1. Introduction

Deoxyribonucleic acid (DNA), functionalized with photoresponsive molecules, has been the subject of interest due to its potential application in nonlinear optical (NLO) effects-based devices [1]. Some of them are closely related to the dynamic holographic grating recording carried out using a degenerate two–wave mixing (DTWM) setup for DNA with cetyltrimethyl-ammonium chloride as matrix and well known photochromic molecules of Disperse Red 1 (DR1) as a dye (DR1:DNA-CTMA thin films). Under the inhomogeneous light illumination the DR1 molecules undergo multiple cycles of trans-cis-trans conformational cycles which promote the build-up of a diffraction grating. The experimental results [2] of dynamic diffraction grating formation show that signal evolution is characterized by a very short time of increase and decay, full reversibility and high stability with weak dependence on wavelength and finally small diffraction efficiency which evolution can be characterized by single–exponential kinetics. Amongst those results the operational time, which can be two orders of magnitude shorter than for “traditional” host-guest gratings, e.g. those based on polystyrene matrix, are potentially attractive for non–linear optical applications.

The origin of different dynamics for the two types of systems is not known. A common opinion is that one of important factors is the nature of binding of azo-dyes to the DNA helix. Studies of circular dichroism [3] showed that the photochromic dye which is doped into the DNA biopolymer, can be aligned by binding in the major or minor grooves of the DNA helix or...
intercalated between the base pairs. Some arguments against this full intercalation were discussed in [4], and confirmed by You et al. [5] who has shown that the dye molecules doped to DNA-CTMA probably do not interact directly with DNA helix and that the CTMA acts as a kind of an interface between DNA double helix and DR1 molecule. A similar physical picture, in what follows referred to as a semi–intercalation hypothesis (cf. Section 3.1), was earlier formulated by some of us on purely theoretical grounds [6,7]. Monte Carlo simulations of the semi-intercalation model combined with analytical arguments [8] have reproduced the main experimental data of [2] (see Sections 3.2 and 3.3 for more details), and provided a strong support to semi-intercalation approach. On the other hand, the theoretical analysis predicted that the dynamics of the grating inscription should have, in general, a more complex pattern than a single-exponential one. Quite recently, we have reported first experimental results [9] which show that a non-exponential dynamics set in on much longer time scales than those of experiments reported in [2]. We conclude that the topic of the temporal patterns of both short–time and long–time dynamics of the inscription of the gratings in DNA biopolymer remains open.

The aim of this paper is twofold: (i), to present new measurements of the dynamics of grating inscription in DR1:DNA-CTMA system in short and long intervals of time and to analyze the emerging temporal patterns; (ii), to formulate, on theoretical grounds, a hypothesis concerning their origin and to present Monte Carlo simulations in its support.

2. Experimental procedure

2.1. Experimental setup

Fig. 1 shows the experimental configuration schematically, which was used for the study of the inscription of diffraction grating using the degenerate two–wave mixing (DTWM) technique. Two s-polarized beams - I and I' - generated by the Ar⁺ laser (cw, P = 300 mW of total laser power, λ = 514.5 nm) were crossing at 2θ angle and interfering in the sample, generating local changes in refractive index of the medium, consistent with the interference pattern. The dynamics of the process of diffraction grating generation, represented by the temporal evolution of the signal power diffracted in the first order of diffraction, was measured with the high–speed photodetector (Thorlabs) connected to a digital oscilloscope (Tektronix, TDS 220). Additionally, a chopper positioned on I’ beam was used in order to study an optical erasure dynamics in a short time scale (milliseconds).

2.2. Sample preparation

To prepare a biopolymeric matrix we used a commercially available purified salmon roe DNA (Sigma - D1626) and complexed it with a cationic surfactant CTMA (cetyltrimethyl-ammonium chloride) replacing all Na⁺ ions of DNA salt. This complex is soluble in many organic solvents including alcohols and can be processed into good optical quality thin films by casting and spin-coating deposition. The conversion of pure DNA material into DNA:CTMA complex was done according to procedure described elsewhere [10,11]. We have prepared butanol solutions of DNA-CTMA and Disperse Red 1 separately and mixed them in order to obtain 2% DR1 in DNA-CTMA w/w in the dry mass. The DR1:DNA-CTMA solution was cast onto glass plates and dried 24 hours in air at room temperature. Thickness of the layer amounted to 4 µm which guarantee measurable diffraction efficiency [2].

