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ScienceDirect
Optical Materials 31 (2009) 501–504
OPTICAL Materials
www.elsevier.com/locate/optmat

Thermal stability of blends containing azo-carbazole derivatives and epoxy resin, designed for nonlinear optical applications

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Received 14 September 2007; accepted 8 November 2007
Available online 8 February 2008

Abstract

Many studies have been intended to synthesize new thermally stable organic materials and polymers for nonlinear optical applications. These materials are most often guest–host systems and present some inconveniences like solvents compatibility for both the matrix and the chromophore. In the present work, we propose to use an epoxy resin as matrix for chromophores. Three blends containing an epoxy resin and azo-carbazole derivatives (either physically dispersed or chemically bound) were studied. They were prepared in form of thin films. We report their nonlinear optical properties investigated by third harmonic generation (THG) by Maker fringes technique, as well as thermal stability of these characteristics. The results show different behaviour for dispersed chromophore in a matrix and covalently bounded chromophore.

Keywords: Carbazole; Epoxy resin; Nonlinear optical properties; THG

1. Introduction

Within the development of the new low cost technologies, organic and polymer materials have been intensively studied and applied in the domain of nonlinear optics (NLO) for at least three past decades. Most often, reported systems consist of a physically dispersed guest chromophore molecules in a host polymer. These polymers should be optically transparent without any nonlinear optical properties like Polymethylmethacrylate (PMMA), Polystyrene (PS), Polycarbonate (PC) and so on. In this way, all nonlinear properties are supposed due to dispersed NLO chromophore. A routine technique to transform the starting materials (polymer and chromophore powders) is dissolving them together in a solvent, adequate for both. Next, from this solution and by mean of spin-coating, thin films are obtained on glass substrate. However, such approach suffers numerous inconveniences. Although spin-coating technique enables good quality film formation, most of the solution is lost during the spinning. Film thickness cannot reach more that few microns, unless the film surface is swirled or cracked. Furthermore, often the choice of common solvent is very limited by polymer and chromophore compatibility. To overcome these problems, the chromophore can be chemically bound to the polymer chain, which resolves problem of chromophore-polymer incompatibilities. Nevertheless, this approach is a work consuming method and the chromophore-polymer rate cannot be changed.

In this paper we proposed an interesting method which allows overcoming all of above-mentioned problems. As polymer matrix, we applied a liquid resin, which served also as solvent for the chromophore. The obtained solution was deposited on glass substrate and was chemically reticulated by introducing (3-ethyl,4-phenyl)amine and forming films of tailored thickness and other dimensions.

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doi:10.1016/j.optmat.2007.11.033

As a part of the carried study, we tested thermal stability of epoxy resin blends containing three chromophores, derivatives of carbazole and azobenzene. The systematic difference between these chromophores consists of the substitution made on the nitrogen atom from the carbazole ring, namely by CH_2CH_3 and $CH_2C_2H_2O$ (epoxy group) moieties. The chromophore bearing the epoxy group was supposed to be incorporated into polymer network during the reticulation. The other two compounds have to be only physically dispersed and were chosen to investigate influence of chemical bonding and steric constraints on the composite thermal stability. These three chromophore molecules were also chosen because of their potential application in optical grating recording.

2. Experimental

2.1. Chemical syntheses

2.1.1. 3-(2′-chloro-4′-nitrophenylazo-)carbazole [CNPA-carbazole]

Concentrated hydrochloric acid (18 ml) was added into suspension of 2-chloro-4-nitroaniline (5.3 g, 0.0264 mol) in water (57 ml). Due to the fact that the aniline derivative is dissolved, a solution is obtained. The solution was then cooled in an ice bath until the reaction mixture temperature dropped to (0 °C, 5 °C). Next, a solution containing sodium nitrite (2.5 g, 0.0264 mol) 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 the diazo derivative, the solution was filtered and added to a suspension of carbazole (4.0 g, 0.024 mol) in *n*-butanol (40 ml) at 40 °C. The mixture was stirred overnight at 40 °C. The dye, 3-(2′-chloro-4′-nitrophenylazo-)carbazole, 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. (Fig. 1).

