Synthesis, Thin Film Deposition and Optical Characterization of Epithiopropylcarbazole Polymer

A. MESHALKIN[1], S. ROBU[1,2], A. PRISACAR[1], L. BETS[3], G. TRIDUH[1], E. ACHIMOVA[1]

[1]*Institute of Applied Physics of Academy of Sciences of Moldova, 5 Academiei str., 2028, Chisinau, Moldova*

[2]*Moldova State University, 60 Alexei Mateevici str., 2009, Chisinau, Moldova*

[3]*Institute of Chemistry of Academy of Sciences of Moldova,3 Academiei str., 2028, Chisinau, Moldova*

alexei@asm.md

Abstract **- Carbazolic copolymer namely epithiopropylcarbazole with glycidyl butyrate have been developed to be used in holographic recording. This paper describes an analysis, from synthesis of the material to its applications, together with the corresponding characterizations. The investigated materials were photosensitive copolymers obtained from epithiopropylcarbazole (ETPC) with glycidyl butyrate (GB). A detailed investigation was undertaken involving infrared spectroscopy in order to establish the chemical structure and the composition of the copolymer. Each step of chemical synthesis was carefully controlled by IR analysis. Spin coating procedure using programmable spin-coater was used to obtain the thin films. The thickness of the polymer film was varied by changing the concentration of polymer solution. It was shown the linear thickness dependence on polymer concentration. Photoinduced phenomena were investigated by UV-VIS and IR spectroscopy. In comparison with other carbazole-containing polymers, copolymer epithiopropylcarbazole with glycidyl butyrate have no changes in UV-VIS transmission spectra after irradiation. And only IR spectroscopy could be applied to distinguish such changes. Holographic recording were applied for recording characteristics investigation. It was shown that via a holographic recording process, it is possible to hide record of holograms and read it only after chemical etching. The surface of etched diffraction gratings were characterized by atomic force microscopy analysis.**

Index Terms **– carbazole-containing copolymer, holographic recording, IR spectroscopy, photoinduced phenomena, thin polymer films.**

I. INTRODUCTION

Carbazole-containing polymers and copolymers have been the subject of intensive investigation in the last 50 years since the discovery of its photoconductivity by Hoegl [1]. In 1957, he established that polyvinylcarbazole sensitised with suitable electron acceptors showed high enough levels of photoconductivity to be useful in practical applications like electrophotography. Since then, numerous carbazole-containing polymers have been described in scientific literature [2-5]. Carbazole-based polymers exhibit photorefractive, optical and charge-transporting properties [6–8]. In particular, carbazolic compounds have attracted wide interest due to their potential applications in areas such as optical data storage and information processing [9]. In the past decade, special attention was paid to the problem of holographic recording with the aim of protecting the documents from falsification or counterfeiting, and reliefographic methods appeared to be a convenient answer to the problem [10]. Security holograms offer a unique solution to product and document counterfeit providing unambiguous visual authentication that requires no external device or reader for verification. The use of small holograms in credit cards, which are made to prevent falsification, has made holograms a well known concept. Holograms show up more and more often on tickets and original covers. Important areas of application are bar-codereaders in shops, warehouses, libraries and so on, which is based on holographic components like optical gratings.

Any material used to record a hologram must respond to exposure to light with a change in its optical properties. In the absorption or amplitude modulating materials the absorption constant changes as a result of exposure, while in phase modulating materials thickness or refractive index changes due to the exposure. In the phase modulating materials, there is no absorption of light and the entire incident light is available for image formation, while the incident light is significantly absorbed in an amplitude modulating material. Thus a phase material can produce a higher efficiency than an amplitude material. Also in phase modulating media, the amount of phase modulation can be made as large as desired. A practical recording media can be considered as a combination of these two. The material should be of high optical quality. The media performance is assessed in terms of parameters like diffraction efficiency (DE), sensitivity, resolution, signal to noise ratio (SNR), temporal stability etc.

Hologram recording in carbazolic polymers can be achieved by several processes using its photorefractive, photoconductive, and/or photochemical properties.

The aim of this work was first to synthesize new carbazole-containing copolymer appropriated to holographic recording. For this purpose the material must have a number of required characteristics. Compared with other holographic materials such as dichromated gelatin and silver halide emulsions, polymers have the great advantage of recording and reading holograms and the spectral sensitivity could be easily shifted to the type of

recording laser used by changing the sensitizing dye. Also these materials possess characteristics such as good light sensitivity, large dynamic range, good optical properties, format flexibility, and low cost.

