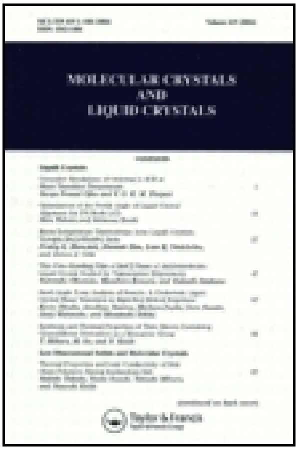


Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photoinduced Gratings in Functionalized Azo-Carbazole Compounds in Picosecond Regime

Robert Czaplicki [a] , Sylvie Dabos-Seignon [a] , Ileana Rau [b] , Oksana Krupka* [a] , Bouchta Sahraoui [a] , Jacek Nizioł [c] , Monika Bednarz [d] , Jan Pielichowski [d] , Aurelia Meghea [b] & Mina Bakasse [e]

[a] Laboratory POMA, University of Angers, Angers Cedex, France

[b] Faculty of Applied Chemistry and Material Science, University Politehnica of Bucharest, Bucharest, Romania

[c] Faculty of Physics and Applied Computer Science, AGH - University of Science and Technology, Cracow, Poland

[d] Department of Polymer Science and Technology, Cracow University of Technology, Cracow, Poland

[e] University of Chouaib Doukkali - Faculty of Sciences BP, El Jadida, Morocco

Version of record first published: 31 Aug 2012.

To cite this article: Robert Czaplicki , Sylvie Dabos-Seignon , Ileana Rau , Oksana Krupka* , Bouchta Sahraoui , Jacek Nizioł , Monika Bednarz , Jan Pielichowski , Aurelia Meghea & Mina Bakasse (2008): Photoinduced Gratings in Functionalized Azo-Carbazole Compounds in Picosecond Regime, Molecular Crystals and Liquid Crystals, 485:1, 1030-1042

Mol. Cryst. Liq. Cryst., Vol. 485, pp. 282/[1030]–294/[1042], 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400801926396

Photoinduced Gratings in Functionalized Azo-Carbazole Compounds in Picosecond Regime

Robert Czaplicki[1], Sylvie Dabos-Seignon[1], Ileana Rau[2], Oksana Krupka[1,*], Bouchta Sahraoui[1], Jacek Niziol[3], Monika Bednarz[4], Jan Pielichowski[4], Aurelia Meghea[2], and Mina Bakasse[5]
[1]Laboratory POMA, University of Angers, Angers Cedex, France
[2]Faculty of Applied Chemistry and Material Science, University Politehnica of Bucharest, Bucharest, Romania
[3]Faculty of Physics and Applied Computer Science, AGH – University of Science and Technology, Cracow, Poland
[4]Department of Polymer Science and Technology, Cracow University of Technology, Cracow, Poland
[5]University of Chouaib Doukkali – Faculty of Sciences BP, El Jadida, Morocco

We report results of diffraction grating inscription on thin films prepared from epoxy resin doped with azo-carbazole based dyes. Diffraction gratings were recorded at the wavelength 532 nm and monitored through intensity of first order of diffraction (632 nm). Atomic force microscope scans of the gratings show that a surface relief grating also appeared.

Keywords: azo-carbazole compounds; picosecond regime; pulsed-laser grating inscription; surface relief gratings

[*] On leave from Kiev National Taras Shevchenko University, Chemistry Department, Ukraine.

Some of the authors (Monika-Bednarz-and-Jacek-Niziol) acknowledge the support by Polish Ministry of Science and Education through the project 3-T08E-083-30. For Bouchta Sahraoui, Mina Bakasse, Aurelia Meghea financial support from FP 6 *Marie Curie Host Fellowship for the Transfer of Knowledge* contract NANOTEC- EST MTKD-CD-2004-014059 is gratefully acknowledged.

The authors thank Professor Andrzej Miniewicz (Wroclaw University of Technology, Poland) and for helpful discussion.

Address correspondence to Robert Czaplicki, POMA Laboratory, UMR CNRS 6136, University of Angers, 2 Boulevard Lavoisier, 49045 Angers, France. E-mail: robert.czaplicki@etud.univ-angers.fr

INTRODUCTION

Organic compounds combine unique electronic and optical properties. Polymers containing azo-benzene dyes either as side groups or physically dispersed, can interact with polarized light. This interaction due to reorientation of the side groups, results in reversible birefringence and dichroism. The *trans* azobenzene derivatives are stable in an elongated molecular form. In contrast, the *cis* azobenzenes are photoinduced isomers, taking a bentform, usually revert back to the *trans* form by thermal or light stimulation [1,2]. Photoinduced isomerisation was studied by many researchers [2–10] and several mechanisms of surface relief grating formation were proposed [1]. Polymers containing the azo groups are able to generate surface relief gratings by irradiation [1,11–13]. This phenomenon enables applications like holographic data storage, optical switching, optical data storage, etc [14].

