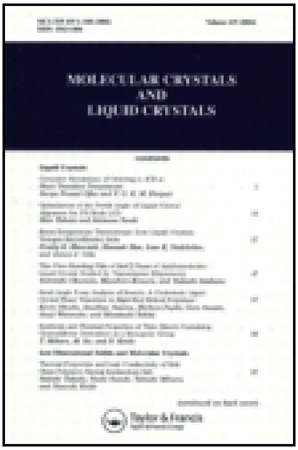

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Temperature Dependence of the Kinetics of Diffraction Gratings Formation in a Polymer Matrix Containing Azobenzene Chromophores: Monte Carlo Simulations and Experiment

Grzegorz Pawlik [a], Antoni C. Mitus [a], Andrzej Miniewicz [b], Anna Sobolewska [b] & Francois Kajzar [c]

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

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

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

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Grzegorz Pawlik
Antoni C. Mitus
Institute of Physics, Wroclaw University of Technology,
Wroclaw, Poland

Andrzej Miniewicz
Anna Sobolewska
Institute of Theoretical and Physical Chemistry,
Wroclaw, University of Technology, Wroclaw, Poland

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

We use the framework of recently formulated kinetic model of temperature-dependent processes accompanying the recording and erasure of diffraction gratings in a polymer matrix doped with azobenzene chrompohores under the illumination with spatially modulated and linearly polarized light to study general features of temperature dependence of time evolution of diffraction efficiency close to the glass transition temperature T_g of the polymer matrix. Bond fluctuation Monte Carlo simulations are used. Basic kinetic results found in simulations are in agreement with preliminary experimental results obtained in degenerate two-wave mixing (DTWM) experiment. We discuss, using Monte Carlo results, the concept of temperature controlled writing of diffraction gratings in a temperature interval close to T_g.

Keywords: diffraction gratings, azobenzene chromophores, Monte Carlo simulations

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Address correspondence to Antoni C. Mitus, Institute of Physics, Wybrte Wyspianskiego 27, Wroclaw, 50-370, Poland. Tel.: 48713202826, Fax: 48713283690, E-mail: antoni.mitus@pwn.wroc.pl

1. OUTLINE OF THE PROBLEM

It is a common belief that temperature effects play substantial role in the kinetics of writing and decay/erasure of diffraction gratings and might be of practical and theoretical interest in the field of photonic devices. Recently [1] we have formulated a simple kinetic model of the temperature-dependent processes accompanying the recording and erasure of diffraction gratings in a polymer matrix doped with azobenzene chrompohores under the illumination with spatially modulated and linearly polarized light. The present approach generalizes the kinetic model for athermal case [2], based on (i), three-channel photoizomerization cycles of *trans–cis* type of azobenzene molecules and (ii), on orientational diffusion, by taking into account an influence of polymer matrix onto those processes. By modeling the "macroscopic" light diffraction efficiency one gets insight into the roles played by "microscopic" processes like angular hole burning, angular redistribution and rotational diffusion at various temperatures. Preliminary results of Monte Carlo simulations of diffraction efficiency [1] prove the capability of the model to produce a large variety of temperature dependent kinetic behaviors.

The aim of this paper is a Monte Carlo study of diffraction efficiency close to (below and above) the glass transition temperature T_g of the polymer matrix, motivated by an interest in temperature-controlled storage of information in photopolymers [1], in analogy to magneto-optic technique [3]. Also, preliminary DTWM experimental results on time dependence of diffraction efficiency for a few temperatures below T_g are presented.

2. THE KINETIC MODEL

The temperature is introduced into the model via an equilibrium thermal motion of the polymer matrix. This motion modifies the transition probabilities of the photoizomerization and angular diffusion of molecular axis of *trans* molecules introduced earlier for an athermal model [2]. We assume, following the lines of [1], that those probabilities (per unit of time) depend on the polymer configuration close to the azo-dye , characterized by the local (in a close vicinity of a photochromic molecule) void size V and by the number of collisions C (per unit of time) of the monomers with the photochromic molecule. The probability of *trans* to *cis* transition reads [1]:

$$p(trans \to cis) = V\,I\,p_{trans\to cis}\cos^2\theta, \tag{1}$$

where I stands for the light intensity and θ is an angle between the long axis of *trans* molecule and the direction of the polarization of the light. The inverse *cis* → *trans* transition probability is also proportional to V, thus [1]:

$$p(cis \to trans) = V\, I\, p_{cis \to trans} \equiv V\, I\, R^{-1} p_{trans \to cis} \tag{2}$$

