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Holographic Recording Media Based on Electron Donor Oligomers

Davidenko N.A.[a], Davidenko I.I.[a], Mokrinskaya E.V.[a], Chuprina N.G.[a], Getmanchuk Yu.P.[a], Kostenko L.I.[b], Kunitskaya L.R.[a], Pavlov V.A.[a], Studzinsky S.L.[a], Tonkopieva L.S.[a]

[a] *Kiev Taras Shevchenko National University*

[b] *L.M.Litvinenko Institute of Physics Organic Chemistryand Coal Fuel Chemistry NAS of Ukraine*

ndav@univ.kiev.ua

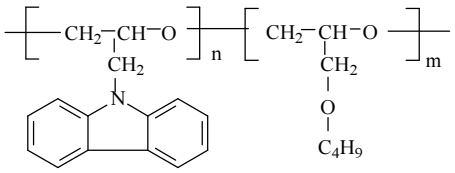
For optical holographic recording by photothermoplastic technique reversible holographic media based on oligomers with hole type of conductivity are used. New carbazole containing radial tetrasubstituted silanes and germanes are described in the present work.

Introduction

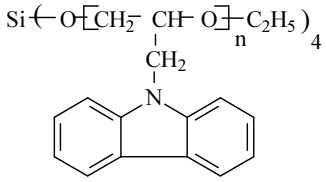
Organic oligomers with electron donor substitutes and compositions based on them (OC) are widely used in electrographic and holographic information recording media [1]. Holographic recording media (HRM) for photothermoplastic (PTP) holographic technique must possess necessary rheological properties, high electrical resistance in darkness, high photoconductivity. However, presently influence of oligomers structure on above mentioned properties is not completely investigated. The aim of the present work is comparative analyses of information properties of HRM based on oligomers with linear and radial molecule structures.

Experimental part

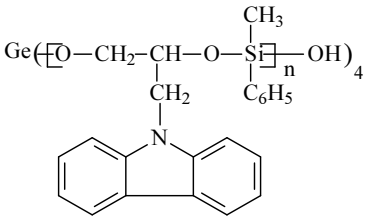
Cooligomer of oligoglycidylcarbazole with butyl glycidyl ether (GCBE) of linear structure and radial structures tetrasubstituted silane (RTS) and tetrasubstituted germane (RTG) were chosen as the base of OC:



GCBE

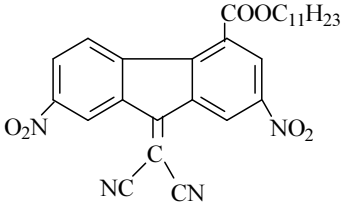


RTS



RTG

Acceptor UDFA was used as the sensitizer of OC photosensitivity.



Intermolecular charge transfer complexes

(CT-complexes) appear while contacted acceptor molecules with carbazole fragments of oligomers in liquid solutions and in solid films. These complexes are the centers of light absorption and photogeneration of charge carriers. For holographic recording by PTP technique HRM was prepared as thin OC film deposited onto transparent electroconducting layer SnO_2 : In_2O_3. Ratio between components was following: oligomer – 97 mas.%, UDFA – 3 mas.%. The thickness (L) of the OC films was 1.1 – 1.2 μm. Measurements of photothermoplastic characteristics of OC were done using known technique of registration of holograms of flat wave front [2]. Spatial frequency was 500 mm^{-1}, light wavelength of the semiconductor laser was 650 nm. Diffraction efficiency (η) of the reconstructed image of the hologram of flat wave front in -1 diffraction order was measured continuously during development process. "Memory" effect on preliminary exposure with light before charge of OC surface in crown discharge was observed in the investigated HRM. Therefore, investigations of η dependency on time (t_1) of exposure before start of charge cycle and development of latent hologram image as well as investigations of η dependency after long time exposure of HRM on time (t_2) of delay before start of charge cycle and development of the latent image. Additional investigations were carried out for ascertainment of the nature of "memory" effect. For these investigations the samples were prepared as the sandwich-structures glass substrate - SnO_2:In_2O_3 – OC film – Ag. The concentration (Q) of non-equilibrium electric charges appearing in OC film volume after its illumination with light without application of external electric field was measured in the samples. Technique of Q determination as well as Q dependency on time (t_1) of illumination and on time (t_2) after illumination was ceased is explained by diagrams on Fig.1. At the beginning, in darkness electric voltage (U) was applied to the sample and kinetics of conductivity current (i_1) was registered using memory oscilloscope.

