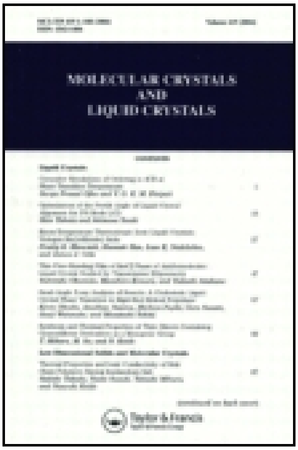

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Carbazole-based Azopolymers for Non-Linear Optics

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Carbazole-based Azopolymers for Non-Linear Optics

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Synthesis of diazo-carbazole chromophore and its epoxy derivative is described. This new material was found suitable for nonlinear optics.

Keywords: azo-chromophores; carbazole; epoxy resins; nonlinear optics

INTRODUCTION

A number of amorphous organic polymers show interesting physicochemical properties, such as low light propagation losses, processability, chemical stability favorizing their application in linear and nonlinear optics. In order to get nonlinear optical properties it is necessary to functionalize these polymers with active nonlinear optical (NLO) chromophores. However very often these materials are used in form of a guest-host system. It limits the content of active chromophores due to the aggregation problems. Also in the case of second-order NLO materials the guest-host systems show poor stability of induced polar order, necessary to exhibit these properties and the concentration

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of active chromophores is limited by already mentioned aggregation problems. It limits the value of second-order NLO susceptibility.

Another approach consists of the introduction of NLO active chromophores into the main polymer chain (main chain polymers), chemically grafting the chromophores (side chain) or using chromophores to bind polymer chains through the thermal- or photo-crosslinking process. Among different chromophores a special attention attracted the azo-aromatic materials [1–3]. This is mainly due to the high values of nonlinear susceptibilities characterising these chromophores and their ability to conformation from trans to cis under the illumination via either one photon or two photon absorption. The structural and dipolar properties of azo units and its content in the sample are factors that play an important role in the orientation processes [4]. Often the azo are blended in an optically inert polymer matrix. Epoxy resins are good candidates for the matrix owing to low optical losses and the possibility they offer to tailor their mechanical and thermal properties by varying the degree of crosslinking.

CHEMICAL SYNTHESIS

The bi-functional chromophores were obtained by the coupling reaction of carbazole (**1**) with diazonium salt of 2-chloro-4-nitroaniline (**2**). The coupling reaction was carried out in biphasic system consisting of water and n-butanol. The obtained 3-(2′-chloro-4′-nitrophenylazo-)-carbazole (**3**) was purified with ethyl acetate [5]. Next the 3-(2′-chloro-4′-nitrophenylazo-)-carbazole (**3**) was converted to epoxy derivative in the reaction with epichlorohydrine (**4**) in acetone in presence of potassium hydroxide, potassium carbonate and tetrabutylammonium bromide (TBAB) as a catalyst. The 3-(2′-chloro-4′-nitrophenylazo-)-9-(2,3-epoxypropylo)-carbazole (**5**) was obtained in form of a red powder with very good yield (Fig. 1). The obtained product was identified by FT-IR and ^{1}HNMR spectroscopies according to data given below.

IR (KBr), cm^{-1}: 3098, 2933 ($\nu_{\mathrm{Ar-H}}$), 1626, 1559 ($\nu_{\mathrm{C=C}}$), 1524, 1341 ($\nu_{\mathrm{NO_2}}$), 1463 ($\nu_{\mathrm{N=N}}$), 1450, 1431 ($\nu_{\mathrm{C-H}}$), 1114 ($\nu_{\mathrm{C-Cl}}$), 896 ($\nu_{\mathrm{C-O-C}}$), 750, 744 (γ_{CH2})

^{1}HNMR (acetone): $\delta = 3{,}45$ (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)

The epoxy functional group in the carbazole moiety plays important role. It enables chemical bonding of the chromophore molecule to the

