Synthesis of Some Carbazole Monomers Designed to Obtain Materials with Photosensitive Properties

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This paper presents the synthesis of some acrylic monomers with pendant carbazole groups. They were copolymerized with N-octyl methacrylate to obtain organic photosensitive materials used in the production of holograms with electrophotographic methods.

Keywords: N-vinylcarbazole, N (2-hydroxymethyl carbazole), N-carbazolyl methlacrylate, octylmethacrylate.

The discovering the photoconductive properties of poly (*N*-vinyl carbazole) (PVK) led to intense research of its use in various applications of great interest such as: optical data storage [1, 2], electroluminescent materials, fluorescent and phosphorescent dyes [3-5], getting the conductive films for optoelectronic applications [4-6], electrophotographic applications, photocopying and holography recording [1, 8-11].

Polyvinyl carbazole exhibits the electro-donor effect and being coupled with an electron acceptor agent such as trinitro- or tetranitrofluorenone becomes a material with high level of photoconductivity, widely used in applications of electrophotographic and holographic imaging in the visible range of spectra [8,12-14]. Secure transmission and storage of data including optical and holographic recording represents a particular importance in protecting of documents and fighting against counterfeit labeling of industrial products and food.

The use of block PVK in such applications is very difficult due to the rigidity of the polymer chain, instead it offers a high degree of friability and an increased value of glass transition temperature *(T_g)* (about 200 °C). These properties represent a significant impediment to use of PVK in applications such as mentioned above. The extremely high rigidity is caused by the large volume of pendant carbazole cycles to the polyvinyl chain [12, 15]. To reduce the rigidity of the polyvinyl chain, the distance of contact between these carbazole cycles should be increased. Thus, by appropriate reactions at the vinylic double bond, the acrylic monomers may be attached, that by polymerization lead to synthesis of some polyacrylates with carbazole nucleus spaced from polymer chain [1,16,17], as exemplified in scheme 1.

In order to improve the mechanical properties it should be increased the mobility of carbazole cycles and their spacing can be achieved by copolymerization, e.g. of N-carbazolyl ethyl methacrylate or N-carbazolyl ethoxy-ethyl methacrylate with different alkyl-methacrylates: CH_2=C(CH_3)-COOR, where R = butyl (C_4H_9), octyl (C_8H_{17}), decyl ($C_{12}H_{25}$), cetyl ($C_{16}H_{33}$).

Increasing the distance between the carbazole cycles and polyvinyl chain and copolymerization with acrylic monomers leads to decrease of carbazole nucleus weight in material, without significantly effect the level of photoconductivity required in electrophotography applications [18].

Experimental part

The following compounds of high purity: carbazole, polyformaldehydes (paraform), methacryloyl chloride of Aldrich origin, were used without other restrictions.

Octyl methacrylate was synthesized by the reaction of n-octanol with methacryloyl chloride.

Toluen, clorbenzen, other solvents, were purification by distillation.

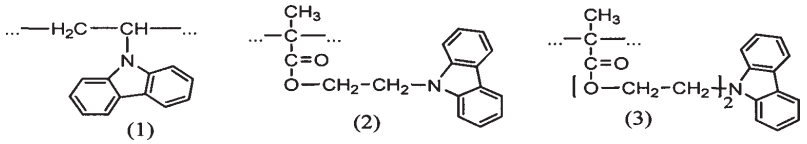
AIBN from Aldrich was used as initiator.

- Elemental analysis was performed on a Vario EL analyzer;
- melting point was determined using an Optronic Kruss KSP-1N apparatus;
- structure of the reaction products was determined by the chromatography on thin layer of silica gel and by the high-performance liquid chromatography (HPLC). The HPLC-1200 device of Agilent Technologies was used.

One way to improve the quality of obtained holograms based on carbazole copolymers is the increasing of photosensitivity degree of the photoconductor material. For this purpose, new monomers with the substituents (Br, or NO_2) have been synthesized in the 3 position of the carbazole nucleus, according to the reaction presented in scheme 2.

It was found that introduction of the bromine in the 3 position of carbazole cycle increases the polymers' photosensitivity by about 7%.