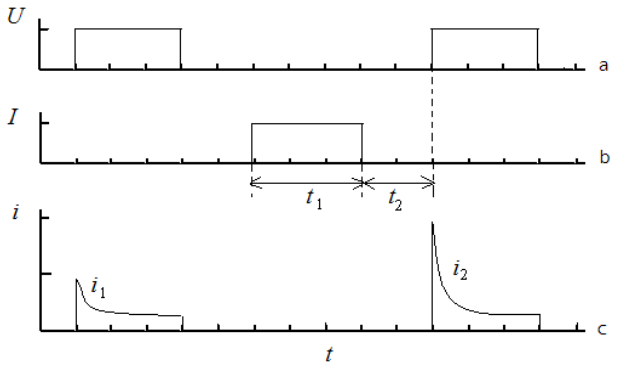


Fig.1. Diagrams of application of electric voltage (*a*), illumination with light (*b*) and measurement of conductivity current (*c*).

Next, electric contacts were connected and the sample was illuminated with light during time interval t_1, then light was switched off and after time interval t_2 electric contacts were disconnected, electric voltage U was applied to the sample and current i_2 kinetics was registered. From these measurements kinetic of Q accumulation and relaxation was determined using expression $Q = \int(i_2 - i_1)dt/eSL$, where e is electron charge, S is the square of the sample.

Results and discussion

It was ascertained that the value η increases at 1.5 and 2 times when in HRM GCBE is substituted by RTS and RTG respectively. Dependencies η(*t*) after start of development of latent image of the hologram are shown in Fig.2. It easily can be seen from Fig.2 that maximal value η is reached for less *t* in HRM with OC based on RTG and RTS as compare to HRM based on GCBE. This fact is evidence that formation of geometric relief of the surface of OC film with RTG and RTS during the process of hologram development happens at less temperatures as compared to GCBE.

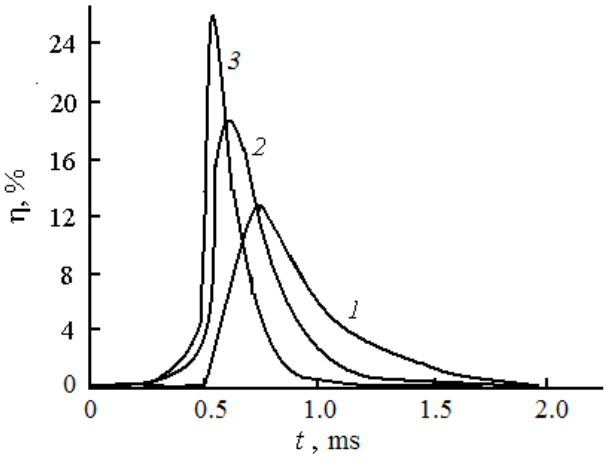


Fig.2. Kinetics of η growth and relaxation after start of development of hologram of flat wave front in HRM with OC based on GCBE (*1*), RTS (*2*) and RTG (*3*).

Dependencies of η on time intervals t_1 and t_2 measured in the samples HRM with OC based on RTG (curves *1*, *3*) and RTS (curves *2*, *4*) are shown in Fig.3. Saturation of the "memory" effect, i.e. reaching of some stationary value in the dependency η(t_1), occurs quicker than its relaxation. Besides, kinetic curves of the dependencies η(t_1) and η(t_2) are symbatic to the dependencies $Q(t_1)$ and $Q(t_2)$ (curves *5*, *6* in Fig.3). In the samples of HRM with OC based on GCBE described "memory" effect was not observed as well as accumulation *Q*.