Materials typically applied in the field of grating recording are optically transparent thermoplastic polymers (polymethacrylates, polycarbonates etc.) containing dyes dispersed on molecular level. The thermoplastics undergo the glass transition in relatively low temperatures – typically between 90 and 120°C. This feature limits laser power, which can be exerted on the surface without the risk of damage. More thermally stable materials are thermosetting resins. Once they are set, it is not possible to melt them any longer. Due to this feature, it is more complicated to transform them into thin films for gratings recording.

In frame of this work, we studied three kinds of thin films prepared from epoxy resin by different methods. The purpose was to find the most adapted to grating recording. As dyes we used tailored azo-functionalized carbazole compounds, already reported for their non-linear optical properties [15]. This choice was done due to their good miscibility with the epoxy resin and lack of visible phase separation.

DYES SYNTHESIS

General

All chemicals, were purchased from either Aldrich or Fluka and used as received with exception of solvents, twice distilled prior to synthesis.

The carbazole azo dyes can be synthesized either by coupling reaction of carbazolediazonium salts with passive compound or by coupling reaction between carbazole or its derivatives and diazonium salts of aromatic amines (very convenient method, which enables synthesis of multiple carbazole azo dyes [16]).

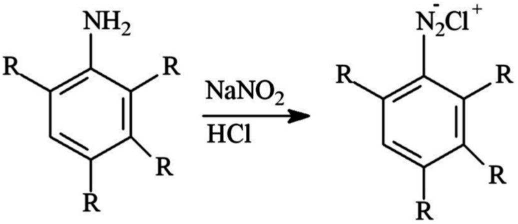


FIGURE 1 Amine diazotization, R = –Cl, $-NO_2$, –CN.

In this work, we follow the second one. At first, the diazonium salts are obtained according to the scheme presented in Figure 1. The next stage – coupling reaction (Fig. 2) is carried out at the interference of a two-phase system. Usually this system form water and an alcohol of low solubility in water (like butanol or isobutanol, less than 15 w% at 15°C) [17,18]. Under these conditions, carbazole and its derivatives easily react with diazonium salts of aromatic amines and the product is a suitable dyes. The dye formation according to this procedure is particularly rapid, even using reactants such as carbazole and its N-alkyl derivative, that normally undergo very hard (if at all) the coupling reaction.

Next, the obtained dye is extracted from the reaction mixture through filtration. Its purity usually is superior to 90%. Sometimes before filtering the dye, it is necessary to evaporate the residue of alcohol by steam distillation. This method provides high yield of the product, generally more than 80%.

Diazo Salt Solution Preparation

Hot, concentrated hydrochloric acid (18 ml) was added into suspension of 2-chloro-4-nitroaniline (5.3 g, 0.0264 mol) in water (57 ml). Then the

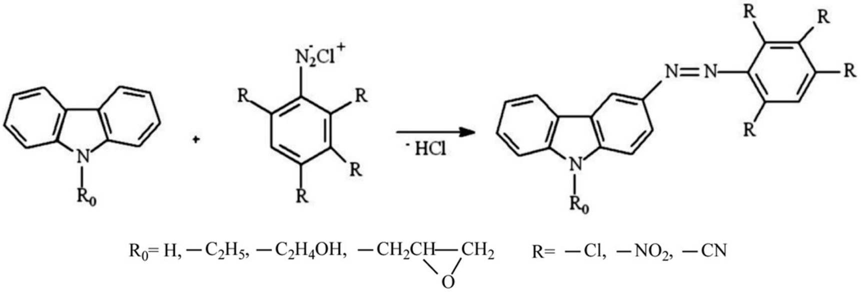


FIGURE 2 Coupling reaction of diazonium salts of aromatic amines with carbazole and its derivatives.