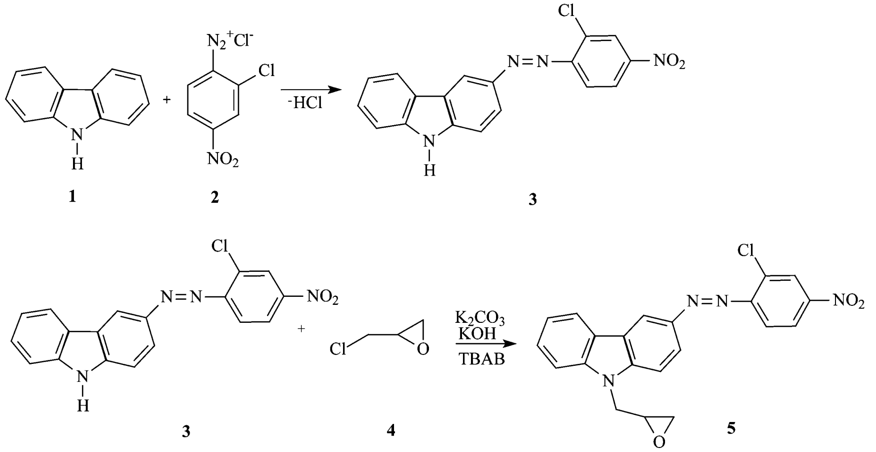

FIGURE 1 Synthesis of 3-(2′-chloro-4′-nitrophenylazo)-carbazole and its epoxy derivative.

resin main chain during crosslinking reaction. In result, the final product is a polymer with homogenously distributed azo-carbazole chromophores. In order to obtain a solid state polymer, the diglicydyl ether of bisphenol A (Araldite PY 3483), 3-(2′-chloro-4′-nitrophenyl-azo-)-9-(2,3-epoxypropylo)-carbazole and p-phenylenediamine (hardener) were homogenized together in proportions 85:5:10 wt. and left in ambient conditions for few days. In this way, the resulting solid state polymer contained 5% wt. of the chromophore. We expected the chromophore to be chemically bound in the reticulated network, according to FT-IR spectra where was no more traces of epoxy groups and characteristic carbazole lines were modified. DSC studies revealed glass transition at around 75°C and no peaks characteristic of melting or recrystallization (during sample cooling). Further inspection under polarization microscope of the modified resine thin film, annealed at a temperature well above T_g, did not show presence of any crystalline object. This was an additional proof that the chromophore groups were chemically bound to the polymer main chain.

PHYSICAL STUDIES

Subsequently, this modified epoxy resin was studied in order to estimate its non-linear optical properties. First, the thin films (ca. 1 μm thick) of the material, prepared by spin-coating technique, were oriented by corona poling technique. Next, they were conditioned in

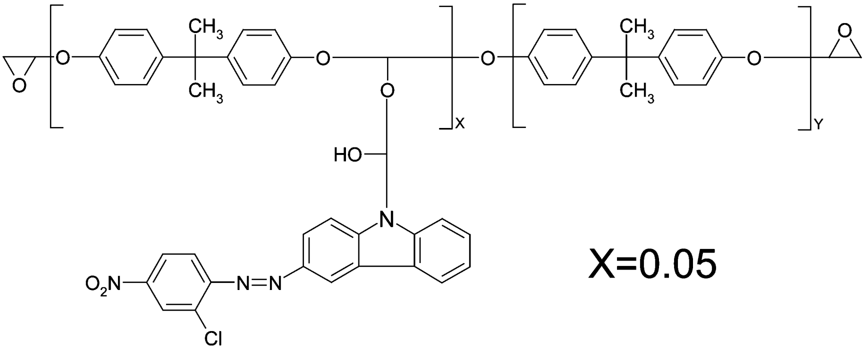

FIGURE 2 Modified epoxy resin.

the usual laboratory environment until their UV-vis absorption, initially gradually growing due to chromophore reorientation, did not attain stable values. This was considered a proof of reaching equilibrium state, which typically persisted for at least few weeks. Then, the nonlinear susceptibility χ^2 was measured using second harmonic generation technique. The experimental set-up used or SHG measurements is shown schematically in Figure 3. The measurements were performed in transmission geometry using a pulse Nd:YAG laser, operating at 1064 nm fundamental wavelength. Further extensive theory and technical details of such experiment can be found in [6]. In an effort to maximize χ^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 χ^2 coefficient was obtained for samples oriented in 70°C at voltage 7 kV during 15 minutes. Values found equaled respectively for *p-p* and *s-p* components χ^2_{pp}= 63.8 pm/V and χ^2_{sp}= 23.6 pm/V. These