In the present work, the studied material was copolymer of epithiopropylcarbazole (ETPC) containing 4% of glycidyl butyrate (GB) and synthesized by free-radical polymerization. The copolymer was synthesized as the host polymer matrix and iodoform CHI_3 was used as the photosensitizing dye. The role of GB was mainly to ensure the film forming properties and surface stability without damaging the holographic response of the material. Additionally, it appeared that the presence of GB in the copolymer induced an effect of film thickness increasing.

II. EXPERIMENTAL

Synthesis of polymer. Copolymer of epithiopropylcarbazole with 4mass% of glycidyl butyrate (ETPC:GB) was selected to ensure the excellent film forming properties and photoinduced properties.

Copolymer used in this investigation was synthesized by polymerization of epoxypropylcarbazole and epithiopropylcarbazole at the presence of 1-3% potassium methylate on the anionic mechanism at temperature 80-120˚C within 2-6 hours. For the full drying they were stored in a vacuum drying chamber at 50˚C up to constant mass. From the characterization by polymer viscosity using calibrated standards results a molecular weight Mw 2000-3000. In Fig. 1 the scheme of chemical synthesis of ETPC monomer is presented.

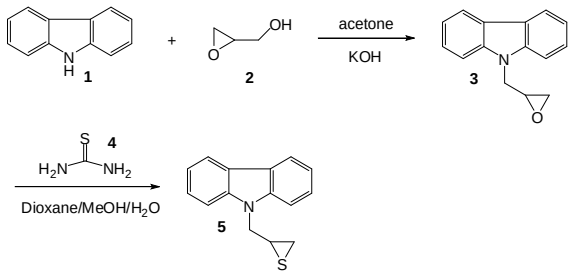
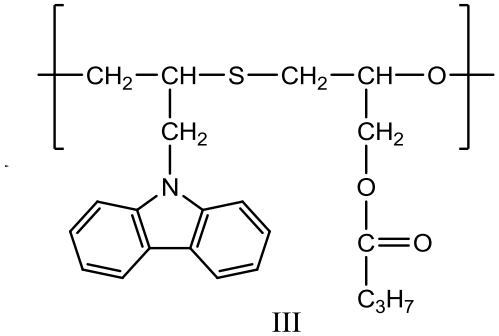


Fig. 1. Chemical synthesis of ETPC monomer: 1 – carbazole; 2 – epichlorhydrin; 3 – epoxypropilcarbazole; 4 – thiourea; 5 – epithiopropylcarbazole.

As the synthesized material is only sensitive in the UV the spectral sensitivity should be shifted to the type of recording laser region. To shift the spectral sensitivity to the blue region of spectrum the sensitizing dye such as iodoform CHI_3 has been introduced into the samples.



III

Fig. 2. Chemical structure of copolymer ETPC:GB.

The dependence of photosensitivity of the deposited films on the content of iodoform CHI3 was studied earlier [14]. It was established that the optimum concentration of the iodoform was 10 mass%.

Formation of polymer films from solution.

A widely used technique to fabricate thin layers is spin-coating. In the first step, the material is poured or sprayed to the center of a glass disk. Next, the disk starts rotating in an axis normal to the surface of the disk. Thereby the material moves outward. In the stationary state, the viscous forces in the fluid dominate the thinning of the layer. Excess material may leave the disk at the edge as droplets. If the material contains a solvent, the solvent may evaporate. Spin-coating may be done at elevated temperatures. Various designs are in use.

In our study the thin polymer films were prepared from homogeneous polymer solution by spin coating procedure using programmable spin-coater "SGS Spincoat G3P-8". The thickness of the polymer film was varied by changing the concentration of polymer solution and the rotation speed of spin coating. In series oa samples, the ETPC:GB concentration was varied (from 2.5 to 12.5 wt% solutions in chloroform $CHCl_3$) at fixed spin speed.

Operation conditions for polymer solution deposited on 5 cm diameter optical glass substrate (BK7) was as follows: 2 cm^2 of liquid dispensed on the disk at rest, subsequently accelerated in about 10 s to 3000 rpm and spun for 20 s. The broad range of thicknesses can be covered by using polymer solution with increasing solids content or for a given solution by changing the final spin speed.

Determination of film thickness.

For the determination of film thickness in this work the modified interferometric PC based measurement based on MII-4 interference microscope was applied.

