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Photoconductive organic materials based on *N*-vinylcarbazole copolymers with higher alkenes as recording media in photonics

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ABSTRACT

With the purpose to obtain novel photoconductive organic materials with improved complex of physical–mechanical properties and high sensitivity value, the possibility of *N*-vinylcarbazole copolymerization with higher alkenes was studied.

The deposited films were 1.0–2.0 pm thin after drying in vacuum. The photosensitivity of the copolymer films is one order of magnitude greater than other carbazole containing copolymers. The investigation of spectral sensitivity was realized. Photosensitivity reaches its maximal value in 400–800 nm wave band.

A photothermoplastic information registration medium was developed using synthesized copolymers. On the prepared photothermoplastic film, were recorded diffraction gratings with diffractional efficiency of 8–10% and resolution of 1000 mm^{-1}, using electrophotographic method. Photographical sensitivity of obtained films allows real time (1–3 s) photographical and holographic image recording.

1. Introduction

Charge- (hole or electron) transport polymeric materials have been widely used in many fields, including electrophotography, organic electroluminescent devices, and others. They also play an important role in electrophotoconductive materials' elaboration, which attract much interest because of the potential application in holographic optical data storage and real time imaging process. Carbazole containing polymers are also well known for their photorefractive properties. Carbazole containing polymers can be used in production of photothermoplastic materials only in case when they correspond to certain requirements: they must be transparent; they must manifest adhesion for support; and they should possess certain thermomechanic and deformational characteristics [1–4].

Poly(*N*-vinylcarbazole) (PVC) is an interesting polymer due to its electric and photoconductive properties. However, it has a high glass transition temperature (T_g > 450 °C), which makes it necessary to use high-processing temperatures. The copolymerization of *N*-vinylcarbazole (VC) with comonomers of lower T_g could lead to materials retaining the properties of PVC with easier processibility. Copolymerization is a common way for controlling T_g, and several theories have been proposed which relate this parameter with the copolymer composition [3–5].

With the purpose to obtain carbazole containing copolymers with improved complex of physical–mechanical properties, the possibility of *N*-vinylcarbazole copolymerization with higher alkenes – octene-1 (OC-1) and hexadecene-1 (HD-1) was studied.

2. Experimental

2.1. N-Vinylcarbazole copolymers' synthesis

The synthesis of *N*-vinylcarbazole copolymers, containing 40–100 mol% *N*-vinylcarbazole, was realized using free radical polymerization method in the presence of 2 mol% of initiator (azobisisobutyronitrile), in toluene, in inert gas atmosphere and in sealed ampoules. Polymerization lasted 6–8 h at 80 °C. All copolymers were purified by double precipitation into methanol. Obtained copolymers were vacuum dried at 40 °C till constant mass. Thermo-mechanical parameters and characteristic viscosity of synthesized copolymers were determined using Hepler's consistometer. The composition of copolymers was obtained from their nitrogen content determined by elemental analysis. Though the variation of nitrogen (%) is not large with composition, this method was con-

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Table 1
Physical–chemical properties of synthesized copolymers of different compositions.

Composition of monomer mixture* (mol%)			Polymerization time (h)	Solvent	Conversion (%)	Temperature (°C)		Copolymer composition (mol%)		
VC	OC-1	HD-1				Glass transition	Flow point	VC	OC-1	HD-1
100	–	–	12	Toluen	94.5	211	~300	100	–	–
60	40	molar	8	Toluen	78.4	109–110	136–139	77.5	22.5	–
50	50	–	6	Toluen/THF	75.6	102–105	135–137	65.4	34.6	–
60	–	40	6	Toluen	71.8	92–94	120–122	79.7	–	20.3
50	–	50	6	Toluen/THF	69.6	84–85	>125	69.9	–	30.1

Polymerizations were realized at 80 °C (toluene solutions) and 70 °C (THF solutions).
* Initiator concentration (AiBN) – 2 mol%.

sidered adequate for our purposes. The composition and other characteristics of synthesized copolymers are presented in Table 1.

2.2. Copolymers' spectral investigations

The structure of synthesized copolymers was investigated using IR and ^{1}H NMR spectroscopy.

IR absorption spectrum of polyvinylcarbazole was compared with IR spectra of *N*-vinylcarbazole–octene-1 (VC:OC-1 molar ratio 50:50) and *N*-vinylcarbazole–hexadecene-1 (VC:HD-1 molar ratio 50:50) copolymers. Absorption band gain between 3150 and 2800 cm^{-1} demonstrates the fact that octene and hexadecene entered copolymerization reaction.

