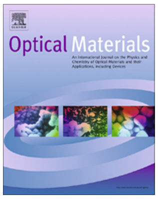
Optical Materials 36 (2014) 892–902

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat



Comparative studies of polyimides with covalently bonded azo-dyes with their supramolecular analoges: Thermo-optical and photoinduced properties

Ewa Schab-Balcerzak [a,*], Jolanta Konieczkowska [a], Mariola Siwy [a], Anna Sobolewska [b], Magdalena Wojtowicz [a], Malgorzata Wiacek [c]

[a] *Centre of Polymer and Carbon Materials, Polish Academy of Sciences, M. Curie-Sklodowska 34, 41-819 Zabrze, Poland*
[b] *Institute of Physical and Theoretical Chemistry, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland*
[c] *Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland*

ARTICLE INFO

Article history:
Received 19 September 2013
Received in revised form 25 November 2013
Accepted 11 December 2013
Available online 14 January 2014

Keywords:
Azopyridine
Polyimides
Hydrogen bonds
Surface relief gratings

ABSTRACT

The paper describes the synthesis and characterization of aromatic polyimides with azopyridine derivatives covalently attached as a side-chain and their supramolecular analoges based on the hydrogen bonds. Moreover, azopolymers differ in the chemical structure of the polymer backbone and the content of the chromophore. Azo-functionalized polymers were obtained by a two-step synthetic approach. This includes the preparation of a precursor with pendant hydroxyl groups followed by the covalent attachment of the chromophore, that is, 4-[4-(6-hydroxyhexyloxy)phenylazo]pyridine to the polyimide backbone. The degree of functionalization of the polymers was estimated by the UV–Vis spectroscopy. Supramolecular films were built on the basis of the hydrogen bonds between the hydroxyl groups of the polymer and azopyridine derivatives, that is, 4-(4-hydroxyphenylazo)pyridine and 4-[4-(6-hydroxyhexyloxy)phenylazo]pyridine. The polymers were characterized and evaluated by FTIR, ^{1}H NMR, X-ray, UV–Vis, DSC and TGA methods.

The synthesized precursor polymers revealed the glass transition temperature (T_g) in the range of 254–366 °C, whereas azopolymers and supramolecular systems exhibited lower T_g within the ranges 129–153 °C and 53–171 °C, respectively. The polymers were easily soluble in common organic solvents enabling to obtain films of a good optical quality. The light-induced optical anisotropy was studied with the help of the holographic recording. The polymer films were investigated by an atomic force microscopy before and after the diffraction grating recording in order to confirm the formation of surface relief gratings. To the best of our knowledge, for the first time the photoinduced anisotropy in polyimides functionalized with azopyridine units has been compared with their supramolecular systems analoges.

1. Introduction

The development of the field of science and technology such as photonic and optoelectronic forces search of new materials. One of the most promising materials for photonic applications are azobenzene-containing polymers named azopolymers [1]. Azobenzene-based chromophores have two isomeric states, a thermodynamically stable *trans* and a metastable *cis* form, which have different properties such as different dipole moments, refraction index and spatial volume [2–5]. They can undergo many successive reversible *trans–cis–trans* photoisomerization cycles under the irradiation with a linearly polarized light, which let to generation of photoinduced optical anisotropy (POA) in the material [2,5,6]. Moreover, the chromophore reorientation is linked with the microscopic mass transport of the polymer chains observed as a free surface modulation and called as a surface relief grating (SRG) [5,7]. The azopolymers have several advantages such as environmental resistance, low dielectric constants, good thermal stability and mechanical strength, low fabrication costs and flexibility in the molecular design, compared with inorganic materials [1,6]. Because of these advantages, some polymers have been extensively investigated for photonic devices such as frequency modulators, optical switches, optical fibers, optical data storage, diffractive optical elements [8,9]. The replacement of the azobenzene moiety by an azopyridine, that can also undergo the *trans–cis* photoisomerization, is another way of the chromophore structure modification [10]. Such chromophore combines the photoactivity of the azobenzene with the ability of the formation of supramolecular systems provided by the pyridyl group, which

---

* Corresponding author. Tel.: +48 32 2716077; fax: +48 32 2712969.
E-mail address: eschab-balcerzak@cmpw-pan.edu.pl (E. Schab-Balcerzak).