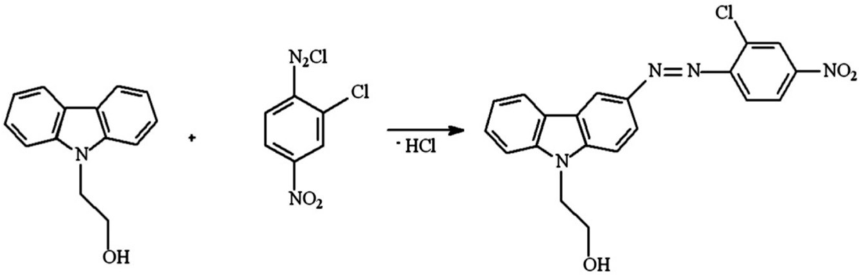


FIGURE 3 Synthesis of 3-(2′,4′-chloronitrophenylazo)-N-(β-hydroxyethyl)-carbazole) (CNHEK).

suspension was cooled in an ice bath until the temperature reached between 0° and +5°C. Then the solution containing sodium nitrite (2.5 g, 0.0264 mol) in water (13 ml) was slowly added to the suspension. The mixture was stirred in the ice bath for 30 min.

3-(2′-chloro-4′-nitrophenylazo)-N-(β-hydroxyethyl)-carbazole (CNHEK)

The filtered diazo solution was run into suspension of N-(β-hydroxyethyl)-carbazole (3 g, 0.0142 mol) in n-butanol (22 ml) at 40°C. The mixture was then stirred overnight at 40°C and meanwhile the dye precipitated. The dye was filtered, well rinsed on the filter (with 16 ml of n-butanol, and then with water) and finally dried. Resulting product, a green-yellow powder was obtained with 80% yield (Fig. 3).

IR (KBr), cm^{-1}. 3095, 2933($\nu_{\mathrm{Ar\text{-}H}}$), 1595($\nu_{\mathrm{N=N}}$), 1626, 1595($\nu_{\mathrm{C=C}}$), 1524, 1323($\nu_{\mathrm{NO_2}}$), 1466, 1439($\nu_{\mathrm{C-H}}$), 1111($\nu_{\mathrm{C-Cl}}$), 748, 733($\gamma_{\mathrm{CH_2}}$)

^{1}HNMR(acetone). $\delta = 4.05$(d, 2 H), 4.63(t, 2 H), 7.31(dt, 1 H), 7.60(dt, 1 H), 7.71(dd, 1 H), 7.82(d, 1 H), 7.96(m, 3 H), 8.31(dd, 1 H), 8.46(d, 1 H), 8.86(d, 1 H)

3-(2′-chloro-4′-nitrophenyloazo-)-N-(2,3-epoxypropyl)-carbazole (CNEPK)

First, the 3-(2′-chloro-4′-nitrophenyloazo-)-N-(2,3-epoxypropyl)-carbazole was obtained. Acetone (100 ml) was added into suspension of 3-(2′-chloro-4′-nitrophenylazo-)carbazole (5.7 g, 0.0158 mol) in epichlorohydrin (7.4 g, 0.0095 mol). The solution was heated up to 35°C and potassium hydroxide (0.9 g, 0.016 mol), potassium carbonate (16 g) and TBAB (tetrabutylammonium bromide) (0.5 g, 0.0095 mol) were added. The mixture, thermostated at 35°C, was stirred vigorously for 6 h. After evaporation of acetone crude product was crystallized

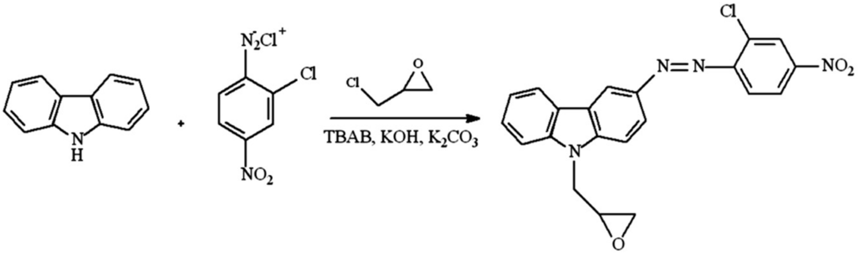


FIGURE 4 Synthesis of 3-(2′-chloro-4′-nitrophenylazo-)-N-(2,3-epoxypropyl)-carbazole (CNEPK).

from methylene chloride, filtered, well rinsed with water and dried. A bright red powder was obtained with 70% yield (Fig. 4).