A thickness characterization of the samples was achieved by a MII-4 interference microscope with CCD-camera recorded the micrographs. The interference pattern of light reflected from a flat reference surface and the investigated sample was recorded in PC. A magnification of 490 times was used. The area from which a data analysis is performed was 0.3 mm diameter circle. This enables a height resolution better than 100 nm [12].

Spectral characterization.

With the purpose of firmly assessing the nature of the synthesized material, a detailed characterization by IR and UV-VIS spectroscope was applied. Before infrared analysis, samples were dried in exsiccator up to constant mass. Infrared spectra of the samples were recorded with a Perkin Elmer FTIR 100 spectrophotometer (4 cm^{-1} and 32 scans).

UV-VIS transmission spectra were recorded on thin polymer films with Specord M40.

Holographic characterization.

A 442 nm He-Cd laser was used for holographic characterization. Diffraction gratings were recorded on these films by keeping the beam ratio as 1:1 and spatial frequency as 1000 lines/mm. After recording wet

chemical treatment was applied for relief formation. Etching treatment was controlled by measuring of DE in transmission mode at the wavelength of 633 nm within the equal time interval.

The special organic solution was chosen as etching agent. It was studied the variation of DE with etching time.

III. RESULTS AND DISCUSSION

Good quality films with different thickness were obtained after a drying period of 24 hrs. The thickness of spin-coated films determined from the fringe pattern in the interferogram was found to be increased with the increase of polymer concentration in solution. It was shown that by raising the polymer concentration from 3 to 15.0 wt%, the final film thickness increase from 760 to 2270 nm at a spin speed of 3000 rpm. Applied methods of thickness measurements have shown a quasi-linear thickness dependence on polymer concentration. (Fig.4.). In case of PEPC deposition the obtained film thickness is changed essential. But linear dependence on polymer concentration remains. Therefore, a smooth polymer films with desired thickness can be fabricated just by controlling the polymer concentration in solution.

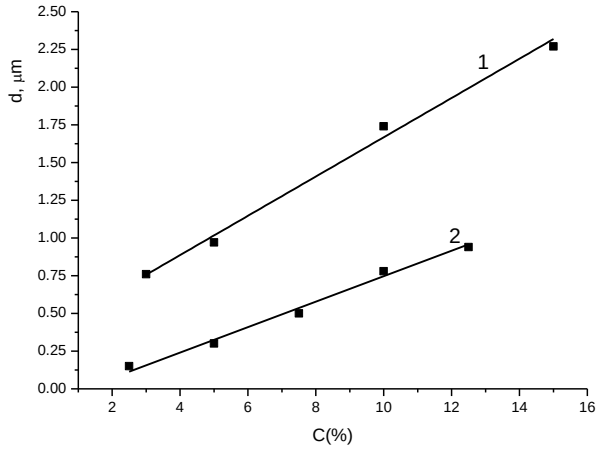
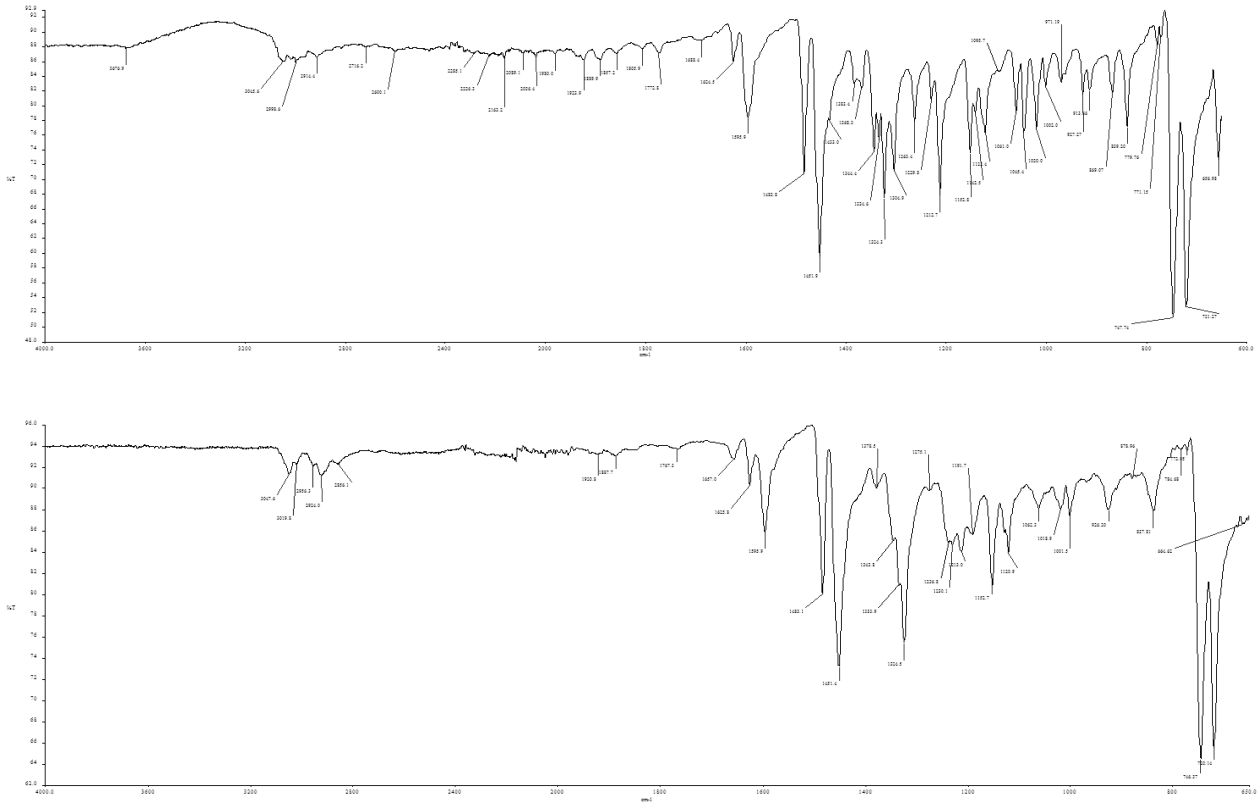