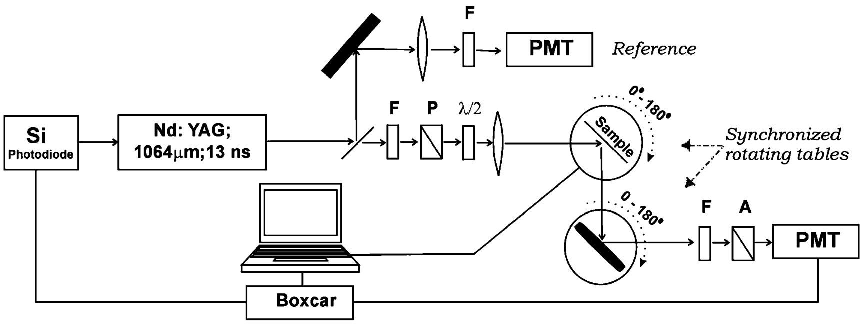

FIGURE 3 Experimental setup, second harmonic generation.

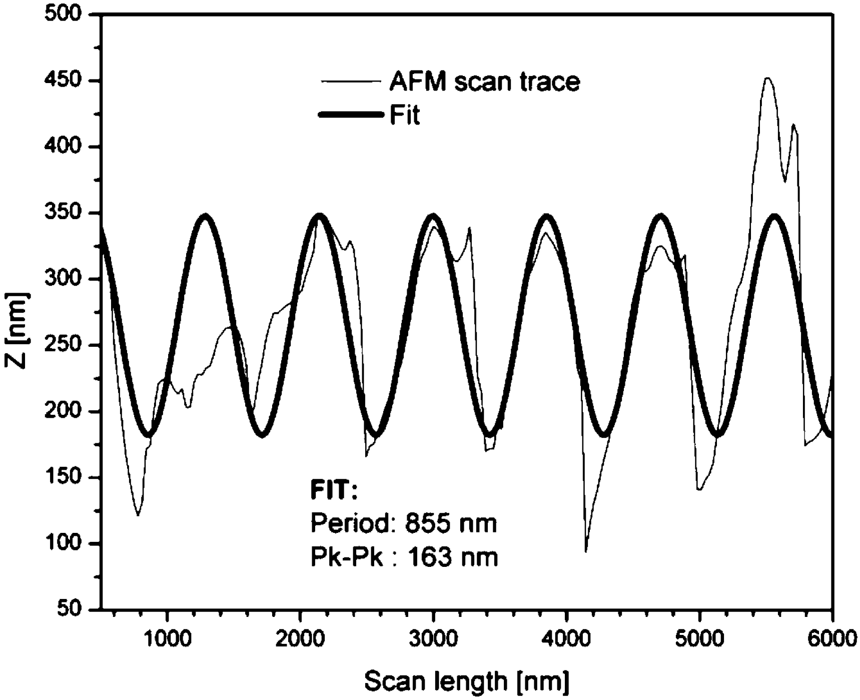

FIGURE 4 A typical cross-section through structured resine thin film obtained by AFM (thinner line) and fitted theoretical curve (thicker line).

results are good in case of polymer materials. It was also checked, that such modified epoxy resins undergo optical structuration – 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 potentially interesting in view of information storage applications. Interference fringes produced with Lloyd mirror were permanently written on the modified resine thin films. A typical cross-section obtained by AFM with superimposed fitted theoretical curve are shown in Figure 4.

CONCLUSIONS

In the frame of this work, it was shown that by means of simple chemistry new interesting and versatile materials for applications in the field of non-linear optic can be obtained. As it will be presented in further reports, the presented approach facilitates formulation of polymers with tailored NLO properties.

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