In a first stage the synthesis of N-(2-hydroxymethyl) carbazole was carried out by treatment of carbazole with ethylene oxide, thus yielding the introduction of a carbon



(1) (2) (3)

Scheme 1. Polymethacrylates with pendant carbazole groups.(1)poly (N-vinylcarbazole); (2) poly (N-carbazolyl ethyl methacrylate); (3) poly (N-carbazolyl ethoxy-ethyl methacrylate)

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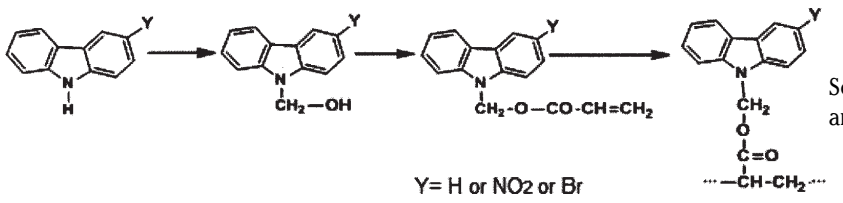
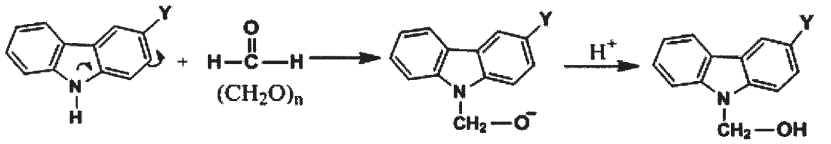


Scheme 2. Scheme of obtaining the acrylic monomers and the polymers with distant carbazole nucleus from the polyvinyl chain.



Scheme 3. Scheme of obtaining N-(2-hydroxymethyl) carbazole

atom linked to the nitrogen carbazole atom [16]. The difficult conditions of reaction, its low rate and reduced yield, led to the abandonment of this process. Thereafter, it is only used for comparative analysis.

Obtaining of the N-(2-hydroxymethyl) carbazole by carbazole reaction with formaldehyde obtained by cleavage of polyformaldehydes (paraform) by heating is more advantageous in terms of cost-effectiveness. Synthesis was carried out in ethanol solution at 60 °C for 1.5 hours. The yield of the synthesis is high (90-95%) and it does not produce secondary reactions.

Considering these results, also the synthesis of N-(2-hydroxymethyl) carbazole derivatives substituted in the 3 position by Br and NO_2 was performed by using of the paraform according to the scheme showed in scheme 3.

As hydroxymethylation is a nucleophilic reaction, in the first stage the carbazole derivatives (Br, NO_2) were treated with potassium hydroxide, thus facilitating the addition of formaldehyde from the paraformic substrate to the carbazole nitrogen atom, according to the scheme 3.

N-(2-hydroxymethyl) carbazole and its derivatives of 3-nitro and 3-bromo hydroxyl carbazole were subjected to the acylation reaction with acryloyl chloride in the presence of hydroquinone as an oxidizing agent giving thus the N-carbazolyl methylacrylate (CMA), 3-nitro and 3-bromo N-carbazolyl acrylates. These monomers were purified by recrystallization from benzene-hexane solution.

It should be noted the high efficiency of the synthesis of these monomers: 92% for CMA, 86% for the brominated derivative and 82% for the carbazole nitroderivative.

Results and discussions

Reactions of carbazole hydroxymethylation and nitration and bromination of N (2-hydroxymethyl) carbazole were monitored by thin layer chromatography on silica gel. The structure of components was confirmed by elemental analysis and by high performance liquid chromatography (HPLC). Through IR spectroscopy have been identified components at the following wavelengths: 3330 cm^{-1} (O-H); 3048 cm^{-1}, 2977 cm-1 (C-H); 1894 cm^{-1} (aromatic cycle); 1699 cm^{-1}, 1627 cm^{-1}, 1598 cm^{-1} (aromatic C-H); 1451 cm^{-1} (C-N); 778 cm^{-1}, 748 cm^{-1}, 722 cm^{-1} (aromatic CH). N-carbazolyl methylacrylate has the following characteristic wavelengths: 3046 cm^{-1}, 2976 cm^{-1} (νC-H), 1728 cm^{-1} (ester νC = O), 1632 cm^{-1}, 1596 cm^{-1} (aromatic νC = C), 949 cm^{-1}, 915 cm^{-1} (alkenes νC = C), 782 cm^{-1}, 753 cm^{-1}, 721 cm^{-1} (aromatic νC-H).

In the method of synthesis of N-(2-hydroxymethyl) carbazole derivatives substituted in the 3 position, when the carbazole nitration or bromination was developed in the first step, it was found that these substituents inhibit the formation of carbazole anions. This phenomenon is due to the electro acceptor effect of these substituents and it favors the subsequent reaction of methylation with paraform, significantly decreased the time of hydroxymethylation reaction up to 5 hours for nitroderivative and up to 3 hours for the brominated compound.