0925-3467/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.optmat.2013.12.017

can readily form hydrogen bonds with proton donors. Aromatic polyimides (PIs) play a key role as materials for many various uses due to their excellent physicochemical properties such as optical and thermal stability in combination with the high glass transition temperature, low susceptibility to the laser damage [11–15]. Moreover, polyimides are investigated as potential materials in the field of optoelectronics and photonics [4,16–20].

Azopolymers can be prepared in three main ways (i) by the dissolution of a guest chromophore in a passive host polymer matrix, (ii) by the covalent attachment of the chromophore to the polymer chain and (iii) by the utilization of different nonconvalent intermolecular interactions including ionic interactions, coordination bonds, hydrogen bonds, π–π interactions between a dye and a polymer backbone [4,21–23]. Each method has advantages as well as drawbacks. The concept based on non-covalent intermolecular interaction is relatively new approach to link the active molecules to the polymer chains, especially for polymers with imide rings, and it is also suitable for SRGs formation [4,24]. Such approach offers several advantages: simple and low costs preparation by mixing compounds, good optical quality films without the aggregation and the phase separation of the chromophore and the polymer matrix [24–27]. It was found that the amplitude of the surface relief grating modulation in the hydrogen-bonded polyimide–dye complexes depends on the polymer backbone and the chromophore chemical structure, and the kind of the polymer functional group, which was described in our previous paper [4]. Thus, this work is a continuation of our effort in the preparation of new photoactive supramolecular azopolyimide systems and their corresponding azopolymers with the chromophore covalently attached to the polymer chain. The complexity of the phenomena which determines the photoinduced effects in organic compounds, especially in polymers, makes difficulties in the estimation of their ability for applications in various fields of photonics. Therefore, the basic research is very important to determine the influence of various factors, coming from the chemical structure of the material on photoinduced optical anisotropy. Thus, our interest is focused on the systematic studies of the relationship between the chemical structure and relevant physical–chemical properties including photoinduced anisotropy from the point of view of application of such materials in the fabrication of photonic structures or for holographic optical information storage. Our investigations may let to better understanding the relationship between the chemical structure and photoinduced phenomena mainly holographic recording of the diffraction grating. The obtained results may allow forming some general relationships between the chemical architecture of new materials and their properties, which would enable the modeling of the chemical structure to obtain a material with specific characteristics. The investigations should be systematically carried out because the different parameters are not independent of each other. Thus, our investigations may have both a basic and cognitive aspect that will contribute to a significant extension of knowledge concerning the investigated type of compounds, as well as application aspect, which may lead to development of new materials with defined properties for photonics and optoelectronics. The azopolymers assemblies were built through the selective paring between poly(etherimide)s and polyimides having a phenolic moiety, that operates as an H-bond donor, and azocompounds, with the function as an H-bond acceptor. The prepared new functionalized poly(etherimide)s and polyimides containing covalently bonded azopyridine units being analoges of supramolecular polymers differ in the content of the chromophore and the polymer backbone structure. The study involves structural (X-ray) and thermal (DSC, TGA) and optical (UV–Vis) properties of obtained azopolymers as well as their ability to record a holographic grating.

As far as we are aware, this is the first time that the comprehensive characterization of hydrogen-bonded polyimide–dye complexes and their covalently functionalized analoges have been reported.

2. Experimental section

2.1. Materials

Triphenylphosphine, 6-chlorohexanol, 4,4′-(4,4′-isopropylidenediphenoxy)bis(phthalic anhydride), *N*-methyl-2-pyrolidone (NMP), o-dichlorobenzene, 4,4′-(hexafluoroisopropylidene)bis(phthalic anhydride) were purchased from Sigma–Aldrich Chemical Co. Phenol, chloride acid, methanol were purchased from POCH. 4-aminopyridine, 4,6-diaminoresorcinol dihydrochloride were purchased from Acros. Diethylazodicarboxylate (DEAD), 2,4-diaminophenol dihydrochloride were purchased from Fluka. N,N-dimethyloformamide (DMF) was purchased from Ubichem.

