematic liquid crystal-like order parameter (second-order Legendre polynomial), which describes the orientation of long axes of *trans* particles, and the calculation of the population of those particles. In this paper we use a simplified, instantaneous [18] kinetics of the physical processes accompanying pulsed inscription. According to it, the characteristic time scales of laser heating pulse and heat distribution in the polymer [12] are quick processes while polymer matrix

evolution is a much slower process. Then, the only result of the former is an instantaneous change of the parameters of the later. More details can be found in Ref. [18].

The grating inscription was done in the following way. We have started from an equilibrium configuration of the polymer matrix at the reduced temperature $T = 0.1$, which constitutes approximately one half of the glass temperature $T_g \approx 0.19 - 0.20$. A pulsed recording, with spatially modulated intensity given by Eq. (1), was applied in a single Monte Carlo step. It has influenced the system in two ways. One was an instantaneous change of the configuration of *trans* and *cis* particles, the second – an instantaneous temperature growth. We have assumed that an increase of temperature was homogeneous along the x-axis (see Reference [12]). The new temperature was $T = 0.12$. After the laser shot, during 25000 MCS the grating has decayed in the darkness. After this period, pulsed inscription was applied once again. After each laser shot the temperature was increased by 0.2. In Ref. [12] other scenarios of temperature increase in the volume were discussed. We have used 5 laser pulses and the final temperature was $T = 0.2$, close to the glass temperature. We stress that we did not calculate the heat distribution in the system and the final temperature profile; instead, we have concentrated on the resulting diffraction efficiency kinetics.

RESULTS

The results of Monte Carlo simulations of the diffraction efficiency of the model azopolymer system with parameters $I_0 = 10, R = 15$, $p_{c\to t} = 0.001,\ p_{diff} = 2 \times 0.05$ are shown in Figure 2. One finds a good qualitative agreement with results of DTWM experiment, see Figure 1. In particular, pulsed heating leads in each step to a strong increase of diffraction efficiency. There are no traces of a sudden drop of diffraction efficiency during pulsed light action, which were reported in our recent study [18]. After the laser shot, the diffraction efficiency decreases during the period of spontaneous erasure, when the system evolves in the darkness. The rate of this decay increases with a number of laser pulses. In spite of a commonly accepted statistics of simulation data used in our study, the grating diffraction efficiency decay is accompanied by large fluctuations, which make an identification of the character of this decay a difficult task. This is clearly seen in Figure 3, which presents the results of an exponential fit to a self-erasure period after pulse number 1.

The simulated curve displays some traces of an exponential behaviour. For this reason we present here another characteristic of a rate of

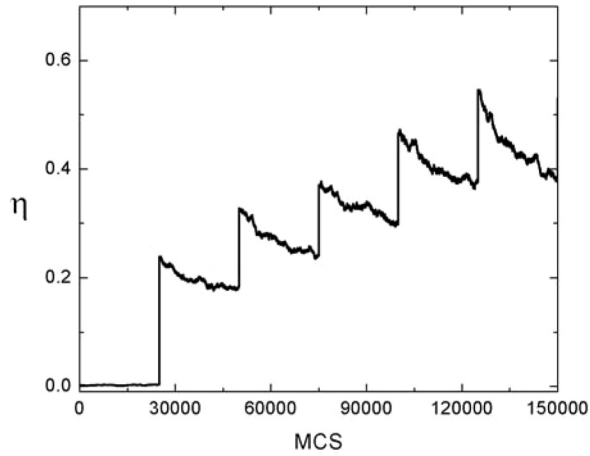

FIGURE 2 Monte Carlo kinetics of diffraction efficiency η during a pulsed grating inscription (for details see text).

the decay, namely an average slope in a decay period, representing the slope of a straight line joining the diffraction efficiency values at the boundaries of self-erasure interval. The results for an inverse average slope are shown in Figure 4. We conclude that our rate of grating self-erasure increases with increasing number of laser pulse,

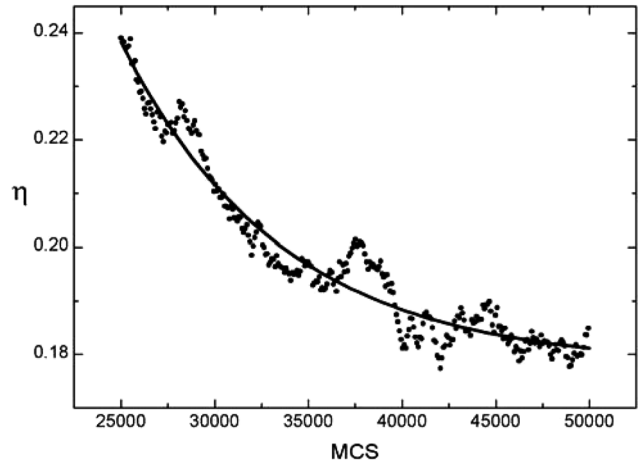

FIGURE 3 Exponential fit of grating diffraction efficiency η decay between two consecutive laser shots number 1 and 2, for grating inscription process depicted in Figure 2.

