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# New modified epoxy resins for nonlinear optics

## RAPID COMMUNICATION

**Summary** — A new epoxy resins modified with azo-carbazole chromophores were obtained. The nonlinear optical properties of these new polymers were investigated.

**Keywords**: carbazole, azo-chromophores, epoxy resins, nonlinear optics.

NOWE MODYFIKOWANE ŻYWICE EPOKSYDOWE DO ZASTOSOWAŃ W OPTYCE NIELINIOWEJ

**Streszczenie** — Otrzymano nowe żywice epoksydowe modyfikowane za pomocą chromoforów azokarbazolowych. Zbadano właściwości nieliniowo optyczne otrzymanych materiałów metodą SHG (*second harmonic generation*). Stwierdzono, że otrzymane kompozyty wykazują stosunkowo duże wartości współczynnika polaryzowalności nieliniowej $\chi^{(2)}$. Zaobserwowano również, że produkty te pod wpływem silnej wiązki światła wykazują efekt nanostrukturyzacji. Otrzymana dzięki temu siatka dyfrakcyjna może służyć do zapisu informacji.

**Słowa kluczowe**: karbazol, chromofory azowe, żywice epoksydowe, optyka nieliniowa.

Polymers are most promising materials for practical applications in the field of optoelectronics and nonlinear optics (NLO). These polymers are typically fashioned as guest-host, main chain, or crosslinked systems. Special attention has been paid to the azo-aromatic polymers because of their potential uses in various optical applications, *i.e.* nonlinear optics, optical information storage, and optical switching [1—3]. Azo-dye-containing organic and polymeric materials exhibit reversible birefringence and linear dichroism which is consequence of reversible *trans-cis* photoisomerization with respect to N=N double bond of azobenzene group. The structural and dipolar properties of azo units and its content in the sample are factors that play important roles during the orientation processes [4].

Epoxy-based polymeric systems, such as those based on bisphenol A, have been utilized extensively in the development of second-order materials owing to the ease of processing and low optical losses in this class of polymers [5—8].

The epoxy derivatives of azo-carbazole chromophores cause a special interest among the carbazolil derivatives because of presence of epoxy functional group in carbazole moiety. This group can react with common curing agents used for epoxy resins. For this reason it is possible to obtain homogenic compositions of azo-carbazole chromophores, diglicydyl ether of bisphenol A and curing agent.

## EXPERIMENTAL

### Materials

The following materials were used in this work:

— carbazole (Fluka Chemie A.G., purity 98 %),

— 2-chloro-4-nitroaniline (Aldrich, purity 97 %),

— tetrabutylammonium bromide (TBAB, Aldrich, purity 99 %),

— low-molecular epoxy resin *i.e.* glicydyl ether of bisphenol A (Araldite PY 3483, Ciba),

— isoforenodiamine (Ciba) used without previous purification.

### Synthesis

#### Preparation of 3-(2′-chloro-4′-nitrophenylazo)carbazole

The bifunctional chromophores were obtained according to equation (1) by the coupling reaction of carbazole [Formula (I) in eq. (1)] with diazonium salt of 2-chloro-4-nitroaniline [Formula (II) in eq. (1)]. This reaction was carried out in biphasic system consisting of water and *n*-butanol.

First concentrated hydrochloric acid (18 mL) was added into suspension of 2-chloro-4-nitroaniline (5.3 g, 0.0264 mole) in water (57 mL) and stirred until the amine dissolved. Then the suspension was cooled in an ice bath

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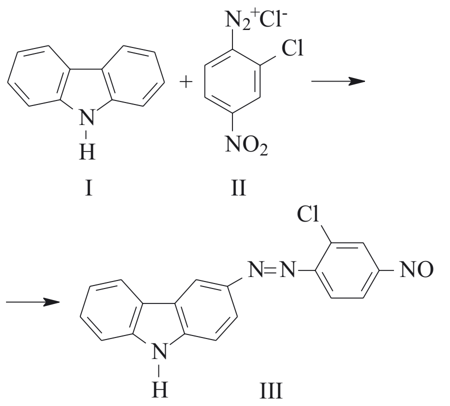