3. Experimental results and discussion

The example of dynamic diffraction grating inscription and erasing in DR1:DNA-CTMA film with Ar⁺ laser (s-s recording polarization configuration, I = I’ = 470 mW cm⁻², 2θ = 6°) and chopper working with frequency of f = 40 Hz is presented in Fig. 2. The dependence of the diffraction efficiency on time was satisfactorily fitted using a single–exponential function which has a rise constant τᵣ ≈ 4 ms, after which the inscription is practically completed. The decay of the grating which occurs after the laser light was turned off is also very steep reflecting the same type of dynamics as in the recording process, but this effect is not the objective of the current study.
In the second experiment, we have repeated those studies but in a much longer interval of 30 seconds with a single light opening procedure without the chopper. We observe, cf. Fig. 3, in addition to a systematic growth of the signal, an oscillatory component with a period of about 6s and with a decreasing amplitude. Its origin is unknown. Some traces of a similar behavior were reported in recent studies [9]. The results of fitting of the data are shown in Fig. 3 and display new interesting features as compared to Fig. 2. The fits pass through the point (0,0) which corresponds to the beginning of the measurements. The single–exponential fit (part (a)) fails completely. The bi–exponential fit (part (b)) is unsatisfactory in the initial phase (few first seconds). It yields two characteristic time scales, $\tau_1 = 0.2$ and $\tau_2 = 90$. More complicated fitting procedures were involved but no simple analytical formulas could be found. Amongst others we have tried one of the functions used in theory of complex systems, namely the stretched exponential function, proportional to $\exp(-t/\tau)^\alpha$. Fitting procedure yields $\alpha = 0.28$ (part (c)). While the fit clearly fails in the initial phase it is acceptable in the long–scale regime. In all three cases the fitting procedures encounter difficulties in the initial, very dynamic phase of the process. The origin of the very steep behavior in the first phase is not known. We point out that the data are rather messy, with large fluctuations present, but the conclusions seem to be sound.

We conclude, accounting for Fig. 2, that the characteristic time scales related to the dynamics of grating inscription differ by at least three orders of magnitude. The shortest one is of the order of magnitude of single ms while the largest is (at least) of one minute. Moreover, the data show that there are intermediate temporal scales in the system. This observation is very different from the case of host–guest systems studied earlier [12,13], where only two principal time scales were found which differed approximately by one order of magnitude, and the bi–exponential fit was satisfactory. The appearance of many time scales which differ by orders of magnitude is a characteristic feature of complex behavior. We are of the opinion that the unusual dynamics of DR1:DNA–CTMA system reflects the underlying complexity of the system. In the next Section we discuss briefly an outline of theoretical studies which can shed some light onto this topic.

4. Semi–intercalation scenario: theory and Monte Carlo simulations

The study of a hypothetically complex behavior of DR1:DNA-CTMA system requires using analytical approach as well as computer modeling. While those studies are in their initial phases and only preliminary results are available, it is worthwhile discussing some important concepts closely related to future studies as well as available theoretical tools.

4.1. Semi–intercalation hypothesis

In the literature it is assumed that the DR1 chromophores can either be doped to the DNA matrix, or intercalated into the nanospaces between the base pairs or aligned by binding in the major or minor grooves of the DNA helix. The semi–intercalation scenario offers a third possibility, see Fig. 4, according to which the dye molecule is only partially intercalated in the DNA-CTMA system, see
Fig. 5 (left). It assumes that each DR1 molecule which has undergone the photo-isomerization cycle trans-cis-trans preserves the memory about its initial orientation in the space and returns exactly to this orientation. This is in contrast with the host-guest model studied earlier [12,13], where the orientational redistribution and diffusion play an important role.

4.2. Monte Carlo modeling

The model has two main components: DNA (polymeric) matrix and semi–intercalated DR1 azo-dyes. We simulate the matrix using bond–fluctuation Monte Carlo method in 3D [14]. In this approach the matrix is represented by a set of “monomers” (corresponding to Kuhn elements) joined by elastic bonds. As a rule, a lattice model is used, where the monomers occupy lattice sites of a simple cubic lattice. The simulations are done close to the glass temperature $T_g$ of the matrix. More details can be found in [13,15,16].

Fig. 6a shows a snapshot of the simulated polymer matrix. A two-dimensional cross-section through the matrix (Fig. 6b) clearly displays the inhomogeneity in the spatial distribution of the monomers.

Each dye molecule must absorb a photon to undergo an isomerization. The absorption probability of molecule in trans form depends on the square of product of electric field of light and molecule transition dipole moment while that of cis form is independent of the orientation of the molecule. The kinetics of the inscription of the grating is modeled by the transition probabilities (per unit of time) for photo-isomerization reactions trans $\Leftrightarrow$ cis of photochromic molecules in a polymer matrix [12,13]:

$$p(\text{trans} \rightarrow \text{cis}) = V I p_{tc} \cos^2 \theta$$

(1)
\[ p(\text{cis} \rightarrow \text{trans}) = VIp_{ct} \]  