$p_{trans \to cis}$ and $p_{cis \to trans}$ denote the probability of the corresponding transition in a single act of an interaction with a photon. As in [1] we assume that the orientation of a long axis of *trans* molecule after *cis* → *trans* transition is chosen randomly. Parameter $R = p_{trans \to cis}/p_{cis \to trans}$ [2] plays an important role in the kinetics of the system; in real experiments its value can be tuned in a wide interval by using various light wavelengths [4]. The redistribution of the orientations $\Omega = (\theta, \phi)$ of long axes of *trans* molecules due to the collisions with monomers is governed by the transition probability for *trans* molecules:

$$p(\Omega \to \Omega + \Delta\Omega) = \begin{cases} p_{diff} VC, & d\Omega \le d\Omega_0 \\ 0, & d\Omega > d\Omega_0 \end{cases}, \tag{3}$$

where p_{diff} is a constant and for $\Delta\Omega$ we take the values from [2]: $\delta\phi = 10^\circ$, $\delta(\cos(\theta)) = 0.1$. Specific expressions for parameters V and C depend on the geometry of model polymer matrix and are given in Section 3A.

3. MONTE CARLO SIMULATION

A. Polymer Matrix: Bond-Fluctuation Method

To study the equilibrium properties (at fixed temperature) of the polymer matrix we apply the lattice bond-fluctuation [5] version of standard importance sampling Monte Carlo method [6,7]. For the sake of simplicity we consider a two-dimensional (2D) case [8] only where the monomers occupy the sites of a two-dimensional square lattice. The azo-dye particles, placed on the same lattice, can rotate in three dimensions. Each node has four neighbors. Because of a geometric constraint on the length of a bond joining two monomers in bond fluctuation method, the number of occupied sites around a central node can be 0, 1 or 2. If the node in question is monomer free, we call it a void. The size of the void V takes the following values: $V=5$ (central plus 4 free neighbors), $V=4$ (central plus 3 free neighbors) or $V=3$ (central plus 2 free neighbors). For an occupied node we put $V=0$.

The temperature-dependent statistics of void sizes and of their lifetimes leads to temperature-dependent photorefractive effects discussed below. Parameter C characterizing the strength of collisions of the dye with the polymer is proportional to the total number of changes δn of the occupation state $n_i = 0$, 1 of four neighbors of the dye molecule by the monomers ($n_i = 1$ for site i with a monomer in it, $n_i = 0$ when site i is monomer-free):

$$C = \sum_{i=1}^{4} |\delta n_i|. \tag{4}$$

Parameter C takes the values $C = 0, 1, \ldots, 4$. More details can be found in [1].

We simulate a 2D system consisting of 120 columns ($x = 1,\ldots,120$) and 400 rows ($y = 1, \ldots, 400$) (cf. Fig. 1). The sites of the square lattice are occupied by 384 polymer chains each consisting of $L = 25$ monomers. The density of the polymer matrix (defined as in Ref. [8]) is high: $\Phi = 0.8$. The equilibrium polymer matrix was simulated at five reduced temperatures (defined as in Ref. [8]): $T = 0.1$, 0.16, 0.20, 0.24 and 0.30. The simulations reported in Ref. [8] lead to the conclusion that the glass transition temperature $\mathrm{T_g}$ for polymer chains with $L = 25$ at polymer density $\Phi = 0.8$ is located close to the temperature $T = 0.2$. In our system, we find a strong increase of average lifetimes of voids close to this temperature, as shown in Figure 2 for $V = 3$. Thus, we interpret the results at $T = 0.10$ and 0.16 as corresponding to the glassy phase, $T = 0.2$ as close to T_g, and $T = 0.24$ as slightly above T_g.

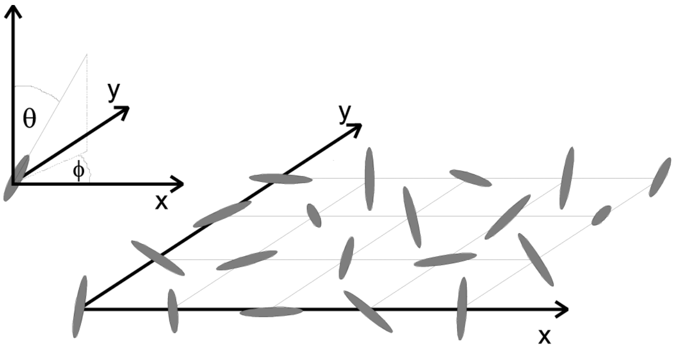

FIGURE 1 Two-dimensional square lattice with chromophores in the nodes (see text).