Fig. 4. Thickness as a function of ETPC:GB solution (1) and PEPC solution (2).

The copolymers were also characterized by investigated by FT-IR spectroscopy. The spectra of the each intermediate material during synthesis have been compared to each other. Carbazole was used as reference for attributions of absorption bands of carbazole rings. IR spectra of monomer ETPC, polymer ETPC and copolymer ETPC:GB are given in Figure 4.



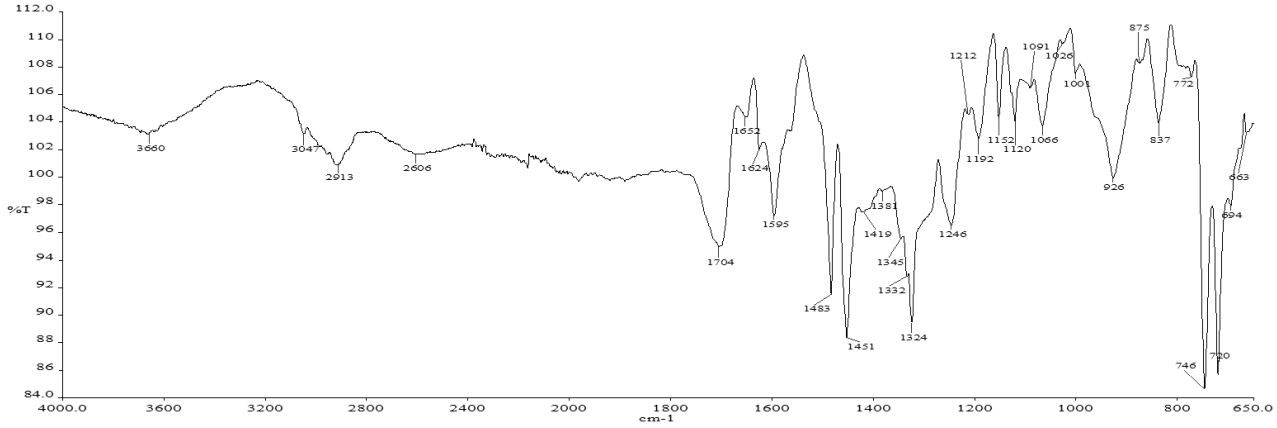


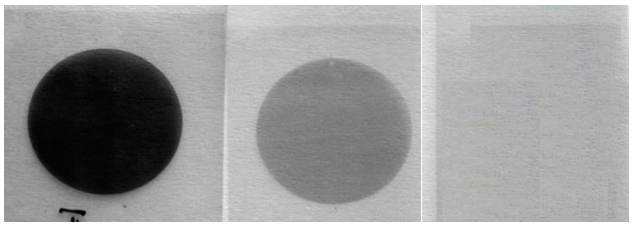
Fig. 5. IR spectra of monomer epithiopropilcarbazole, polymer epithiopropilcarbazole, and copolymer epithiopropylcarbazole with glycidyl butyrate.