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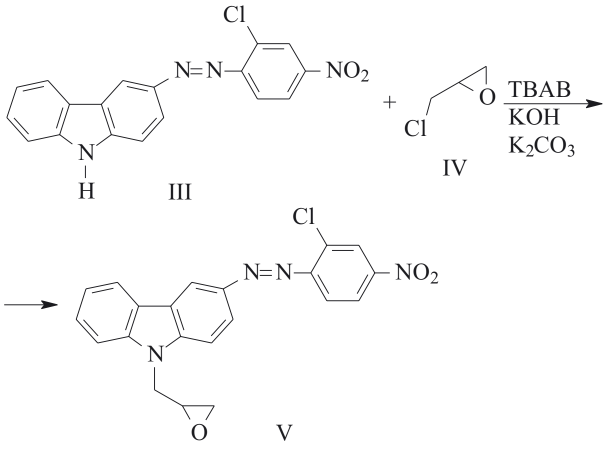


(2)

until the reaction mixture temperature dropped to about 0 °C. Next a solution containing sodium nitrite (2.5 g, 0.0264 mole) in water (13 mL) was added slowly to the suspension, and it was allowed to stir in the ice bath for 30 min. After the formation of diazo derivative, the solution was filtered and added slowly to a suspension of carbazole (4.0 g, 0.024 mole) in *n*-butanol (40 mL) at 40 °C. The mixture was stirred overnight at 40 °C. The dye 3-(2-chloro-4-nitrophenylazo)carbazole [Formula (III) in eq. (1)], which precipitated from the solution was then filtered off and well rinsed on the filter paper with 16 mL of *n*-butanol and then with water, and dried. Finally, 3-(2′-chloro-4′-nitrophenylazo)carbazole in the form of an orange powder was obtained with 78 % yield.

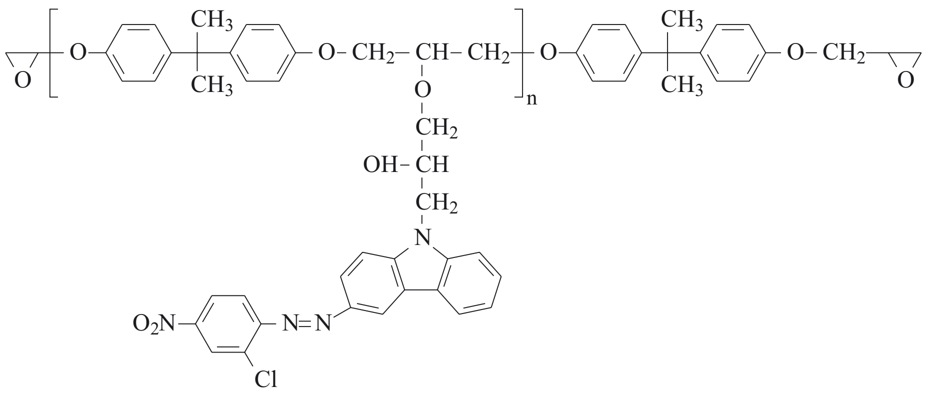
#### Preparation of 3-(2′-chloro-4′-nitrophenylazo)-9-(2,3-epoxypropyl)carbazole

3-(2′-Chloro-4′-nitrophenylazo)carbazole was converted according to equation (2) to epoxy derivative in the reaction with epichlorohydrine [Formula (IV) in eq. (2)] in acetone in the presence of potassium hydroxide, potassium carbonate and tetrabutylammonium bromide (TBAB) as a catalyst.

Acetone (100 mL) was added into the suspension of 3-(2′-chloro-4′-nitrophenylazo)carbazole (5.7g, 0.0158 mol) in epichlorohydrine (7.4 g, 0.0095 mol). The solution was heated up to 40 °C and potassium hydroxide (0.9 g, 0.016 mol), potassium carbonate (16 g) and tetrabutylammonium bromide (TBAB) (0.5 g, 0.0095 mol) was added. The mixture was stirred vigorously at 40 °C for 8 h. The dye, which was precipitated, was filtered off, and was well rinsed, first with acetone, and then with water, and dried. 3-(2′-Chloro-4′-nitrophenylazo)-9-(2,3-epoxypropyl)carbazole [Formula (V) in eq. (2)] in the form of a red powder was obtained with 70 % yield.