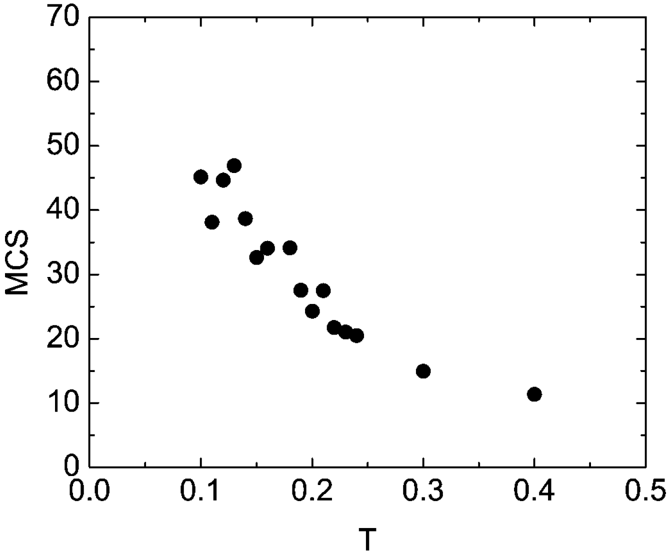

FIGURE 2 Plot of temperature dependence of lifetimes in MCS units of the voids with $V = 3$.

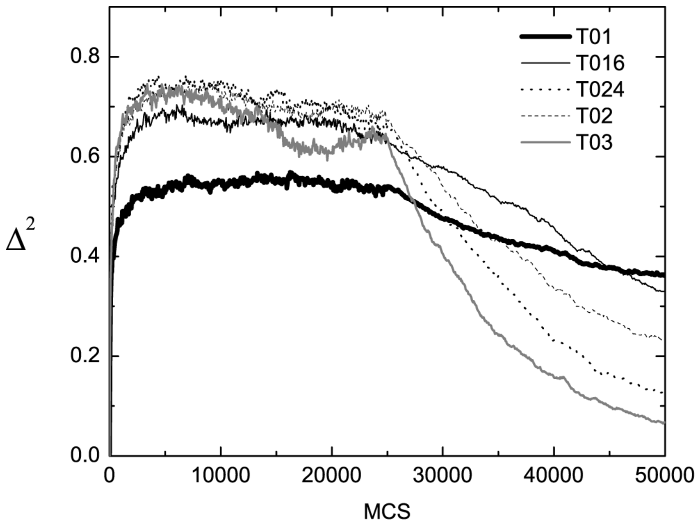

FIGURE 3 Time evolution of $\Delta^2 \propto \eta$ during writing and self-erasure of the gratings simulated for polymers with chains consisting of $L = 25$ monomeric units for temperatures $T = 0.10$, 0.16, 0.20, 0.24 and 0.30 ($p_{cis \to trans} = 0.001$, $R = 5.0$, $p_{diff} = 0.05$).

B. Optical Field Setup and Calculation of Diffraction Efficiency

The polymer matrix forms a background in which processes leading to light induced anisotropy take place. The optical field setup corresponds to the conditions of a two-wave mixing experiment, see [2]. During writing of the grating the light field intensity varies along the x axis:

$$I(x) = I_0(1 + \sin(qx)), \tag{5}$$

where q stands for the grating wave-vector; the light of I_0 intensity ($I_0 = 1$ arbitrary units) is linearly polarized along the z axis. We use a single period of light modulation along the x-dimension of our system. During self-erasure of the grating the light is completely turned off:

$$I(x) = 0. \tag{6}$$

In the Monte Carlo simulation during one Monte Carlo step (MCS) for the polymer matrix all of the dyes undergo a single act of interaction with the light according to the probabilities described in Section 2.

The central point of our interest lies in the study of the kinetics of diffraction efficiency defined in DTWM experiment as $\eta(t) = I_{diff}/I_{in}$, where I_{diff} and I_{in} are diffracted and incident light intensities, respectively, and t represents time. Under a small signal approximation and neglecting the absorption grating contribution to the diffraction efficiency, η for light scattering on a periodic sinusoidal grating of Δn refractive index amplitude is proportional (in Raman–Nath regime), to its square: $\eta \propto (\Delta n)^2$ [9]. This quantity can be calculated from Monte Carlo simulations. In the case when the anisotropic optical properties are due only to the *trans* molecules, we use expression for η (based on Kuzyk's approach [10]), proposed recently in [2]:

$$\eta \propto (\Delta)^2, \tag{7}$$

where parameter Δ is directly proportional to the photoinduced refractive index amplitude Δn in studied photochromic system:

$$\begin{aligned}\Delta = {} & N_d^{trans}(x_{\max}) \cdot (1 + 2\langle P_2\rangle(x_{\max})) \\ & - N_d^{trans}(x_{\min}) \cdot (1 + 2\langle P_2\rangle(x_{\min})).\end{aligned} \tag{8}$$