In the first step of synthesis of N-(2-hydroxymethyl) carbazole also was found that the presence of hydroxymethyl groups in the 3 position increases the electron density of the cycle, thereby enhancing its degree of aromatization. Accordingly, reducing the electro-donor effect of carbazole cycle leads to increase in speed and efficiency of electrophilic substitution reaction of nitration and bromination in the 3 position.

It should be noted that increasing of the carbazole compound aromatization unfavors production of the reaction also in the 6 position, thereby increasing the yield of the monosubstutuited N-(2-hydroxymethyl) carbazole synthesis.

Analyzing the two variants of synthesis we believe that the process of hydroxymethylation followed by nitration or bromination is the proper way to prepare the derivatives of the N-(2-hydroxymethyl) carbazole substituted in the 3 position.

Final purification of the synthesized compounds has been achieved in most cases by means of the chromatographic method on silica gel column.

By acylation of N-(2-hydroxymethyl) carbazole with acryloyl chloride was obtained N- carbazoil methylacrylate (CMA) with high efficiency, as previously mentioned. This monomer has a pendant carbazole cycle removed from vinyl group, so that through polymerization of polymer chains was obtained a degree of freedom increased compared to that of polyvinyl carbazole. For even greater flexibility of the polymer chain the CMA was copolymerized with octyl methacrylate (OMA) in ratios 40:60, 50:50 and 60:40 mol%.

The copolymerization was carried out by free radical mechanism in toluene at 80 °C, for 6 hours, using 2, 2'-azo-bis-isobutyronitrile (AIBN) as initiator. The CMA-OMA copolymers have been separated from the toluene synthesis solution by precipitation with methanol in excess, filtered and dried under vacuum in the dark. Inherent viscosity (η) and glass transition temperature (T_g) are shown in the following table:

Table 1
CHARACTERISTICS OF THE SYNTHESIZED COPOLYMERS

Nr.	Copolymers (mol %)	[η]	T_g, °C
1	CMA:OMA (40:60)	0.25	75-76
2	CMA:OMA (50:50)	0.23	78-79
3	CMA:OMA (60:40)	0.23	82-83

From the data presented in table, it can be seen that these carbazole copolymers have greatly improved properties of thermal machinability compared to PVK.

In order to test the photosensitive properties of copolymers were obtained films from 10% solution of chlorobenzene that were deposited on a transparent glass substrate coated with a thin layer of SnO_2. After evaporation of the solvent in air, advanced desolvation was performed in a vacuum oven at 40 °C.

Tests have established the real photosensitivity in range of 400-700 nm – the characteristic interval for carbazole photopolymers used for recording holograms by electrophotographic method.

Conclusions

Obtaining the carbazole monomers with nucleus removed from polymerizable vinyl group was carried out in two stages of synthesis starting from carbazole.

In the first stage, was realized hydroxymethylation of carbazole using paraform, the process being easier to manage and free of danger compared to that using ethylene oxide process. Additionally, this method has the advantage of obtaining the N-(2-hydroxymethyl) carbazole with high efficiency and without of reaction by products.

In the second stage, the acylation reaction of N-(2-hydroxymethyl) carbazole with acryloyl chloride was carried out. As a result, the N-carbazole methacrylate monomer at a high reaction yield of 92% was obtained.

Synthesis study of the of 3-nitro and 3-bromo derivatives of N-(2-hydroxymethyl) carbazole determined that producing them by nitration and bromination of hydroxymethyl compound is most advantageous method of preparation due to the increased speed of reaction and the significant reduction of reactants attack in the 6 position of the carbazole nucleus.

The acylation of nitro and bromine hydroxymethyl carbazole derivatives with acryloyl chloride is carried out with an increased efficiency of 86% for 3-nitro-N-carbazolyl methacrylate and 82% for 3-bromo-N-carbazolyl methacrylate.

Copolymers of such carbazole monomers with octyl methacrylate demonstrate photosensitivity in range 400-700 nm and possess good thermoprocessibility. These properties of copolymers permit to recommend them as good materials for recording holograms via electro-photographic methods.

In conclusion, due to the accessibility of raw materials, facile process of synthesis and high yield of preparation, we believe that synthesis of carbazole monomer is profitable both in economic terms and in its use for obtaining of copolymers with holographic applications.

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