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Author: Jolanta Konieczkowska, Anna Kozanecka-Szmigiel, Karolina Bujak, Dariusz Szmigiel, Jan Grzegorz Małecki, Ewa Schab-Balcerzak

Citation style: Konieczkowska Jolanta, Kozanecka-Szmigiel Anna, Bujak Karolina, Szmigiel Dariusz, Małecki Jan Grzegorz, Schab-Balcerzak Ewa. (2021). Photoresponsive behaviour of “T-type” azopolyimides. The unexpected high efficiency of diffraction gratings, modulations and stability of the SRG in azopoly(ether imide). "Materials Science and Engineering B: Advanced Functional Solid-state Materials" (Vol. 273 (2021), art. no. 115387, s. 1-7), DOI:10.1016/j.mseb.2021.115387



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Photoresponsive behaviour of “T-type” azopolyimides. The unexpected high efficiency of diffraction gratings, modulations and stability of the SRG in azopoly(ether imide)

Jolanta Konieczkowska^{a,*}, Anna Kozanecka-Szmigiel^b, Karolina Bujak^c, Dariusz Szmigiel^d, Jan Grzegorz Małecki^c, Ewa Schab-Balcerzak^a

^a Centre of Polymer and Carbon Materials Polish Academy of Sciences, 34 M. Curie-Skłodowska Str, 41-819 Zabrze, Poland

^b Faculty of Physics, Warsaw University of Technology, 75 Koszykowa Str, 00-662 Warszawa, Poland

^c Institute of Chemistry, University of Silesia, Szkolna 9 Str, 40-006 Katowice, Poland

^d Łukasiewicz Research Network – Institute of Microelectronics and Photonics al, Lotnikow 32/46, 02-668 Warszawa, Poland

ARTICLE INFO

Keywords:

Azopolyimides
Azopyridine
Photoinduced optical anisotropy
Surface relief gratings

ABSTRACT

In this paper, we compare the light-induced properties of three “T-type” polyimide containing azobenzene chromophores with the properties of their structural counterparts containing azopyridine moieties. The processes of photoinduced birefringence generation and surface relief grating (SRG) formation are efficient in azobenzene polyimides, while in the azopyridine analogues the processes are non-detectable. Density functional theory calculations performed to reveal a possible structural reason for the lack of optical response in the azopyridine materials showed a formation of intramolecular H-bonds. Azopoly(ether imide) with 2,2'-diphenylpropane structure despite relatively low chromophore content exhibited one of the highest diffraction efficiency (ca. 20%) and the largest modulation of the SRG (260 nm) as have ever been observed for azopolyimides. Two years after inscription, modulation of the SRG was still observed without a decrease in the relief depth, which is important in applications requiring long-term stability of SRGs.

1. Introduction

Advanced amorphous azopolymers are a wide group of materials with N = N moieties in their chemical structures. In the past decades, this class of polymers was intensively investigated in the field of photonics and optoelectronic applications [1,2]. Irradiation of azopolymer layers by polarized light can generate dichroism, photoinduced birefringence, diffraction gratings with macroscopic mass migration resulting in the formation of sinusoidal deformations called surface relief gratings (SRGs), and photomechanical effect (in free-standing polymer films) [1–3]. Inscription of bulk birefringence and SRGs gratings in azopolymers allows applying them as recording materials in holographic devices e.g. for production of the holographic versatile discs (HVDs), holographic versatile cards (HVCs), holographic versatile libraries or fingerprint holograms [4]. In 2008 InPhase® company introduced the first commercially-viable holographic storage device and HVDs. Holographic discs were characterized by a large recording capacity of up to 1.6 TB with a data transfer rate of 120 MB/s (cost 120 – 180 \$). For this

reason, companies that register and store large amounts of data e.g. record companies, film production companies, accounting firms, are increasingly interested in such storage technology. In all of the holographic-based devices, the long-time stability of the record is required cause that the SRGs generated in photosensitive materials should be stable for years. One of the main goals of holographic data recording technologies is to minimize the cost of the device's production while keeping the large and stable photoinduced properties of the used materials.