### Modification of epoxy resins

Obtained epoxy derivative of diazo-carbazole chromophore was used to modification of diglicydyl ether of bisphenol A epoxy resins into new polymeric materials for nonlinear optics. The polymer was prepared by mixing together the epoxy resin, azo-carbazole chromophore and the setting agent (isoforenodiamine) in proportions 85:5:10 by weight. The final product have the chromophore segments chemically bounded in the reticulated network of epoxy resin [Formula (VI)].



(VI)

### Method of testing

Products were analysed by IR spectroscopy (KBr technique, range from 400 $cm^{-1}$ to 4000 $cm^{-1}$) using BIO RAD FTS 165 and by $^1$H NMR (acetone as a solvent) using Tesla 487C spectrometer.

The modified epoxy resin was studied in order to find its non-linear optical properties. First, thin films (*ca.*

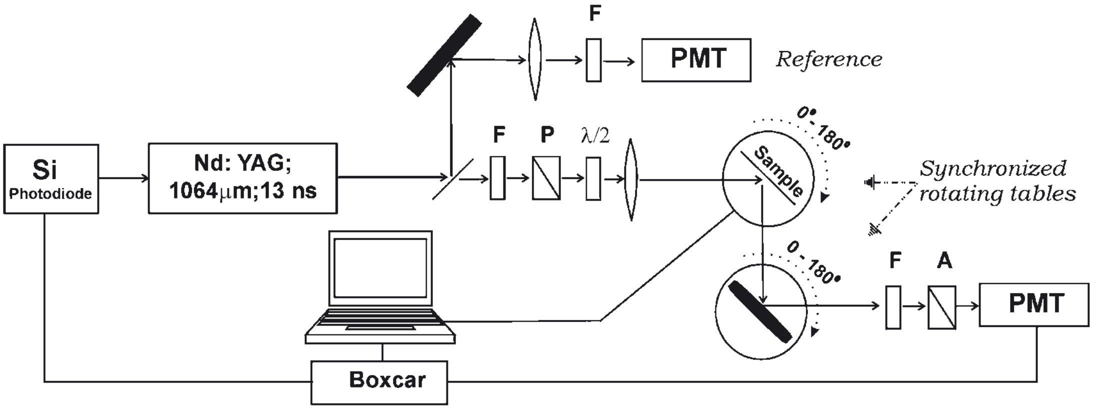


*Fig. 1. Second Harmonic Generation experimental setup*

1 μm) of modified resin (composition of epoxy resin, azo-carbazole chromophore and isoforenodiamine) prepared by spin-coating technique, were oriented by corona poling. Next, they were conditioned in the usual laboratory environment until their UV-vis absorption, initially gradually growing due to chromophore reorientation, reached stable values. This last one was considered as a proof of aquilibrium state reaching, which typically persisted for at least few weeks. Then the nonlinear susceptibility $\chi^{(2)}$ was measured using second harmonic generation (SHG) technique.

The SHG measurements were performed in transmission geometry using a pulse Nd:YAG laser, operating at 1064 nm fundamental wavelength. The experimental setup is shown schematically in Fig. 1. Further extensive theory and technical details of such experiment can be found in [11].

Resin thin films were investigated by Atomic Force Microscopy (AFM) [12].

## RESULTS AND DISCUSSION

### Characteristics of the synthesized chromophores

Purified 3-(2′-chloro-4′-nitrophenylazo)carbazole have melting temperature 245 °C.

In IR spectra of this chromophore the following bands were observed: 3432 cm$^{-1}$ ($\nu_{N-H}$); 3103 and 2975 cm$^{-1}$ ($\nu_{Ar-H}$); 1606 cm$^{-1}$ ($\nu_{N=N}$); 1626, 1595 and 1579 cm$^{-1}$ ($\nu_{C=C}$); 1519, 1342 cm$^{-1}$ ($\nu_{NO2}$); 1120 cm$^{-1}$ ($\nu_{C-Cl}$).

$^{1}$H NMR analysis showed the following chemical shifts of protons (in ppm): 7.30 (dt, 1H), 7.49 (dt, 1H), 7.70 (dd, 1H), 7.93 (d, 1H), 8.12 (m, 3H), 8.27 (dd, 1H), 8.43 (d, 1H), 8.83 (d, 1H).