2.2. Experimental methods

^1H NMR spectra were recorded on an Avance II 600 MHz Ultra Shield Plus (Bruker) Spectrometer in DMSO-d_6 and $CHCl_3$-d as solvents and TMS as the internal standard. FTIR spectra were recorded on a SpectrumOne Perkin Elmer Spectrometer in the transmission mode using KBr pallets. UV–Vis spectra were recorded in NMP solution of the polymers and as films on the glass substrate using a V-570 UV–Vis–NIR Spectrophotometer (Jasco Inc.). The X-ray diffraction patterns of solid samples were recorded using Cu Kα radiation on a wide-angle HZG-4 diffractometer (Carl Zeiss Jena) working in the typical Bragg geometry. Differential scanning calorimetry (DSC) was performed with a TA-DSC 2010 apparatus (TA Instruments) under nitrogen using a heating/cooling cycles. Thermogravimetric analyses (TGA) were performed on a Pyris-1 Perkin Elmer apparatus at a heating rate of 10 °/min under nitrogen. Molecular weight and dispersity of the polymers were obtained by means of the size exclusion chromatography (SEC) on a Shimadzu Prominance UFLC instrument at 40 °C on a Shodex 300 mm × 8 mm OHpac column using THF as a solvent. Polystyrene was used as the calibration standard. The measurements of the light-induced optical anisotropy were performed using a holographic recording setup described elsewhere [27] employing an Ar^+ laser working at line $\lambda = 514.5$ nm. The identical experimental conditions were applied for all polymers. The recording beams intensities were the same and equal to ca. 280 mW/cm^2. The period of the gratings was $\Lambda \cong 2.0\ \mu m$. Diffraction gratings were recorded for *p*–*p* polarization configuration, and the exposure time lasted 60 min. The topography of the polymer surface was examined by an atomic force microscopy (Dimension V scanning probe microscope, Veeco) working in a tapping mode.

2.3. Synthesis of chromophores

Chromophores 4-(4-hydroxyphenylazo)pyridine (denoted as **AzPy-1**) and 4-[4-(6-hydroxyhexyloxy)phenylazo]pyridine (denoted as **AzPy-2**) were prepared via the same procedure as described in our previous publication [4].

AzPy-1: ^1H NMR (DMSO-d_6, δ, ppm): 6.96 (d, ArH, 2H), 7,65 (d, ArH, 2H), 7.85 (d, ArH, 2H), 8,74 (d, ArH, 2H), 10.59 (s, —OH, 1H). FTIR (KBr, cm^{-1}): 3043 (—OH), 1595 (—N=N—), 1579 (—C=C—), 1009 (pyridine). Yield: 30%. $M_p = 262$ °C. λ_{max} (UV–Vis, NMP) = 366 nm.

AzPy-2: ^1H NMR (DMSO-d_6, δ, ppm): 1.36–1.43 (m, $OCH_2\mathbf{(CH_2)_3}CH_2CH_2OH$, 6H), 1.72–1.75 (m, $OCH_2(CH_2)_3\mathbf{CH_2}CH_2OH$, 2H), 3.37–3.41 (m, $OCH_2(CH_2)_3CH_2\mathbf{CH_2}OH$, 2H), 4.09 (t, $O\mathbf{CH_2}(CH_2)_3CH_2CH_2OH$, 2H), 4.32 (t, $OCH_2(CH_2)_3CH_2CH_2\mathbf{OH}$, 1H), 7.14 (d, ArH, 2H), 7.68 (d, ArH, 2H), 7.92 (d, ArH, 2H), 8.77 (d, ArH, 2H). FTIR (KBr,