IR (KBr), cm^{-1}. 2933($\nu_{\text{Ar-H}}$), 1596($\nu_{\text{N=N}}$), 1626, 1559($\nu_{\text{C=C}}$), 1524, 1341(ν_{NO_2}), 1465, 1450, 1431($\nu_{\text{C-H}}$), 1114($\nu_{\text{C-Cl}}$), 896($\nu_{\text{C-O-C}}$)750, 744(γ_{CH_2})

^{1}HNMR(acetone). $\delta = 3.45$(d, 2 H), 4.56(t, 2 H), 7.36(dt, 1 H), 7.57(dt, 1 H), 7.75(dd, 1 H), 7.87(d, 1 H), 7.98(m, 3 H), 8.33(dd, 1 H), 8.48(d, 1 H), 8.88(d, 1 H)

3-(3,4-dicyanophenylazo)-N-(2,3-epoxypropyl)-carbazole (DCEPK)

The first step of 3-(3,4-dicyanophenylazo)-N-(2,3-epoxypropyl)-carbazole synthesis (Fig. 5) was analogous to this of described above dyes. Further, the freshly obtained diazo-compound was suspended in acetone and treated with epichlorohydrine in presence of potassium hydroxide, potassium carbonate and tetrabutylammonium bromide (TBAB) at 40°C for 8 h. The epoxy functionalized chromophore, collected by filtration, was washed with acetone and water and finally dried.

IR (KBr), cm^{-1}. 3072($\nu_{\text{Ar-H}}$), 2230(ν_{CN}), 1603($\nu_{\text{N=N}}$), 1627($\nu_{\text{C=C}}$), 1467, 1455, 1431($\nu_{\text{C-H}}$), 900($\nu_{\text{C-O-C}}$), 751, 736(γ_{CH_2})

^{1}HNMR(acetone). $\delta = 4.05$(d, 2 H), 7.34(dt, 1 H), 7.50(dt, 1 H), 7.71(dd, 1 H), 8.12(d, 1 H), 8.26(m, 3 H), 8.33(dd, 1 H), 8.44(d, 1 H), 8.84(d, 1 H)

Polymer Synthesis (ER + CNEPK)

In the next stage, 5% wt. of the dye was added to epoxy resin, known as “Epidian 6” (brand name of the product based on bisphenol A from

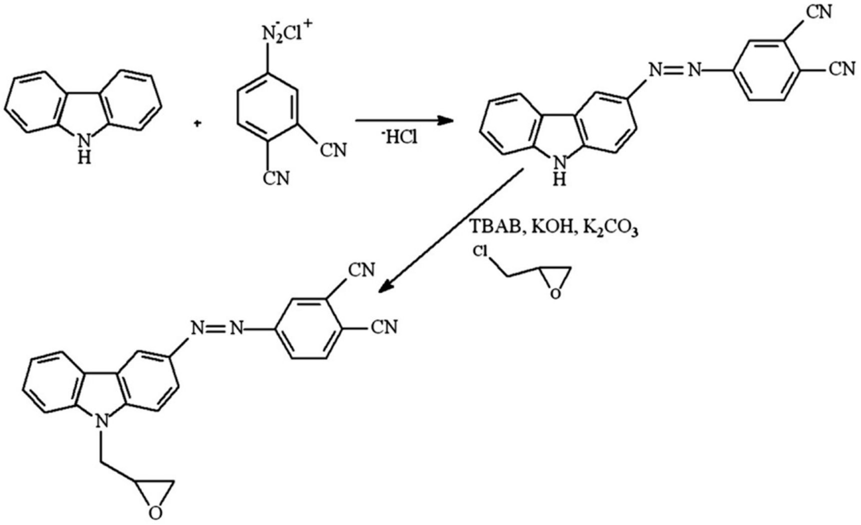


FIGURE 5 Synthesis of 3-(3,4-dicyanophenylazo)-N-(2,3-epoxypropylo)-carbazole (DCEPK).

Z.Ch. Organika-Sarzyna, Poland) and heated at 120°C with a small quantity of 2-methyl-imidazole (setting agent). This curing reaction was carried one hour. FTIR and NMR spectroscopies results of this material supported the structure shown in Figure 6. The resulting material was not a completely set polymer, (forming long-range network) but had a glass transition of $T_g = 95°C$ and was soluble in typical organic solvents.

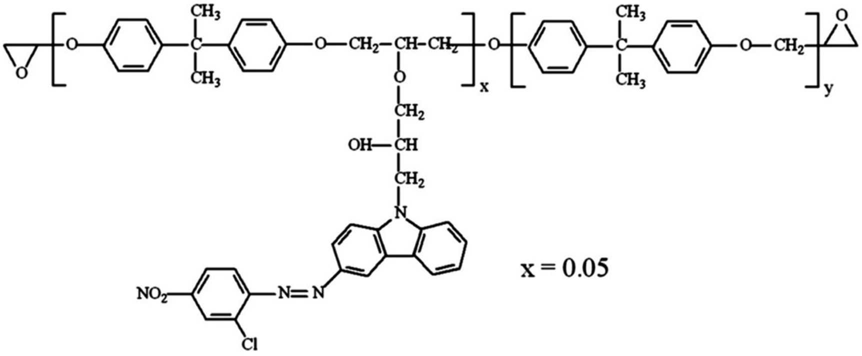


FIGURE 6 Structure of the synthesized polymer (ER + CNEPK).

