ISSN 1027-5495. Functional Materials, 22, No.4 (2015), p. 543-546.
doi:http://dx.doi.org/10.15407/fm22.04.543

Synthesis and investigation of information media based on halogen-containing oligomers

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Received May 20, 2015

New carbazolyl containing oligomeric (CO) photosemiconductors which contain "heavy" bromine and iodine atoms were synthesized by cationic polymerization. In order to reduce the softening temperature of respective CO to the photothermoplastic holographic information recording method required level, the cationic copolymerization of corresponding bromine-containing carbazolyl monomers with butyl glycidyl ether and α-naphthyl glycidyl ether was carried out. The informational properties of the holographic recording media based on obtained oligomeric composites films for the photothermoplastic method of holograms recording were investigated.

Keywords: carbazolyl containing oligomerics, holographic recording media; photoconductivity, photothermoplastic method of holograms recording.

Катионной полимеризацией получены новые карбазолилсодержащие олигомерные (КО) фотополупроводники, содержащие тяжелые атомы брома и йода. Для снижения температуры размягчения КО до уровня, необходимого при фототермопластической записи информации, осуществлена катионная сополимеризация с бутилглицидиловым и α-нафтилглицидиловым эфирами. Исследованы информационные свойства регистрирующих сред для фототермопластического способа записи голограмм с пленками полученных олигомерных композитов.

Синтез та дослідження інформаційних середовищ на основі галогенвмісних олігомерів. *О.В.Мокринська, С.Л.Студзинський, М.Г.Чуприна.*

Катіонною полімеризацією одержано нові карбазолілвмісні олігомерні (КО) фотонапівпровідники, що містять важкі атоми брому та йоду. Для зниження температури розм'якшення КО до рівня, необхідного при фототермопластичному запису інформації, здійснено катіонну кополімеризацію з бутилгліцидиловим та α-нафтилглицидиловим етерами. Досліджено інформаційні властивості реєструючих середовищ для фототермопластичного способу запису голограм з плівками отриманих композитів.

1. Introduction

Oligomeric composites films (OCF) based on carbazolyl containing oligomers (CO) doped with organic dyes can be used in electrographic and reversible holographic recording media (HRM), solar energy photoelectric converters, electroluminescent devices [1]. The wide application of such OCF is due to the presence in the corresponding oligomeric structures of carbazolyl side substituents, which form energetic transport band of non-equilibrium holes. The OCF photoconductivity in the visible range of the spectrum is provided by additives of organic dyes, photoexcited molecules of which are capable to perform of photogeneration of the non-equilibrium charge carriers.

It is known that "heavy" or magnetic atoms in structure of the polymer chain fragments or dopant's molecules can considerably affect the OCF photoconductivity owing to their influence on the photogener-

ated charge pairs spin conversion or non-equilibrium charge carriers transfer between the polymer chain fragments.

Halogen atoms introduction into the photosemiconducting oligomers aromatic nuclei leads to their absorption region widening and increase of photosensitivity in photothermoplastic (PTP) method of information recording [2, 3].

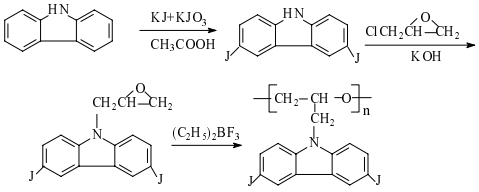
The aim of this work was to study influence of heavy atoms on the holographic properties of OCF and also the halogen-containing oligomers and cooligomers ability to the PTP holographic recording application.

2. Experimental

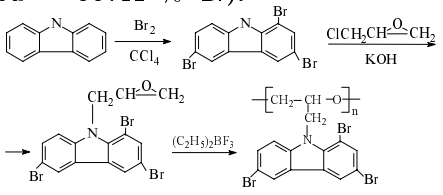
2.1 Synthesis

We obtained iodine- and bromine-containing carbazole-based oligomers. The carbazole molecules contain two reactive sites which are the most favourable for the electrophilic attack, namely, C-3- and C-6 positions. C-1 and C-8 positions of the carbazole nucleus are slightly less reactive in the electrophilic substitution reactions than C-3 or C-6. Under halogenation conditions, the substitution reaction initially occurs at 3-position and then at 6-position of carbazole ring [4]. By using cationic polymerization, we synthesized iodine-containing 3,6-diiodoglycidylcarbazole oligomer (o-di-JGC).

