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Synthesis of biphenyl derivative and its application as dichroic materials in poly (vinyl alcohol) polarizing films

Siyamak Shahab [a, **], Hora A. Almodarresiyeh [a], Ljudmila Filippovich [a], Rakesh Kumar [b, *], Mahdieh Darroudi [c], Fatemeh Haji Hajikolaee [d]

[a] Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, 13 Surganov Str., Minsk 220072, Belarus
[b] Department of Chemistry, DAV University, Jalandhar, 144001, Punjab India
[c] Department of Organic Chemistry, University of Mazandaran, 47416 Babolsar, Iran
[d] Tajan High Education Institute, 47617-96486, Ghaemshahr, Mazandaran, Iran

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ABSTRACT

In the present work, first time on the basis of polyvinyl alcohol (PVA) and new designed structure (Potassium 2,2′-([1,1′-biphenyl]-4,4′-diylbis(azanediyl))diacetate) (I) thermostable polarizing film was created. The structure (I) was first modeled and then synthesized and obtained polarizing film absorbing at $\lambda_{max} = 300$ nm used for electronic applications. Polarizing efficiency (PE) of polarizing film is 96% at stretching degree (R_s) 4.0. On the basis of PVA, Potassium 2,2′-([1,1′-biphenyl]-4,4′-diylbis(azanediyl)) diacetate (I), Sodium 2-hydroxy-5-((2-methoxy-4-((4-sulfonatophenyl)diazenyl)phenyl)diazenyl)benzoate (II) and commercial dye (Congo Red) thermostable polarizing film for wide spectral range of spectrum ($\lambda_{max} = 288–561$ nm) was developed. During the work it was established that oriented PVA-films is phenomenon of *anisotropy of thermal conductivity* ($\lambda_{||}/\lambda_{\perp}$). It is very important for creation of thermostable polarizing films. Thermal conductivity in a direction of orientation ($\lambda_{||}$) is higher than in a direction perpendicular orientations ($\lambda_{\perp}$). The optimization of the molecule (1) was carried out by Density Functional Theory (DFT) using B3LYP/6-311 + G* method. Electronic absorption spectrum of the molecule (I) in dimethylformamide (DMF) solution was calculated using TDB3LYP/6-311 + G* level. The nature of absorption bands in the UV spectral region was interpreted.

1. Introduction

The polarizer film presents a uniaxial oriented polymeric film containing dichroic substance. Light-polarizing films are the basis of sheet polarizers which are traditionally used in processes of manufacturing of liquid crystal indicators for displaying devices. They are constituted usually from polymer matrix, e.g., Polyethylene or polyvinyl alcohol containing uniaxial oriented Dichroic dyes, or iodine [1,2]. The most used polarizers are the H-type polarizers which contain molecular iodine as a dichroic agent. They are excellent in the initial polarization performance but are weak against water or heat. L-type polarizers contain a dichroic dye or mixture of the dyes as a polarizing element [3,4]. They have better durability against water and heat as compared to polarizing films using iodine, but are inferior in polarizing ability. Examples of dichroic molecules include dye compounds, such as azo dyes or as well as iodine have a high polarization degree (90–99%) and can be maintained in a wide range of temperatures. Dichroic dyes when employed as polarizing films are generally used in combination with other dyes, having absorption in a particular wavelength range to provide the polarizing films with a neutral color and wide range spectra [5,6]. PVA-films are easily exposed to uniaxial orientation, then it become optically anisotropic and partially polarize passing light beams. These properties of PVA have defined theoretical and practical interest in it from the point of view of their use for the manufacturing of film polarizers. The majority of films with dichroic dyes finding practical application polarize light in a visible area (400–550 nm) electromagnetic spectrum where the basic strips of absorption of molecules with stretched chains of the interfaced double bond conjugation are located [1–3]. There are not

* Corresponding author.
** Corresponding author.
E-mail addresses: siyamak.shahab@yahoo.com (S. Shahab), h_al1994@yahoo.com (H.A. Almodarresiyeh), luda1977@list.ru (L. Filippovich), rakesh_nitj@yahoo.co.in (R. Kumar).

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thermostable polarizing films on the basis of PVA and dichroic dyes absorbing at $\lambda_{max} = 280–300$ nm. In this work on the basis of PVA, new synthesized structure (Potassium 2,2′-([1,1′-biphenyl]-4,4′-diylbis(azanediyl))diacetate) and synthesized earlier dichroic dyes (II) and Congo Red thermostable polarizing film absorbing in wide spectral range (UV and Vis) of the spectrum ($\lambda_{max} = 288–561$ nm) was developed.

2. Experimental details

2.1. Reagent and apparatus

All chemicals used were of analytical reagent grade. PVA used in this work was «Mowiol 28–99» (Hoëchst Akiengesllschaft Co., Germany). The dyes which were used as dichroic agents are mentioned in Table 1. The commercial azo dye Congo Red (III) was purchased from "Sigma–Aldrich Co." and used without further purification. Water-soluble azo dye (II) was synthesized in accordance with the known procedure usually used for preparation of azo compounds [6]. Heat conductivity of films was measured on the complex equipment LC – 201 (Alfa Laval Group, Sweden) using indicator method for the determination of heat conductivity of polymer materials and films.