Synthesized 3-(2′-chloro-4′-nitrophenylazo)-9-(2,3-epoxypropyl)carbazole melted in the range of temperature 208—210 °C.

The structure of this product was confirmed by IR and $^{1}$H NMR analyses. The IR spectra contain the following bands: 3098, 2933 cm$^{-1}$ ($\nu_{Ar-H}$); 1626, 1559 cm$^{-1}$ ($\nu_{C=C}$); 1524, 1341 cm$^{-1}$ ($\nu_{NO2}$); 1463 cm$^{-1}$ ($\nu_{N=N}$); 1450, 1431 cm$^{-1}$ ($\nu_{C-H}$); 1114 cm$^{-1}$ ($\nu_{C-Cl}$); 896 cm$^{-1}$ ($\nu_{C-O-C}$); 750, 744 cm$^{-1}$ ($\gamma_{CH2}$).

In $^{1}$H NMR spectra the peaks with following chemical shifts (in ppm) were observed: 3.45 (d, 2H), 4.56 (t, 2H), 7.36 (dt, 1H), 7.57 (dt, 1H), 7.75 (dd, 1H), 7.87 (d, 1H), 7.98 (m, 3H), 8.33 (dd, 1H), 8.48 (d, 1H), 8.88 (d, 1H).

### Characterization of modified epoxy resin

In an effort to maximize $\chi^{(2)}$ value of the investigated materials three factors were varied — the applied electric field, the sample temperature and the procedure duration time. Among all samples tested the best value of $\chi^{(2)}$ coefficient was obtained for samples oriented in 70 °C at voltage 7 kV during 15 minutes.

Normally $\chi^{(2)}$ is a third rank tensor, but in materials poled like reported here, only two components are not vanishing. They are denoted by *pp* and *sp* subscripts according to polarizations of the fundamental and the harmonic light beams and theoretically $\chi^{(2)}_{sp}$, should be roughly a third part of $\chi^{(2)}_{pp}$ [11]. Values found in this

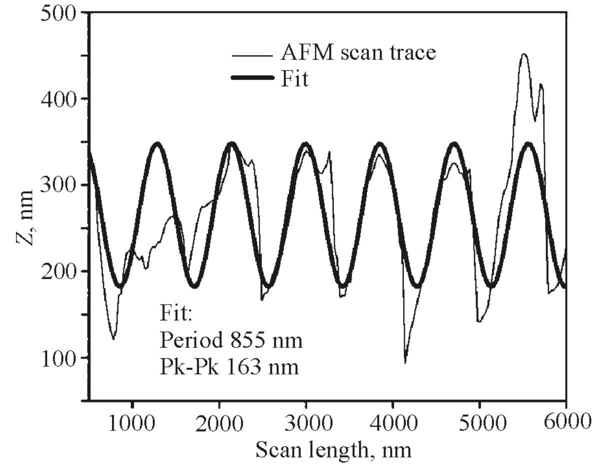


*Fig. 2. Typical cross-section through structured resin thin film obtained by AFM (thinner line) and fitted theoretical curve (thicker line)*

study were $\chi^{(2)}_{pp}$ = 63.8 pm/V and $\chi^{(2)}_{sp}$ = 23.6 pm/V. These magnitudes are pretty high for such kind of systems.

It was also confirmed, that such modified epoxy resins undergo optical structuration — a stable deformation of polymer film surface upon strong light beam illumination. In result, diffraction patterns can be recorded on the polymer film surface, what is interesting from the point of view of information storage application. By mean of Lloyd mirror interference gratings were permanently written on modified resin thin films. For illustrative purpose a typical cross-section of the recorded grating curve obtained by AFM is shown in Fig. 2. Theoretical sin-curve fit (superimposed on experimental data) was used to calculate peak-to-peak amplitude of the recorded grating, which was found roughly half of the film thickness. This high value proves potential for application of such type modified resins.

## CONCLUSIONS

In frame of this work, it was shown that by mean of simple chemistry new interesting and versatile materials for applications in the field of non-linear optics can be obtained.

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