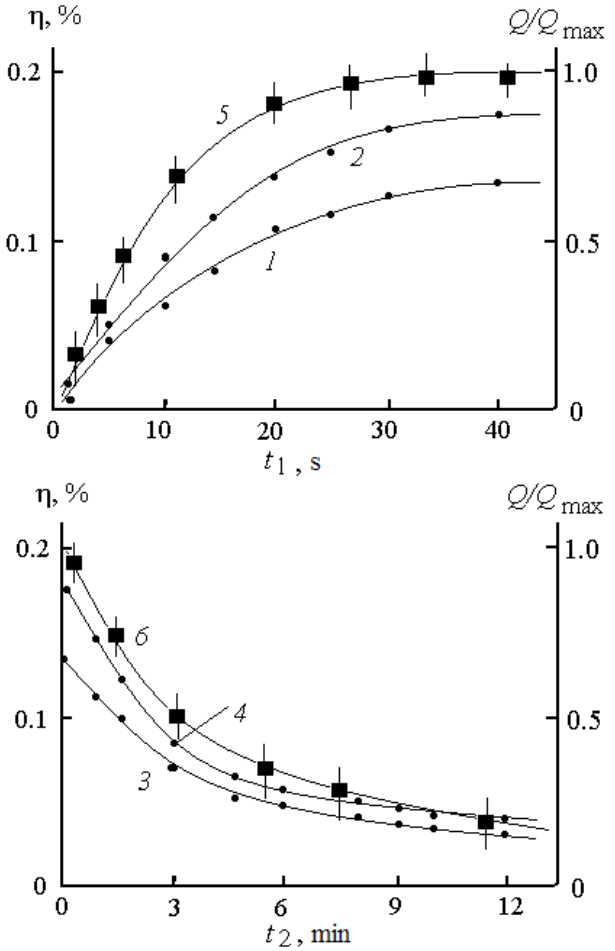


Fig.3. Dependencies η(t_1) (1, 2) and η(t_2) (3, 4) in HRM with OC based on RTS (1, 3) and RTG (2, 4) and dependencies $Q/Q_{max}(t_1)$ (5) and $Q/Q_{max}(t_2)$ (6) in the samples SnO_2:In_2O_3 – OK – Ag with OC based on RTS and RTG.

It is well-known that radial polymers possess unusual low viscosity even at very high molecular mass. Radial polymers with hard chains always more plastic as compare to their linear analogs. Similar properties are characteristic for oligomers as well. The film of linear cooligomers begins slowly deform within

wide temperature range 35 – 80 ^{o}C and next quickly flows (curve 1 on Fig.2). The film of radial oligomer abruptly transits into the liquid state at the temperature ≥ 60 ^{o}C (curves 2, 3 on Fig.2). This fact increases sensitivity and η when radial oligomer is used. Accumulation of volume electric charge can involve growth of sensitivity as well. Formation of volume charge in the OC films under illumination with light can be attributed at least to two reasons.

Firstly, if $|I_{gc}|>|I_{gd}|$ (I_{gc} is the ionization potential of a photogeneration centre, I_{gd} is the ionization potential of a donor fragment) then after photoexcitation of the photogeneration centre and appearance of hole at carbazole fragment energetic barrier exists for return electronic transition. Value of this barrier is proportional to the energies difference $|I_{gc}|-|I_{gd}|$. Such effect before was observed [2] when dyes were used as the sensitizers for which $|I_{gc}|>|I_{gd}|$. In our case CT-complexes are the photogeneration centers. These centers consist of carbazole fragments identical ones through which transport of non-equilibrium holes occurs. Earlier [3] it was shown that barrier for holes recombination during annihilation of charge pairs is small and life time of the charge pairs is ~ 10^{-7} s.

The second reason can be attributed to energetic traps which capture photogenerated charges and hold them during long time. Physical dimers (excimers) of sandwich type of carbazole fragments can serve as these traps. For them |Igd| is at ~ 0.3 less than for carbazolyl fragments which are not included in dimers [4]. Dimers are formed by end carbazolyl groups due to their more favorable steric position for interaction with neighboring fragments. In the molecules of radial oligomers RTG and RTS the number of end carbazolyl fragments in 2 times more as compare to linear GCBE. Therefore, probability of dimers formation also larger in the films of radial oligomers. This fact explains observed “memory” effect in HRM and formation of long-lived photoinduced volume electric charge in OC based on RTG, RTS and its absence (or less value) in OC based on GCBE.

Conclusions

Optimal properties of OC for HRM depend not only on ratio between donor ionization potential acceptor affinity to electron, but olso on the shape of their macromolecules. Plastic and rheological properties of the films are better for radial oligomers than for oligomers with linear structure. Under growth of the number of end carbazolyl fragments in oligomer macromolecules effect of holographic “memory” was observed. It can be explained by accumulation of volume charge in energetic traps which ones are formed by dimers of end carbazolyl groups. Possibility of formation of long-lived photoinduced electric charge in OC is of interest for development of new materials for optoelectronics and molecular electronics.

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