where \( V \) denotes a local (in a close vicinity of a photochromic molecule) void (free volume), see Sect. 3.4, \( I \) – light intensity, \( \theta \) - an angle which the long axis of the molecule makes with the polarization direction of the light, and \( p_{\omega}, p_{\alpha} \) denote the probabilities of a photoisomerization in a single act of interaction with light. We define parameter \( R = \frac{p_{\alpha}}{p_{\omega}} \) which is proportional to the ratio of products of absorbances and quantum yields for transitions \( \text{trans} \rightarrow \text{cis} \) and \( \text{cis} \rightarrow \text{trans} \), respectively. The intensity of linearly polarized light along the \( z \)-direction, propagating in the \( y \)-direction, varies along \( x \)-axis: \( I(x) = \frac{1}{2}(1 + \sin(qx + \pi)) \), where \( q \) stands for the wave-vector of the optical grating. More information can be found in the review paper [17] and in [12]. A multiply excited dye molecule can move along the field gradients. This movement is however possible only when a molecule finds a void in the matrix sufficient in its size to occupy a new position. The voids number and their distribution characterize the probability for a molecule to leave its current position and to occupy a new one. Short-range as well long-range interactions play a decisive role in molecular transport. This transport is much slower than the fast molecular photoisomerisation event and can yield for transitions \( \text{trans} \rightarrow \text{cis} \) and \( \text{cis} \rightarrow \text{trans} \), respectively, the value of parameter \( V \) by 1. For more details see the review paper [17]. We have found [9] that the spatial distribution of void \( V \) forms a complex mosaic where, on one hand, voids with \( V = 0 \) can be the neighbors of the voids with \( V = 7 \) and, on the other hand, some unknown type of spatial correlations is clearly present, see Figs. 6c, 6d. The probabilistic characterization of the random field \( V(\mathbf{r}) \) and of its dynamics constitutes a challenging task in the physics of polymers.

In the context of the hypothetical complexity in the dynamics of DR1:DNA-CTMA biopolymer it is important to prove that the random field \( V(\mathbf{r}) \) contains large scale spatial inhomogeneities in the distribution of the monomers. In the case when no significant inhomogeneities were present, the dynamics of local reorientations of the DR1 molecules due to the interaction with optical field and due to DNA chain motions would be of the same type throughout the system, and no complex temporal patterns would be observed. On the contrary, if there are local volumes with much more spatial freedom than in other local volumes where the DR1 motion is hindered by the DNA chain, then the system will display a large variety of „quick” and „slow” processes, inevitably leading to complex system–like temporal patterns. Partial confirmation of this hypothesis follows from the analysis of various two–point correlation functions introduced recently in [19]. Fig. 7 shows the plots of the correlation function \( g_2(r, V, V) \) which is directly proportional to the conditional probability to find a void \( V \) at distance \( r \) from another void \( V \). In the case of \( V=3 \) (Fig. 7(left)) we find a shell-like pattern typical for the liquids. The case of \( V=6 \) (Fig. 7(right)) is very different: one observes the correlations which gradually decay with increasing distance. This implies that the voids with a negligible amount of steric interactions \( V=6 \) have a strong tendency to form small clusters well separated from cells with strong steric hindrances (a similar conclusion was drawn for \( V=7 \) in [9]). In those clusters “quick” processes, not limited by steric interactions, take place. The correlations of this kind are absent for voids with...
larger sterical hindrances ($V=3$) and the dynamics of the chromophores in such areas is hindered. In particular, most of DNA chains are surrounded by cells with $V = 0$ which form a kind of a tube which, in turn, promotes strong steric interactions and gives rise to "slow" processes [9].

5. Conclusions

We have shown that the temporal patterns governing the dynamics of the holographic grating inscription are very different in the initial phase and over a longer interval of time. In the first case, the dynamics is single-exponential while long-time pattern indicates the presence of a complex-type behavior. Single exponential, bi-exponential and stretched-exponential fits are unsatisfactory. We find the presence of time scales different by 3-4 orders of magnitude. We ascribe their origin to a hypothetically complex dynamics of local free volume (voids) in the polymer matrix and formulate a theoretical approach, based on Monte Carlo modeling and semi-intercalation scenario, oriented onto the study of complex behavior of DR1:DNA-CTMA system. Preliminary results of the theoretical modeling indicate the presence of inhomogeneities in the spatial distribution of local free volume, which is recognized as one of the sources of complexity [20,21]. Further systematic studies, both experimental and theoretical, are necessary to bring more clarity to this topic.

Figure 6. A snapshot of a polymer system modeled by Monte Carlo simulations (a), 2D cross-section of polymeric system (b), map of local free volume parameter $V$ (c), and part of this map scaled up (d).

Figure 7. Correlation functions $g_2(r,3,3)$ (left) and $g_2(r,6,6)$ (right), see text for more details.
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