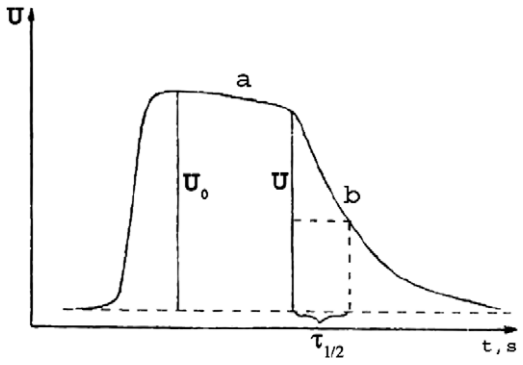

Fig. 1. Kinetic of surface potential evolution after electrical corona discharge was applied.

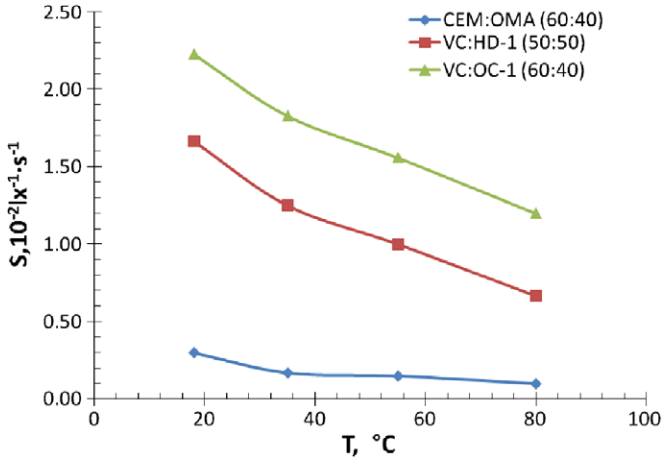

Fig. 2. The temperature dependence of electrophotosensibility of photoconductive films deposited from copolymers with certain molar ratio of components.

The copolymerization reaction between *N*-vinylcarbazole and hexadecene-1 was proved using ^{1}H NMR spectroscopy. The presence of hexadecene units in copolymers structure is confirmed by the apparition of significant signal at 1.27 ppm specific to multiple methylenic groups.

2.3. Film deposition

Photoconductive thin films were deposited on flexible metallized polyethyleneterephthalate support from toluene solutions of copolymers. 10 mass% copolymers' solutions sensitized with

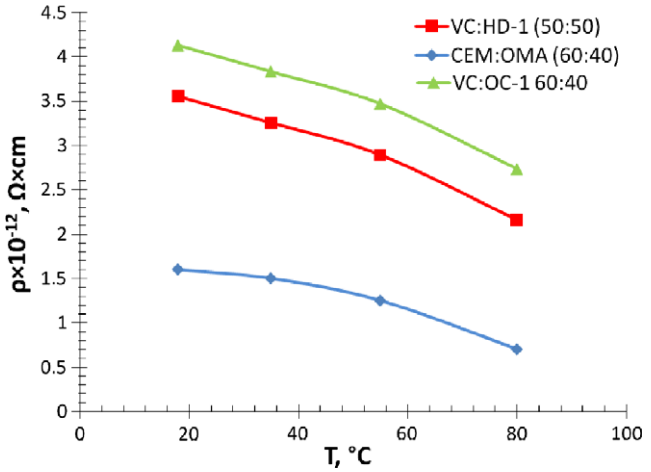

Fig. 3. The temperature dependence of specific resistance of photoconductive films deposited from copolymers with certain molar ratio of components.

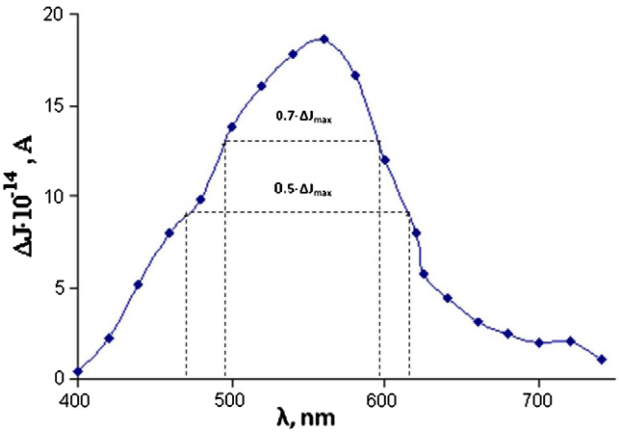

Fig. 4. The spectral dependence of photoconductivity for VC:HD-1 (50:50) film.