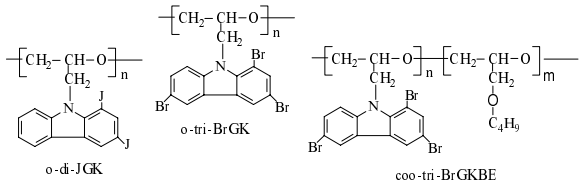
In order to obtain the monomer, method of direct iodination of carbazole (iodate/iodide method) was used [5]. Mixture of KJ and KJO_3 (iodate/iodide mixture) was used as an iodinating agent. The iodination was carried out in acetic acid medium (observed — 62.75 % J; calculated — 62.71 % J):



We also synthesized bromine-containing 1,3,6-tribromoglycidylcarbazole oligomer (*o*-tri-BrGC). In order to obtain the initial monomer, direct carbazole bromination in the carbon tetrachloride medium method was used [6] (observed — 59.37 % Br; calculated — 59.41 % Br):

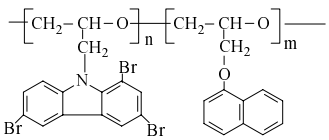


However, the halogen-containing oligomers were too high-melting substances and, as a consequence, these oligomers were unsuitable for the PTP recording of holograms (*o*-tri-BrGC with softening point of ~155°C and *o*-di-JGC with the softening point of ~175°C, respectively). In order to reduce the softening temperature of CO to the level required for PTP holographic recording successful application, we carried out the cationic copolymerization of corresponding bromine-containing monomer with butyl glycidyl ether (butyl glycidyl ether/1,3,6-tribromoglycidylcarbazole molar ratio was 11/1). As a result, cooligomer coo-tri-BrGCBE (with the softening point of 60–65°C) was formed.



Usually, plasticization of CO leads to decrease in electron-donor condensed aromatic nuclei concentration in the photosemiconductor, that causes delay in the charging potential dark decay and reduces photosensitivity.

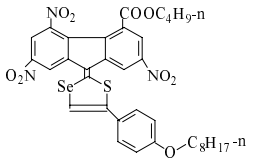
We obtained and studied the new cooligomer (coo-tri-BrGC-NGE with the softening point of 73–83°C) in which α-naphthyl glycidyl ether was used as an internal plasticizer (α-naphthyl glycidyl ether/1,3,6-tribromoglycidylcarbazole molar ratio was 1/1).



The introduction of naphthyl nuclei significantly decreases the softening temperature of bromine-containing oligomer. In this case the respective HRM are characterized by high recording quality due to the conjugated aromatic conservation systems in the chain.

2.2 Samples and experimental methods

The organic dye ICTC1 with intramolecular charge transfer was used as sensitizer of film HRM photoconductivity (3 mass %).



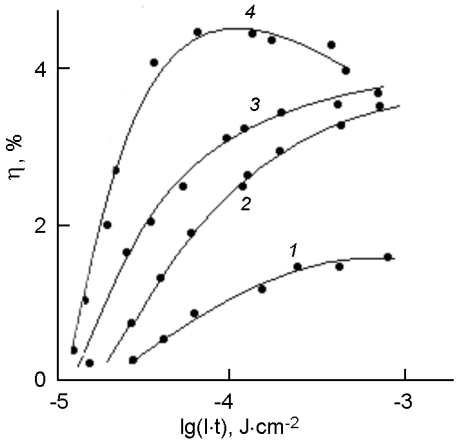


Fig. 1. Dependences of η_{max} on lg($I$$E cdott_{irr}) for HRM based on films of: *1* — o-di-JGC + 3 wt. % ICTC1, *2* — o-tri-BrGC + 3 wt. % ICTC1, *3* — coo-tri-BrGCBE + 3 wt. % ICTC1, *4* — coo-tri-BrGC-NGE + 3 wt. % ICTC1.

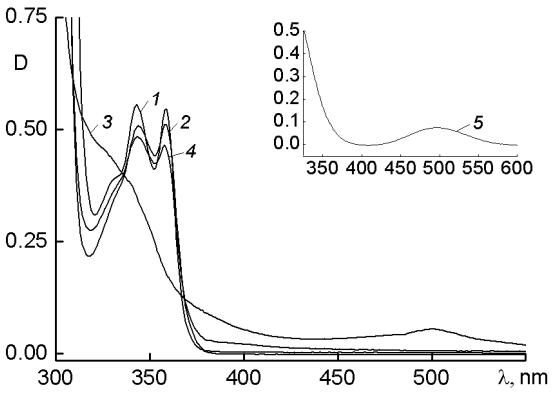


Fig. 2. Absorption spectra of oligomers solutions in toluene: *1* — non-irradiated o-di-JGC, *2* — non-irradiated o-tri-BrGC, *3* — irradiated o-di-JGC, *4* — irradiated o-tri-BrGC, *5* — iodine silution.