The experimental UV absorption spectrum of the molecule was recorded on UV–Visible Spectrophotometer Cary 300 (Varian, USA). The optical transmission spectra were measured in polarized light with UV-NIR Spectrophotometer HR4000 (Ocean optics, USA). IR spectrum of films was measured by a spectrophotometer of Protégé 460 (Nicolet, US). The experimental FT-IR spectrum was recorded by KBr pellet method with spectral resolution 2 cm^{-1}. ^1H NMR spectrum was recorded in DMSO-d_6 by NMR AVANCE-500 spectrometer (Bruker, Germany) with a working frequency of 600 Hz (1H). During calibration of the chemical shifts as the internal standard the residual signal of the solvent is used.

2.2. Synthesis of potassium 2,2′-([1,1′-biphenyl]-4,4′-diylbis(azanediyl))diacetate

Compound (I) was prepared by adding 5.52 g (0.03 mol) of benzidine and 7.73 g (0.06 mol) of ethyl chloroacetate. The mixture was heated to 80 °C and then reaction temperature increased to 120 °C for 0.5 h. Unreacted benzidine was extracted by 50 ml of boiling benzene; the precipitate was filtered and recrystallized from 600 ml distilled water. The light brown product does not melt at 250 °C but turns into a black mass. The resulting solution was stirred at room temperature and in the presence of potassium carbonate then it is transformed into potassium 2,2′-([1,1′-biphenyl]-4,4′-diylbis(azanediyl))diacetate (Fig. 1). Experimental IR Spectrum of the dye (I) is presented in Table 2 and Fig. S1.

Experimental ^1H NMR Spectrum: δ: (DMSO-d6, ppm) at 7.68 MHz (m, 4H, Ar), 7.27 MHz (d, 2H, Ar), 6.67 MHz (d, 2H, Ar), 4.12 MHz (dd, 2H, NH), 3.38 MHz (d, 2H, CH_2), 1.32 MHz (d, 1H, CH_2), and 1.19 MHz (d, 1H, CH_3) (Fig. S2).

2.3. Preparation

The PVA films were prepared from 10% PVA solutions, containing the Potassium 2,2′-([1,1′-biphenyl]-4,4′-diylbis(azanediyl)) diacetate (I), Sodium 2-hydroxy-5-((2-methoxy-4-((4-sulfonatophenyl)diazenyl)phenyl)diazenyl)benzoate (II), Congo Red (III), gelling and plasticizing agents. The films was cast on the polished glasses and dried in the closed box at temperature 20–22 °C. Uniaxial orientation was done in the 4% boric acid (H_3BO_3) solution at 42–45 °C. The washed film was dried for 30 min at temperature 60–63 °C. The value of stretching degree (R_s) was determined as the ratio between length of the films after and before uniaxial stretching. The thickness of the resulting films was between 50 and 55 μm

3. Optical properties

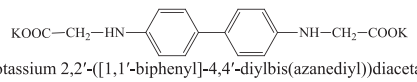
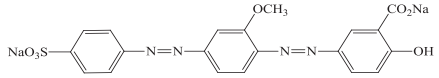
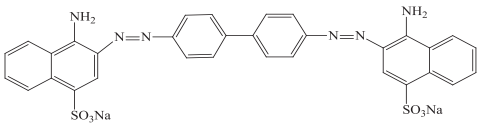
The main optical properties of polarizing films such as Transmittance ($T_\perp$, $T_\parallel$) and Polarizing efficiency (PE) were evaluated at the absorption maximum of the polarizing films according to Eq. (1) [1].

$$PE = \left(T_\perp - T_\parallel\right) \Big/ \left(T_\perp + T_\parallel\right) * 100 \quad (1)$$

Where, $T_\parallel$, $T_\perp$– Transmittance for linearly polarized light parallel ($_\parallel$) and perpendicular ($_\perp$) to the drawing direction of the colored film.

Polarizing efficiency of colored oriented PVA-films depend on the concentration of injected dye and stretching degree (Rs) of the film, therefore the optimum concentration of the compounds (I), (II), (III) in PVA-film were obtained (Table S1). Changes in concentration of compounds from 0.1 to 0.3 wt. % in a PVA-film show that with increasing concentration of the compounds, maximum light

Table 1
Chemical structure of investigated dyes in dimethylformamide (DMF) with their λ_{max} (nm).

Dye	Structure	λ_{max}, nm
(I)	Potassium 2,2′-([1,1′-biphenyl]-4,4′-diylbis(azanediyl))diacetate  Potassium 2,2′-([1,1′-biphenyl]-4,4′-diylbis(azanediyl))diacetate	297
(II)	Sodium 2-hydroxy-5-((2-methoxy-4-((4-sulfonatophenyl)diazenyl) phenyl)diazenyl)benzoate  Sodium 2-hydroxy-5-((2-methoxy-4-((4-sulfonatophenyl)diazenyl) phenyl)diazenyl)benzoate	450
(III)	Congo Red  Congo Red	500