Polyimides (PIs) are one of the most important classes of heat-resistant polymers that are characterized by the presence of both phenyl and heterocyclic imide rings. The first commercial use of polyimide was in the late 1960s when DuPont® introduced a material called Kapton®, which is still used. The synthesis route of PIs is an important aspect from the point of view of commercial use. This class of materials can be synthesized by a one-step polycondensation reaction of diamine and dianhydride in an organic solvent with no use of high-expensive or toxic catalysts. Moreover, water is the only by-product of the synthesis

* Corresponding author.

E-mail address: jkonieczkowska@cmpw-pan.edu.pl (J. Konieczkowska).

<https://doi.org/10.1016/j.mseb.2021.115387>

Received 29 March 2021; Received in revised form 7 July 2021; Accepted 2 August 2021

Available online 19 August 2021

0921-5107/© 2021 The Author(s).

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reaction [5,6]. Easy and relatively non-toxic synthesis of PIs reduces the costs of material production and keeps the environment safe. Polyimides exhibit good physicochemical properties important from the point of view potential applications in photonic and optoelectronic devices i.e. high thermal and chemical resistance that can prevent unwanted destruction of the photoinduced phenomenon, long-term durability, mechanical strength and relatively good solubility in polar organic solvents [7]. Three decades of research on azopolyimides (azoPIs) have provided a great deal of knowledge about the influence of their chemical structure on photoinduced properties [5,6]. Despite huge knowledge about physicochemical properties of azoPIs, the design of materials that show high glass transition temperatures, good solubility in low-boiling solvents together with excellent photoinduced properties (e.g. high and stable birefringence or large diffraction gratings efficiency with high and stable modulations of SRGs), and that could be synthesized in easy and cheap reactions using commercially available compounds, is still a challenge.

Azochromophores can be attached to the polymer backbone with the formation of covalent bonds or non-covalent interactions between polymer matrix (host) and azo compound (guest). In functionalized polymers, azochromophores can be incorporated to the main-chain of the polymer structure (main-chain polymers), attached to the side-chain by a long aliphatic spacer (side-chain polymers), or both as the moieties in the main and side-chain ("T-type" polymers), where one of the aromatic rings of the azocompound is incorporated as a part of the main body of the polymer structure, while -N = N-Ph group is localized in the side-chain [5]. "T-type" polyimides seem to be one of the most interesting class of azopolyimides for potential application in photonic and optoelectronic devices. These polymers exhibit high thermal stability and glass transition temperatures, relatively good solubility in polar solvents, as well as high and stable birefringence [8,9], which allows to use them, e.g. as layers for the alignment of the liquid crystal mixture in the liquid crystal (LC) cells [10,11] or in preparation of LC 2D and 3D holographic gratings [12].

Based on the previous reports it can be noticed that azopyridine chromophores exhibit a faster and more efficient *trans-cis* and *cis-trans* isomerization than their azobenzene analogues in solution [13–18]. We showed, that polyimides with azopyridine moieties can generate photoinduced birefringence, diffraction gratings and SRGs with similar efficiency as their azobenzene-functionalized analogues [19–25]. Depending on the chemical structure of polyimide backbone and azopyridine compound, the photoinduced birefringence was in the range of 0.004–0.025 [21,23], the largest diffraction efficiencies of the diffraction gratings (η), generated using a degenerate two-wave mixing technique, not exceed 2.59% with sinusoidal modulations of the SRGs up to 100 nm [22,23]. "T-type" polyimides with azopyridine groups were carried out only in our previous work [25], where the modulations of the SRGs were up to 200 nm using a diffraction phase mask for the record. Considering the azobenzene-functionalized polyimides it can be concluded that, in most cases, η and amplitude of the SRGs do not exceed 2% and 115 nm, respectively [6]. The exceptions are two poly(amide imide)s with a high content of azobenzene groups in the repeating units, where the diffraction efficiencies were 31.5 and 43.8%, with modulations of the SRGs equal 178 and 260 nm [26,27].