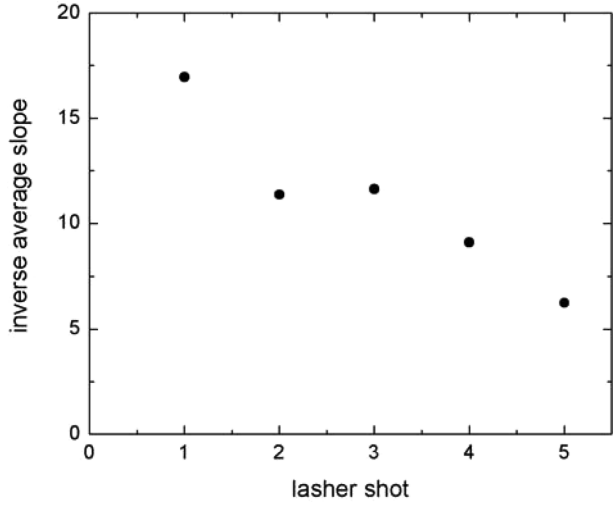

FIGURE 4 Inverse average slope for grating diffraction efficiency decay between consecutive pulses, as a function of pulse number.

in qualitative agreement with experimental data, shown as Inset in Figure 1.

DISCUSSION

Using a previously proposed Monte Carlo method of simulations of temperature-dependent effects in azo-polymers, we have modelled a process of a pulsed diffraction grating inscription and erasure in a doped azopolymer, in a good qualitative agreement with DTWM experimental data. The main interest of our study was concentrated on the optical aspects, while the temperature profile due to laser heating was assumed to be known. Because of strong fluctuations in the calculated diffraction efficiency, we could not obtain a reliable exponential fit to the data. Nevertheless, we have observed an increase of the rate of decay of the grating with increasing number of laser pulse, in agreement with experimental data.

Our results support the concept of Monte Carlo based analysis and design of photonic processes related to temperature-dependent grating inscription in azo-polymers. Preliminary simulations show that the results are very sensitive to the actual value of the parameters. This fact suggests that a systematical analysis of the system may contribute to a better understanding of the role of various parameters of

the model and their correspondence to the parameters of real systems. Let us point out that Monte Carlo modelling has revealed some interesting results of applicational importance related to the anchoring strength in nematic liquid crystal cells [20]. Systematic studies of our system are at progress now; the results will be published elsewhere. The methods presented in this paper can be used for a study of a temperature-controlled increase of the speed of diffraction grating writing (information storage) in azo-polymers (for preliminary results see Ref. [18]), which is in the centre of interest because of its potential applications, in particular in information processing.

ACKNOWLEDGEMENT

We would like to thank the S.C.I.A.M. (Service commun d'Imageries at Analyses Microscopiques, Université d'Angers) for technical help.

REFERENCES

[1] Allen, M. P. & Tildesley, D. (1987). *Computer Simulation of Liquids*, Clarendon Press: Oxford.
[2] Todorov, T., Nikolova, L., & Tomova, N. (1984). *Appl. Opt.*, *23*, 4309.
[3] Kim, D. Y., Tripathy, S. K., Li, L., & Kumar, J. (1995). *Appl. Phys. Lett.*, *66*, 1166.
[4] Sekkat, Z. & Knoll, W. (Eds.) (2002). *Photoreactive Organic Thin Films*, Academic Press: USA.
[5] Dumont, M., Sekkat, Z., Loucif-Saibi, R., Nakatani, K., & Delaire, J. A. (1993). *Sci Technol – Sec. B: Nonlinear Optics*, *5*, 395.
[6] Sekkat, Z., Wood, J., Geerta, Y., & Knoll, W. (1995). *J. Phys. Chem.*, *99*, 17226.
[7] Dumont, M. & El Osman, A. (1999). *J. Chem. Phys.*, *245*, 437.
[8] Sekkat, Z., Yasumatsu, D., & Kawata, S. (2002). *J. Phys. Chem. B*, *106*(48), 12407.
[9] Rochon, P., Batalla, E., & Natansohn, A. (1995). *Appl. Phys. Lett.*, *66*, 136.
[10] Kim, D., Tripathy, Y., Li, S. K., & Kumar, L. (1995). *J. Appl. Phys. Lett.*, *66*, 1166
[11] Barrett, C. J., Natansohn, A. L., & Rochon, P. L. (1996). *J. Phys. Chem.*, *100*, 8836.
[12] Yager, K. G. & Barrett, C. J. (2004). *J. Chem. Phys.*, *120*, 1089.
[13] Pawlik, G., Mitus, A. C., Miniewicz, A., & Kajzar, F. (2003). *J. Chem. Phys.*, *119*, 6789.
[14] Pawlik, G., Mitus, A. C., Miniewicz, A., & Kajzar, F. (2004). *J. Nonl. Opt. Phys. Mat.*, *13*, 481.
[15] Mitus, A. C., Pawlik, G., Miniewicz, A., Sobolewska, A., & Kajzar, E. (2004). *SPIE Int. Soc. Opt. Eng.*, *5517*, 207.
[16] Pawlik, G., Mitus, A. C., Miniewicz, A., Sobolewska, A., & Kajzar, F. (2005). *Mol. Cryst. Liq. Cryst.*, *426*, 243.
[17] Tsunashima, S. (2001). *J. Phys. D.: Appl. Phys.*, *34*, R87.
[18] Mitus, A. C., Pawlik, G., Iwaszko, M., Sahraoui, B., Miniewicz, A., & Kajzar, F. (2005). *Nonlinear Optics, Quantum Optics, 34*, 141.
[19] Carmesin, I. & Kremer, K. (1988). *Macromolecules*, *21*, 2819.
[20] Komorowska, K., Pawlik, G., Mitus, A. C., & Miniewicz, A. (2001). *J. Appl. Phys.*, *90*, 1836.