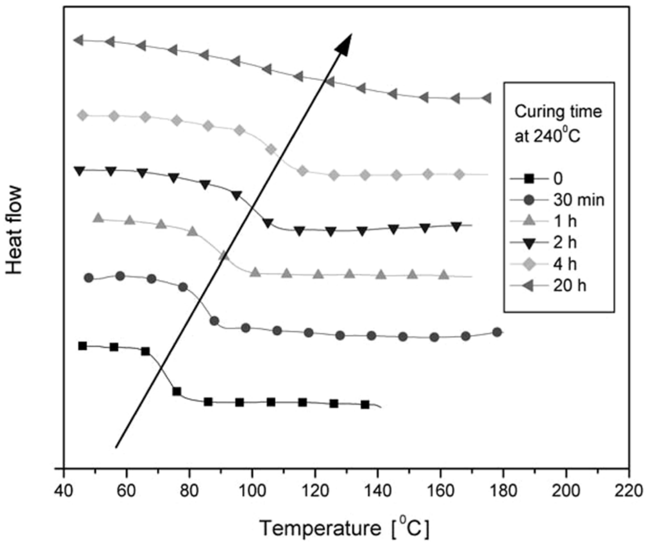


FIGURE 7 Results of thermal conditioning of ER + CNEPK resin.

A sample of this compound was conditioned in elevated temperatures (up to 240°C, however it was still well below the compound decomposition). Prolonged heating shifted always the T_g point towards higher temperatures. Figure 7 shows an example. The sample was kept in an furnace at 240°C and continually undergo the DSC calorimetry to monitor the glass transition shift. With prolonging time of conditioning the T_g rose and completely disappeared after c.a. 20 hours. These characteristics can be understood as the result of complete thermosetting. It means that prolonged heating helps to preserve physical form (recorded grating) of the sample.

Thin Film Preparation

Three types of films were prepared – from resin with already coupled dye molecules (ER + CNEPK), from pristine resin and dye containing epoxy group (DCEPK) and from pristine resin and dye without epoxy group (CNHEK – in this case the dye rest only physically dispersed).

Thin films were prepared as follows. Resin ER + CNEPK was dissolved in 1,1,2 trichloroethane and deposited by spin-coating. The CNHEK and DCEPK dyes were dissolved in warm epidian resin in desired proportions, leading to same molar content of the dye as in case of ER + CNEPK. The stoichiometric amount of the hardening agent – 4,4-diaminodiphenylene methane was added. The mixtures was either squeezed between two microscope glass slides or smeared over one. In this later case, free surface of obtained films was enough glassy. At the end, all samples were kept in the furnace at 240°C for 24 hours, to accomplish their setting, according to findings presented in Figure 7.

We supposed that compound DCEPK (initially bearing epoxy group) after this process was chemically bound to the polymer network while CNHEK remained physically dispersed. Further we will use abbreviation ER + CNHEK and ER + DCEPK for films containing given dyes.

Spectral Characterization

UV-vis absorption spectra of the thin films are presented in Figure 8. As expected all films show a peak around 425–440 nm characteristic for azochromophores.

Absorption at the wavelength 632 nm was insignificant, therefore a YAG laser at 532 nm was used as the writing beam, and a He-Ne laser at 632.8 nm was chosen as the reading beam.

EXPERIMENTAL

The schematic experimental setup of the grating experiment is shown in Figure 9 and it has been described in details by R. Czaplicki *et al.* [20].

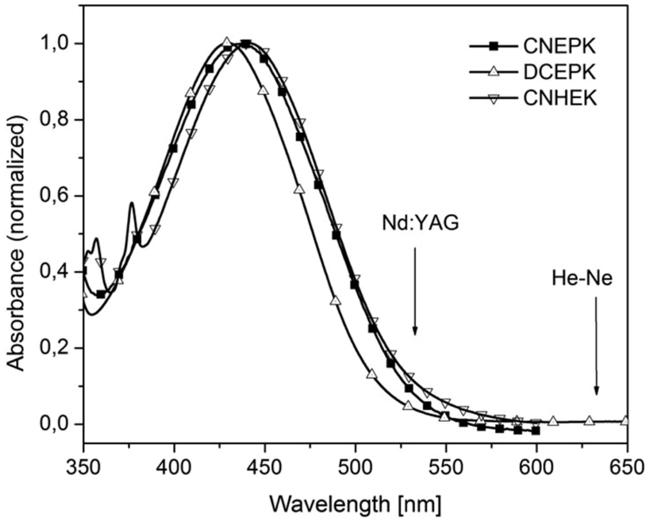


FIGURE 8 UV-vis spectras of prepared thin films.