Attributions of infrared absorption bands in comparison with pure carbazole are reported in Table 1. Each organic group has been identified on the basis of literature data [11]. The obtained data confirmed the chemical structure of copolymer. The absorbance of the carbazolic band at 1122, 1484, 1596, 1624 cm^{-1} (ring stretch) has been measured for copolymer and pure carbazole. The results show a good agreement between the infrared measurements and the expected values.

Table 1. Attribution of infrared absorption bands (cm^{-1}).

Monomer ETPC	Polymer ETPC	Copolymer ETPC:GB	Attribution
3045	3047	3047	Aromatic C-H stretch
	2924		CH_2 antisymetric stretch
	2856		CH_2 symetric stretch
		1704	C=O stretch
1624	1625	1625	Ring stretch
1596	1596	1596	Ring stretch
1484	1483	1483	Ring stretch
1452	1451	1451	"scissors" CH_2 bend overlapped with "sideways" ring stretch
1383	1378	1381	CH_3"umbrella" symmetric bend
1334	1334	1332	$C_{aromatic}$-N stretch
1324	1324	1324	CH bend
		1246	C(O)-O-C stretch
1230	1230		$C_{carbazole}$-N stretch
1152	1152	1152	C-C main chain or CH_2 rocking
1122	1120	1120	carbazole
1020	1018	1026	Ortho-substituted aromatic cycle
747	746	746	Out-of-plane bending of aromatic C-H
721	720	720	Concerted rocking of the CH_2

Photos of irradiated by laser exposure and optical absorption spectra of ETPC:GB film in comparison to polymers PEPC and ETPC are shown in Fig. 6. and Fig. 7. correspondingly. ***a*** – PEPC; ***b*** – ETPC; ***c*** – ETPC:GB.



a ***b*** ***c***

Fig. 6. Photos of irradiated by laser exposure films of a – PEPC; b – ETPC; c – ETPC:GB.

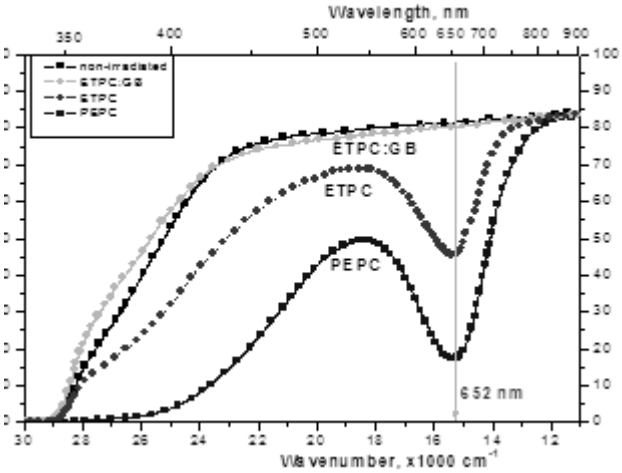


Fig. 7. Optical absorption spectra of ETPC:GB film on laser exposure in comparison to polymers PEPC and ETPC.

It was established that the investigating polymer films demonstrate the etching selectivity of the recorded diffraction gratings. Etching treatment was controlled by measuring of η in transmission mode at the wavelength of 633 nm within the equal time interval.

After recording the diffraction efficiency (η) of all samples was less than 0.1%. Diffraction efficiency dependence on etching time is presented in Table 2 [3].

Table 2. Diffraction efficiency of etching polymer films.

Sample composition	Etching time, s		
	5	10	15
PEPC	2%	2.7%	9.8%
ETPC	11%	24%	26%
ETPC:GB	20%	35%	41%

Mechanism of Grating Formation

The mechanism of grating formation can be explained as follows. On exposing to the interference pattern, the CHI_3 molecules get excited and electron transfer takes place between carbazole ring and CHI_3 [3].This reaction produce carbazole radical and this radical initiates the polymerization reaction.

Polymerization takes place at the region of constructive interference and as a result this polymerization (crosslinking) contribute to the structurization of copolymer [3]. This structurization takes place without changing the refractive index and transmittance of film which leads to the hidden grating formation. The grating formation can be revealed only by wet selective etching.

The measurements of surface profile by atomic force microscope AFM NANOStationII have proved the non-sinusoidal form of gratings recorded on ETPC:GB film. The relief profile showed the same spatial periodicity (~1 μm) as the light pattern spacing. The depth of surface profile after etching in the organic solution varied from 50 nm to 100 nm [3].