IR (KBr), cm^{-1}: 3420(ν_{N-H}), 3103(ν_{Ar-H}), 2975(ν_{Ar-H}), 1606($\nu_{-N=N-}$), 1626, 1595, 1579($\nu_{C=C}$), 1519, 1342(ν_{NO_2}), 1120(ν_{C-Cl}).

2.1.2. 3-(2′-chloro-4′-nitrophenylazo-)-N-ethylcarbazole [CNPA-ethylcarbazole]

It was prepared in the similar manner as 3-(2′-chloro-4′-nitrophenylazo)-carbazole, from concentrated hydrochloric acid (18 ml), 2-chloro-4-nitroaniline (5.3 g, 0.0264 mol), sodium nitrite (2.5 g, 0.0264 mol), and *N*-ethylcarbazole (4.68 g, 0.024 mol) in an iso-butanol solution (40 ml). Yield 78%.

IR (KBr), cm^{-1}: 3051, 2976(ν_{Ar-H}), 1595($\nu_{N=N}$), 1626, 1579($\nu_{C=C}$), 1518, 1337(ν_{NO_2}), 1479, 1450, 1430(ν_{C-H-}), 1111(ν_{C-Cl}), 743, 726(γ_{CH2}).

^{1}HNMR (acetone): $\delta = 7.30$(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).

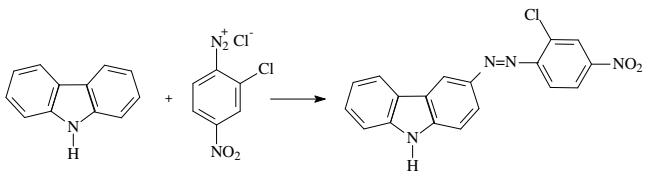

Fig. 1. CNPA-carbazole synthesis. (Similar routine was applied to synthesise CNPA-ethylcarbazole).

2.1.3. 3-(2′-chloro-4′-nitrophenylazo-)N-(2,3-epoxypropyl)-carbazole [CNPA-epoxypropylcarbazole]

Acetone (100 ml) was added into the suspension of 3-(2′-chloro-4′-nitrophenylazo-)carbazole (5.7 g, 0.0158 mol) in 1-chloro-2,3-epoxypropane also named epichlorohydrin (7.4 g, 0.0095 mol). The solution was heated up to 35 °C and potassium hydroxide (0.9 g, 0.016 mol), potassium carbonate (16 g) and TBAB (tetrabutylammonium bromide) (0.5 g, 0.0095 mol) were added. The mixture was stirred vigorously at 35 °C for 6 h. After evaporation of acetone, crude product was crystallized from methylene chloride. The dye, which was precipitated, was filtered off, and well rinsed with water, and dried. The bright red powder was obtained with 70% yield. (Fig. 2).

IR (KBr), cm^{-1}:3098, 2933(ν_{Ar-H}), 1596($\nu_{N=N}$), 1626, 1559($\nu_{C=C}$), 1524, 1341(ν_{NO_2}), 1463($\nu_{N=N}$), 1465, 1450, 1431(ν_{C-H}), 1114(ν_{C-Cl}), 896(ν_{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).

Blend samples were prepared by dissolution of the synthesized chromophores in an epoxy resin, sold as "Epidian 6" (brand name of the product based on bisphenol A, purchased from Organika-Sarzyna Inc., Poland). A stoichiometrically adequate amount of (3-ethyl,4-phenyl)amine was then slowly added to the blend solution, homogenized and poured on microscope slides and left overnight to completely reticulate. The films obtained by this procedure were few tens micrometer thick, transparent and had smooth, defect-free surface.

2.2. Thermal and nonlinear optical properties

All measurements were performed at room temperature and at ambient atmosphere. Nonlinear optical properties of these carbazole derivatives were investigated using the third harmonic generation (THG) by Maker fringes technique. The THG process is nonlinear process in which a fundamental beam at the wavelength λ generates through the nonlinear polarization of the medium, a coherent beam at a shorter wavelength $\lambda/3$. The experiment was performed using a Q-switch NdYAG laser (Continuum) working at 1064 nm wavelength, 16 ps pulse duration and 10 Hz rate emission. Third harmonic signals resulting from the samples were filtered and collected by a photomultiplicator tube (Hamamatsu R1828).