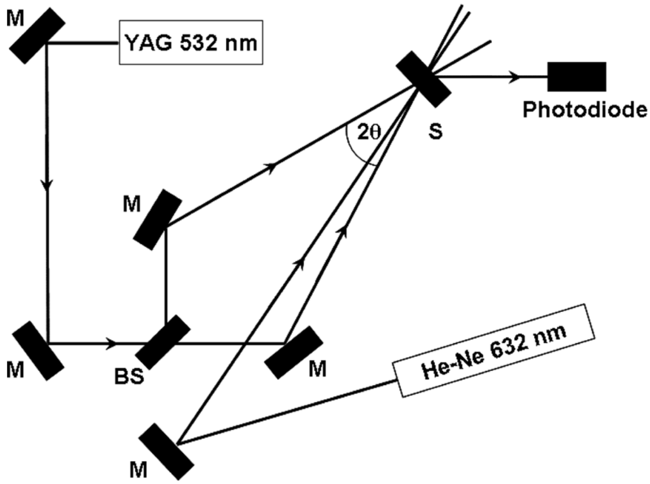


FIGURE 9 Schematic setup of the grating experiment, M – mirrors, BS – beam splitter, S – sample.

Diffracting gratings were recorded by two 30 ps pulses laser beams at wavelength of 532 nm from Q-switched, mode-locked Nd:YAG laser with pulse energy 1.2 mJ and repetition 10 Hz. Grating formation was monitored by He-Ne (30 mW) laser operating at 632.8 nm by measuring the power (by photodiode Centronic Series OSI 5) of the first-order diffraction peak in the transmission mode. The signal from the photodiode was observed on digital oscilloscope (Tektronix TDS 3054). The sample (S) was mounted on a fixed stage.

The surface structure of the grating of polymer film was investigated by Atomic Force Microscopy (with microscope Pico SPM of Molecular Imagining).

RESULT AND DISCUSSIONS

The s-s polarization configuration was set. We worked within the Bragg light scattering regime and we observed only one order of diffraction [21]. The chosen laser wavelength (532 nm) was absorbed in the sample and induced *trans-cis* isomerization process of azobenzene derivatives [2].

Figure 10 shows the pulsed laser grating recording for ER + CNHEK, ER + CNEPK and ER + DCEPK compounds. The observed dynamics of the diffraction signal, which is directly connected to the inscription of grating, shows nonlinear dependence. We can notice that

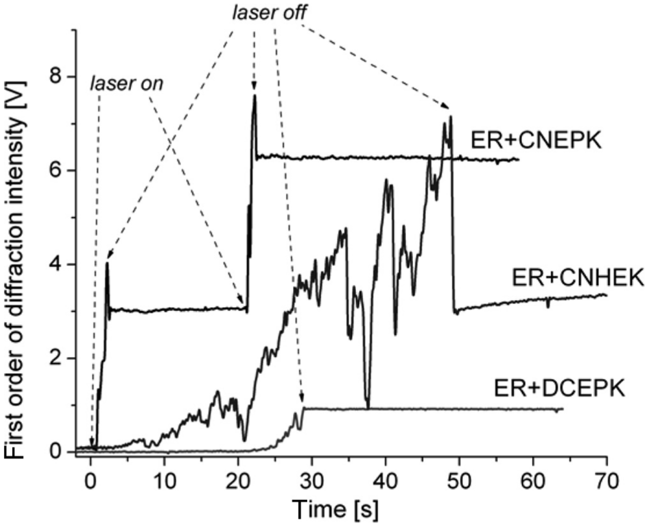


FIGURE 10 Example of grating build-up process in compounds ER + CNHEK, ER + CNEPK and ER + DCEPK using 30 ps pulses of 532 nm with 1 Hz repetition rate and monitored by He-Ne laser (large time scale).

inscription of grating is very fast in all cases and irreversible (stable signal of first order of diffraction during 14 hours after switching off the inscribing laser light). Samples prepared from ER + CNHEK and ER + DCEPK had their surfaces limited by two squeezing glass plates and we can suppose that in these cases there were no surface relief grating formation. However, one of our sample (ER + CNEPK) was free to the deform and surface relief grating could be formed. Due to applied s-s polarisation, we observed intensity grating [1].

During the recording in ER + CNEPK thin film we observed fast build-up of grating (immediately after switching on laser light). After switching off the inscribing laser light we noticed very fast fall (c.a. 20%) of the signal intensity, then the signal stabilized at the attained value. After switching on 532 nm reading beams once again we observed continuation of recording of grating (Fig. 10) in the same manner.