Formula (8) relates the diffraction efficiency to the (i), local orientational order parameter $P_2(\cos\theta) = \frac{1}{2}(3\cos^2\theta - 1)$ for *trans* molecules and (ii), to local values of the concentration of molecules in *trans* states $N_d^{trans}(x)$; those parameters are readily calculated from Monte Carlo simulations. x_{min} and x_{max} denote, the rows with minimal and maximal, respectively, values of orientational order parameter $\langle P_2 \rangle$.

C. Results

Figure 3 displays the Monte Carlo "time" (i.e., number of Monte Carlo Steps) dependence of parameter $\Delta^2 \propto \eta$ (see (7)) for the following values of the parameters: $p_{cis \to trans} = 0.001$, $R = 5.0$, $p_{diff} = 0.05$, for polymers with $L = 25$, at temperatures $T = 0.10$, 0.16, 0.20, 0.24 and 0.30. The writing using the modulated light intensity (5) took place in the time interval 0–25000 MCS; afterwards the writing beams were turned off. The rate of the growth of the grating in its initial phase is large; this phenomenon was discussed in [2] in the context of a rapid growth of *cis* population. As expected, see Figure 4, the higher the temperature the higher the growth rate. In the second phase of the writing η reaches a plateau. Saturation value η of diffraction efficiency (Δ^2 in Fig. 3) depends on temperature. It takes noticeably smaller values at low temperature $T = 0.1 \approx 0.5T_g$. The values of η for temperatures close the T_g are weakly dependent on temperature; at still higher temperature $T = 0.3$ slightly different behavior of η sets in. The decay of

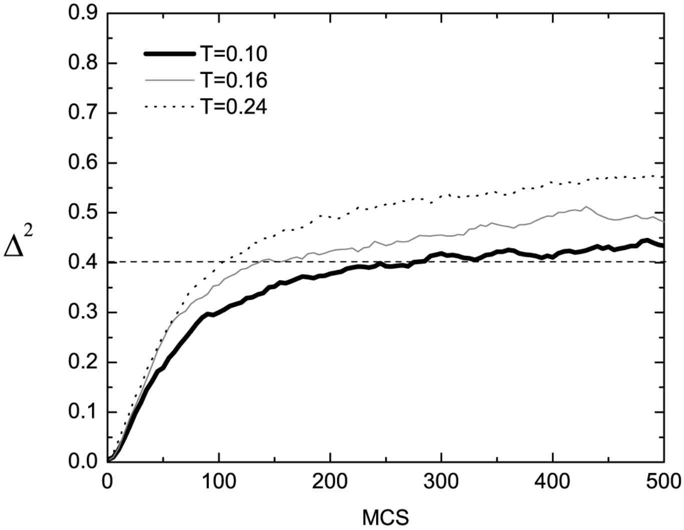

FIGURE 4 Initial phase of grating build-up process simulated with the parameters as in Figure 3. (horizontal line is explained in the text).

the grating (after 25000 MCS elapsed) follows the pattern found during the initial stages of building-up of the grating: the higher temperature the faster decay rate. Contrary to the case of η, the decay rates are strongly dependent on the temperature, even close to the glass temperature. We note that the times in which a substantial decay occurs are much larger than the times in which the grating was built. This effect is especially well pronounced for low temperature $T = 0.1$ and can be easily understood, because for the grating self-erasure ($I(x) = 0$) no photoinduced *trans-cis* phtoisomerization occurs and the process is governed by the molecular rotational diffusion only. In the next Section we discuss the observed temperature effects in the context of their applications in photonics.

4. DISCUSSION: TEMPERATURE-CONTROLLED WRITING

The main interest of the paper is focused on temperature dependence of the time evolution of the diffraction efficiency during diffraction grating build-up and decay. As expected, the speed of writing of the grating and its decay rate in darkness increases with increasing temperature. Stability of the grating after switching the writing beam off is directly related to the value of temperature difference $T_g - T$, where T stands for the temperature of the polymer matrix. Stability of the grating increases with decreasing value of T. This effect is also found in DTWM experiment. In Figure 5 we present the preliminary results of the temperature dependence of light intensity in the first order of diffraction in azobenzene functionalized polyester with glass temperature $T_g = 58°\text{C}$. The grating was written using *s-s* polarized beams from Ar^+ laser with light wavelength $\lambda = 488\,\text{nm}$; afterwards, one of the writing beams was turned off. Measurements were done at three temperatures, $T = 21.3°\text{C}$, 25.6°C and 30.4°C. The curves were fitted using one exponential function. The dependence of relaxation times τ against temperature T calculated in this way are shown in the inset. We find a strong systematical decrease of those times with increasing temperature. Further systematical experiments, in particular oriented onto the study of the initial phase of writing of the grating and on dye-doped polymers are at progress now. Some experimental studies on temperature dependence of η were reported in [11].