Such substances are characterized by sufficiently high extinction coefficient in the visible region, efficient charge carriers photogeneration ability and good plasticizing properties for their application in the OCF-based holographic recording materials (HRM) [4]. The samples for investigation were prepared as structures with free surface of the oligomer film: glass substrate — SnO_2:In_2O_3 (ITO) sublayer — OCF. To record the PTP holograms the HRM were prepared in the thin films form by casting the corresponding toluene solutions onto glass substrates covered by a transparent electroconductive ITO-sublayer with resistance of 20 Ω/sq. The oligomer/ICTC1 mass ratio of the components amounts was 97/3. Working area of the HRM film was 40×40 mm^2. Thicknesses of the HRM films were measured by MII-4 interference microscope. The OCF thickness was 1.1–1.2 μm; it was optimum for the PTP method of holograms recording. The prepared samples of the HRM films were characterized by measuring the spectral and information characteristics.

The absorption spectra of oligomers solutions were measured using "Varian Gary 50" spectrophotometer.

SVD-120 mercury lamp was used as a radiation source.

The OCF photothermoplastic characteristics measurements were carried out by using holograms of planar wavefront recording as described previously [4]. The holograms of planar wavefront were recorded on the HRM with 650 nm light from a semiconductor laser (the spatial frequency of hologram recording was ~ 500 mm^{-1}). The controlled parameter was the diffraction efficiency (η) of the recorded planar-wavefront hologram determined in −1 diffraction order, which is proportional to depth (h) of the relief on the HRM film surface after development of latent image in the HRM [4]. The value of η was measure with a photodetector connected to the input of storage oscilloscope Tektronix TDS1001B. The external triggering of the oscilloscope was formed by the leading edge of development pulse. To determine the maximum attainable value of the diffraction efficiency (η_{max}), the hologram was developed starting from the initial temperature T = 293 K to temperature above the temperature of hologram erasure and complete healing the geometric relief of the HRM film surface. The holograms were recorded at 1:1 intensity ratio of the reference to the object beam. In the course of the hologram development, the diffraction efficiency of the restored image of the hologram of planar wavefront was continuously measured, which permitted the detection of η_{max}. From the results of these measurements, dependence of η_{max} on exposure ($I \cdot t$) was determined, where I — is light intensity, and t — is time of the exposure (Fig. 1).

3. Results and discussion

It was established that, as expected, the higher holographic sensitivity was observed for coo-tri-BrGC-NGE-based recording materials (Fig. 1). This fact is also connected with greater plasticity of these films as

compared to o-tri-BrGC and *o*-di-JGC-based films due to the presence of flexible butyl glycidyl or α-naphthyl glycidyl ether fragments in the structure of respective oligomer molecules. It was found that the holographic sensitivity of the HRM decreased at the transition from *o*-tri-BrGC to o-di-JGC. Such decrease is not connected with the rheological properties of the HRM films and is due to their electroconducting and photoconducting properties change. Because of concentration of carbazolyl fragments which provide the non-equilibrium charge carriers transport in the *o*-tri-BrGC and *o*-di-JGC films is the same, the electro- and photoconducting properties change is unambiguously connected with the halogen atom nature. The holographic sensitivity decreasing is explained by photochemical transformations, namely photoinduced iodine atom elimination that leads to the irreversible changes in the composition properties. The processes of photooxidation are well-known for carbazolyl-containing polymers [8, 9]. Irradiation of the polymers solutions or films leads to broadening of the spectrum structure in the polymer intrinsic absorption region due to the photooxides formation. Figure 2 presents the optical absorption spectra of non-irradiated (curves *1* and *2*) and irradiated (curves *3* and *4*) *o*-di-JGC and *o*-tri-BrGC solutions in toluene. The photochemical elimination of iodine atoms was carried out under oligimers solutions irradiation during 30 minutes. The irradiation of *o*-di-JGC solution in the JGC-groups intrinsic absorption region leads to broadening of the respective absorption spectra structure. Simultaneously, the new band with the maximum at 500 nm appears in the visible range of the spectrum. The long-wave absorption with the maximum at $\lambda \sim 500$ nm is also observed in the spectra of the non-irradiated *o*-di-JGC doped with molecular iodine additives (curve *5*).

4. Conclusions

The results of our investigations show that the halogen-containing cooligomers can be efficiently used as the HRM basic components for the PTP method of hologram recording. For development of the new cooligomer-based photothermoplastic materials the comonomer-plasticizer nature effect on the HRM properties should be considered. The best information characteristics were found for coo-tri-BrGC-NGE-based HRM. The iodine-containing oligomers application is undesirable due to the iodine atoms photoelimination which leads to the irreversible changes in the composition properties.

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