In the case of ER + CNHEK compound, we observed fast build-up of grating (but not so fast as in case of ER + CNEPK sample) followed by a large decrease (c.a. 60%) before signal stabilized. In addition the recorded signal was very noisy. It could be attributed to thermally induced processes concerning the epoxy matrix as well as relaxation phenomena of the dye molecules, not bound chemically to the matrix.

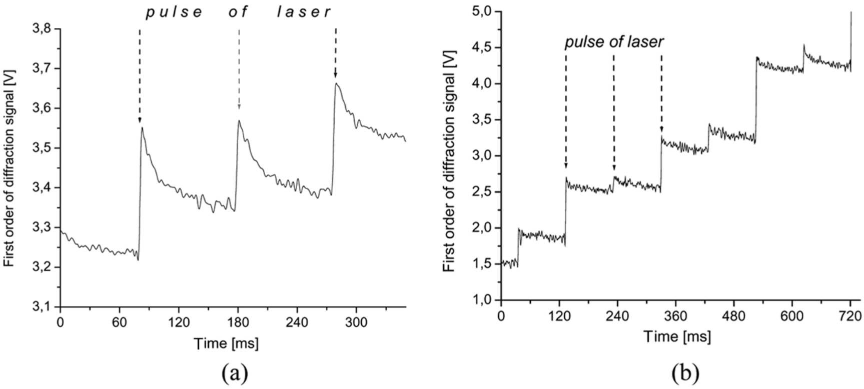


FIGURE 11 Kinetics of grating build-up process in compounds (a) ER + CNEPK and (b) ER + DCEPK (short time scale). Signal from the sample containing CNHEPK was too noisy to be representatively shown at this time scale.

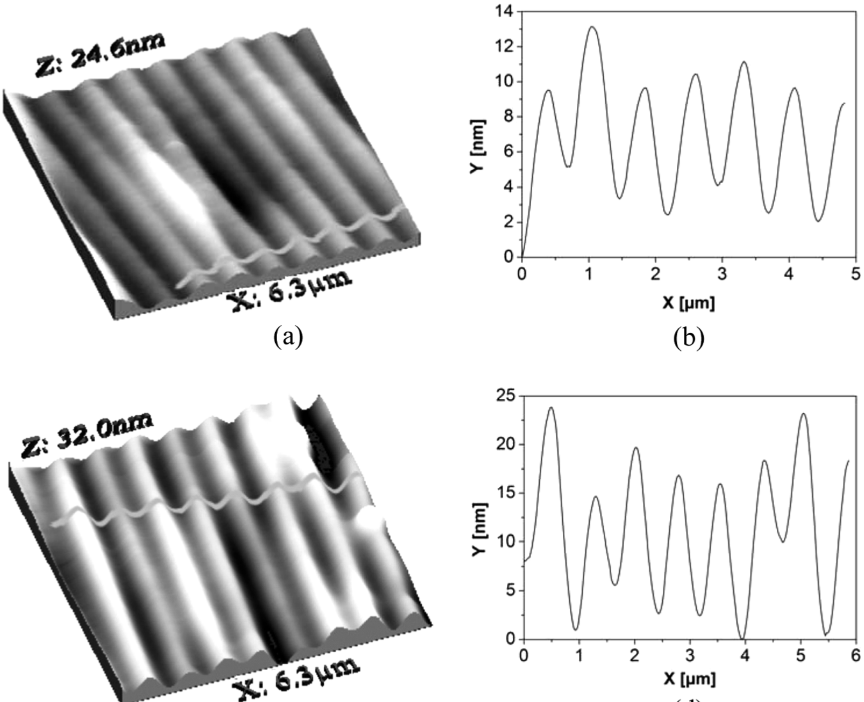
In case of the sample ER + DCEPK the process of recording grating was slower than in the case of ER + CNHEK and ER + CNEPK compounds. After switching on inscribing laser light (532 nm) build-up process of grating started after c.a. 25 s and rapidly progressed. After switching off the laser, the recorded grating rest stable without visible intensity decrease of the signal (Fig. 10).

Described above behaviour was observed more or less in a reproducible manner and did not depend on physical form of samples (squeezed between two glass slides or one surface free).