This result can be explained by the fact that laser action does not change the visible transmittance of the film during the recording time. So no changes in absorption/transmission on visible spectra and no changes in refractive index were observed. It leads to formation of hidden gratings that can be revealed after etching.

IV. CONCLUSION

This paper presents a study of ETPC, from the material synthesis to its use as holographic recording media for hidden recording. Firstly, syntheses and characterizations of carbazolic monomer, polymer and copolymer were carried out. Their chemical structure was examined implementing IR analytical technique. The syntheses yielding carbazole containing copolymers are rather complex from the first step, the monomer synthesis, to the final copolymer elaboration. By IR techniques, it was possible to firmly assess the structure and the composition of the various participants in the synthesis process. The implemented approach gives access to a precise characterization of copolymers; this is a crucial point when considering their wide use as photosensitive materials to record holograms. Secondly, hidden holographic recording in visible spectra was carried out with the synthesized materials. Hologram recording provides the possibility of hologram recording and reading after the selective etching. The comparison between PEPC, ETPC and ETPC:GB films showed that ETPC is advantageous, giving rise to better results in terms of diffraction efficiency. Experimentally, it is possible to record holograms with a diffraction efficiency up to 40%.

The new feature which was observed on ETPC:GB films was the formation of hidden gratings: after recording by laser exposure, no image of gratings were visually observed. The image of gratings appeared only after the etching.

ACKNOWLEDGMENTS

The financial support from the supreme council for science and technological development of the Academy of Sciences of Moldova project no. 11.817.05.03A "Chalcogenide semiconductormaterials, metallo-organic compounds, and molecular magnets for recording media, sensors, optoelectronic and photovoltaic applications" is greatly acknowledged.

REFERENCES

[1] H. Hoegl, "On photoelectric effects in polymers and their sensitization by dopants", Journal of Physical Chemistry, vol. 69, no. 3, pp. 755–766, 1965.

[2] J. V. Grazulevicius, P. Strohriegl, J. Pielichowski, and K. Pielichowski, "Carbazole-containing polymers: synthesis, properties and applications", Progress in Polymer Science, vol. 28, no. 9, pp. 1297–1353, 2003.

[3] A. Andries, V. Abaskin, E. Achimova, A. Meshalkin, A. Prisacar, S. Sergheev, S. Robu, L. Vlad, "Application of carbazole-containing polymer materials as recording media", Physica Status Solidi (A), vol. 208, no. 8, pp.1837-1840, 2011.

[4] B. Mailhot-Jensen, S. Robu, A. Rivaton, J. Pilichowski, A. Chirita, E. Chilat, G. Dragalina, "Carbazole Containing Copolymers: Synthesis, Characterization, and Applications in Reversible Holographic Recording," International Journal of Photoenergy, vol. 2010, Article ID 945242, 11 pages, 2010.

[5] J. Li, A.C. Grimsdale, "Carbazole-based polymers for organic photovoltaic devices", Chem. Soc. Rev., vol. 39, no. 7, pp.2399-2410, 2010.

[6] K. Meerholz, B. L. Volodin, Sandalphon, B. Kippelen, N. Peyghambarlan, "A photorefractive polymer with high optical gain and diffraction efficiency near 100%", Nature, vol. 371, no. 6497, pp. 497–500, 1994.

[7] D. P. West, M. D. Rahn, C. Im, H. Bassler, "Hole transport through chromophores in a photorefractive polymer composite based on poly(N-vinylcarbazole)", Chemical Physics Letters, vol. 326, no. 5-6, pp. 407–412, 2000.

[8] I. K. Moon, C.-S. Choi, N. Kim, "Synthesis and characterization of novel photoconducting carbazole derivatives in main-chain polymers for photorefractive applications", Polymer, vol. 48, no. 12, pp. 3461–3467, 2007.

[9] V. Bivol, S. Robu, G. Dragalina ; L. Bostan, A. Prisacari, A. Coban, "New photoresists from carbazol-containing photopolymers", Proc. SPIE 4087, Applications of Photonic Technology 4, 754, 2000.

[10] V. Bivol, S. Robu, A. Andriesh, T. Necsoiu, "Characterization of the photostructurable media from carbazol-containing copolymers and thermo-cross-linking media from vynil-containing copolymers", Proc. SPIE 4430, ROMOPTO 2000: Sixth Conference on Optics, 754, 2001.

[11] D. Lin-Vien, N. B. Colthup, W. G. Fateley, and J. G. Grasselli, The Handbook of IR and Raman Characteristic Frequencies of Organic Molecules, Academic Press, San Diego, Calif, USA, 1991.