Observed behavior is desirable in designing materials for holographic optical storage. Below, we discuss briefly a temperature-controlled writing of the grating in analogy to optothermal writing used in magnetooptic storage [3], where a laser pulse delivers a heat necessary to rise a temperature of a magnetic medium close to Curie temperature enabling magnetic polarization reversal. The general

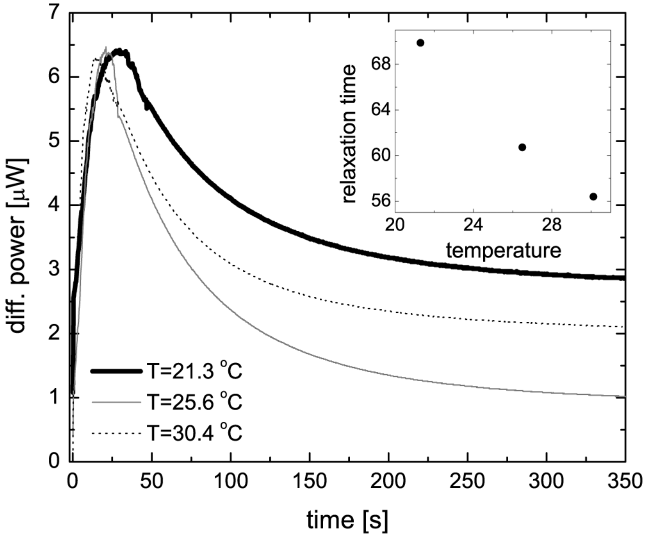

FIGURE 5 Time evolution of (non-normalized) diffraction efficiency during writing and decay of the grating in a DTWM experiment in azobenzene functionalized polyester at various temperatures. Inset: dependence of fitted relaxation times on temperature.

idea is to write the information in polymer by holographic method at higher temperature where the process occurs faster and afterwards to cool the system down in order to freeze a molecular orientation. Such an procedure can give a stable (long-lived) information storage in high T_g polmyers. As in the case of magnetooptic recording of data a pulse of strongly absorbed light from a suitable laser can heat the polymer to temperature at which recording is faster.

Let us discuss briefly, on a semi-quantitative level, the increase of writing speed, using the data of Figure 4. The gain depends crucially on the required level Δ^2 of diffraction grating amplitude (or equivalently of η). In the very initial phase (Fig. 4), constituting approximately *0.01* of the time needed to reach the saturation, there is little difference between writing at different temperatures. If, however, the required value of Δ^2 is large, the situation changes dramatically. For example, the time necessary to build the grating with $\Delta^2 = 0.4$ is three times shorter at $T = 0.24$ and two times shorter at $T = 0.16$ than the corresponding time at $T = 0.1$. This gain grows rapidly with increasing value of Δ^2. We find that a large enhancement of writing speed can be obtained at temperatures lower than T_g, thus avoiding the glass transition process. This is a very important observation, because while in our scenario there is no problem with heating of the matrix, the cooling down of the system in order to obtain a stable grating may be non-trivial because of the very complex nature of dynamic and kinetic processes accompanying this transition. On the contrary, cooling down the polymer in the glass state to, say, $T = 0.1$ creates no such problems. The self-erasure process which occurs afterwards is much slower than writing process (Fig. 3) and thus the grating is stable over a large time interval. As discussed in Section 2C, the decay rate depends strongly on the difference of temperatures $T_g - T$ and thus driving the system to lower temperatures is necessary.

The erasure process can be enhanced in the same way, by increasing the temperature of the polymer. As directly seen from Figure 4 the relaxation times change their values at least by one order of magnitude when heating the polymer beyond glass temperature, which makes the erasure process much faster.

We point out that the gain in the speed of writing depends on parameter R; preliminary results were presented in [1]. A systematical study is necessary to estimate a maximal gain in writing speed. Those topics, as well as corresponding experimental studies are at progress now; the results will be presented elsewhere.

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