Each pulse of laser contributed to grating growth. Examples of this phenomenon are shown in Figure 11. Each laser pulse was followed by relaxation. This relaxation was smaller in case of ER + DCEPK and more pronounced in case of ER + CNEPK (Fig. 11(b)). Differences in height of steps seen in Figure 11 were due to instability of power. Figure 12 shows typical example of the three dimensional view of the surface relief grating. The relief grating has a regular sinusoidal shape up to 15 nm depth. The grating spacing (Λ), measured from AFM, was about 0.76 µm and was consistent with the theoretically ones calculated using Eq. (1):

$$\Lambda = \lambda/(2\sin\theta) \tag{1}$$

where λ is the wavelength of the writing beam, 2θ is the angle between the two writing beams [19].



(a) (b)

(c) (d)

FIGURE 12 (a), (c) AFM three-dimensional view of azo carbazole compound (ER + CNEPK) with inscribed SRG and (b), (d) surface profile of the grating.

From the Figure 12 (a) it can be seen also that the material exhibited partial burning after long illumination with high energy (central part of image).

CONCLUSIONS

In this work we used ps pulsed laser and we have successfully inscribed and studied permanent surface relief gratings into functionalized azo-carbazole compounds in the form of thin film between two glass plates and film deposited on glass substrate. This behavior is also confirmed by the relief observed and studied by AFM topography. Direct AFM measurements confirmed expectations of the simple formula (1). This study also proved that good reproducible results can be obtained when the resin for thin films is pre-polymerized, already contains chemically bound dye groups. Other tested morphologies lead to poorer properties. However obtained results show the damage of the compound and did not explain the very good mechanism of inscription of gratings, therefore further investigation is needed.

REFERENCES

[1] Yager, K. G. & Barrett, C. J. (2001). *Cur. Op. Sol. Stat. Mat. Sci.*, *5*, 487.

[2] Cojocariu, C. & Rochon, P. (2004). *Pure Appl. Chem.*, *76*, 1479.

[3] Todorov, T., Nikolova, L., & Tomova, N. (1984). *Appl. Opt.*, *23*, 4309.

[4] Barrett, C. J., Natansohn, A. L., & Rochon, P. L. (1996). *J. Phys. Chem.*, *100*, 8836.

[5] Sek, D., Schab-Balcerzak, E., Solyga, M., & Miniewicz, A. (2002). *Synth. Met.*, *127*, 89.

[6] Loucif-Saibi, R., Nakatani, K., Delaire, J. A., Dumont, M., Sekkat, Z. (1993). *Chem. Mater.*, *5*, 229.

[7] Kumar, J., Li, L., Jiang, X. L., Kim, D., Lee, T. S., Tripathy, S. (1998). *Appl. Phys. Lett.*, *72*, 2096.

[8] Lefin, P., Fiorini, C., & Nunzi, J-M. (1998). *Pure Appl. Opt.*, *7*, 71.

[9] Viswanathan, N. K., Balasubramanin, S., Li, L., Tripathy, S. K., Kumar, J. (1999). *Jpn. J. Appl. Phys.*, *38*, 5928.

[10] Dumont, M. & Osman, A. E. (1999). *Chem. Phys.*, *245*, 437.

[11] Kim, D. Y., Tripathy, S. K., Li, L., & Kumar, J. (1995). *Appl. Phys. Lett.*, *66*, 1166.

[12] Kim, D. Y., Li, L., Jiang, X. L., Shivshankar, V., Kumar, J., Tripathy, S. (1995). *Macromolecules*, *28*, 8835.

[13] Viswanathan, N. K., Balasubramanin, S., Li, L., Kumar, J., Tripathy, S. K. (1998). *J. Phys. Chem. B*, *102*, 6064.

[14] Hagen, R. & Bieringer, T. (2001). *Adv. Mater.*, *13*, 1805.

[15] Niziol, J., Kajzar, F., Rau, I., Bednarz, M., Pielichowski, J., Pielichowski, K. (2006). *Mol. Cryst. Liq. Cryst.*, *447*, 167.

[16] Chrząszcz, R. (1986). Barwniki karbazolowe, *Zeszyt Naukowy PK nr 2*, Kraków.

[17] USA Patent 4 313 872, 1982.

[18] European Patent 0 028 464, 1981.

[19] Taunaumang, H., Solyga, M., Tija, M. O., & Miniewicz, A. (2004). *Thin Solid Films*, *461*, 316.

[20] Czaplicki, R., Dabos-Seignon, S., Kajzar, F., Bakasse, M., Nizioł, J., Bednarz, M., & Sahraoui, B. (2006). *Proceedings of IEEE Conference on 8-th International Conference on Transparent Optical Networks ICTON 2006 (Nottingham, United Kingdom, 2006)*, 283.

[21] Moharam, M. G., Gaylord, T. K., Magnusson, R. (1980). *Opt. Commun.*, *32*, 19.