Continuing our many years of investigations in explaining the photo-generated behaviour of azopolyimides, this work aims to show the differences in photoresponse of "T-type" polyimides contained azobenzene or azopyridine moieties. In particular, to determine the yield of *cis-trans* isomerization, values and stability of the photoinduced birefringence, efficiency of the diffraction gratings inscription, and sinusoidal deformation of SRGs using a degenerate two-wave mixing technique. It should be noticed, that the photoinduced birefringence has not been studied for "T-type" polyimides with azopyridine moieties. Our studies showed that the photoinduced response does not exist in azopyridine-functionalized polyimides, which can be a result of the intramolecular H-bonds between azo groups and polymer backbone

and/or *trans-cis* isomerization mechanism of azopyridine compound. Together with the low photoresponse of azopyridine-containing polyimides, we unexpectedly observed one of the highest diffraction efficiency (ca. 20%) and the largest modulation of the SRG ($d = 260$ nm) reported so far in the literature for azobenzene-functionalized polyimides. It is the first time when the large efficiency of the diffraction grating and high modulation of the SRG was observed for polyimide with relatively low content of azochromophore in the repeating unit. Moreover, modulation of the SRG for poly(ether imide) was highly stable. Two years after SRG inscription, any decrease in the modulation depth was not observed.

This paper is organized as follows. The main body of the article presents the structural characterization of the studied azopolyimides as well as their physico-chemical properties, i.e., solubility in organic solvents, thermal and optical properties, including the efficiency of the *trans-cis* transitions. Then, the results of the measurements on photo-induced birefringence generation and surface relief grating inscription are given and discussed in the context of the DFT calculations indicating the formation of the intramolecular H-bonds in some of the materials. The details of the synthetic route of the azopolyimides, and the technics used to characterize prepared materials are included in [Supporting Information](#).

2. Results and discussion

In this work, two series of "T-type" azopolyimides were investigated. Presented materials were prepared from two azochromophores i.e. azobenzene (2,4-diamino-4'-azobenzene) or azopyridine ((4-[(E)-(pyridin-4-yl)diazenyl]benzene-1,3-diamine) derivatives and three different dianhydrides containing ether (4,4'-(4,4'-isopropylidenediphenoxy)-bis(phthalic anhydride), 4,4'-oxydiphthalic anhydride) or ester (2,2'-[N'-phenylethylamine-di(4-estro-1,2-dicarboxylic)]anhydride) groups. The chemical structures of the studied azopolyimides are depicted in [Fig. 1](#). Polyimides **PI-AzPy-3** and **PI-Az-3** are new materials, while the other polyimides were synthesized and characterized in our previous works [25,28,29]. The designed chemical architectures of the polymers allowed studying the effect of the main chain structure and influence of the introduction of the pyridine ring to azochromophore on photoinduced properties.

2.1. Polymer characterization

The chemical structures of new azopolyimides **PI-Az-3** and **PI-AzPy-3** were determined by ^1H NMR, FTIR spectroscopies, and elemental analysis. ^1H NMR spectra showed signals in the range 7.39 – 8.77 ppm corresponding to the aromatic rings for all PIs. FTIR spectra exhibited absorption bands at 1780 cm^{-1} and 1720 cm^{-1} characteristic for the asymmetric and symmetric stretching vibrations of the carbonyl group in the imide ring. The absorption peaks at 1365 cm^{-1} and 744 cm^{-1} were attributed to C-N stretching and deformation vibration of the imide ring, respectively. Polyimide **PI-AzPy-3** with a derivative of azopyridine exhibited absorption at 928 cm^{-1} attributed to the pyridine ring. The elemental analysis exhibited ca. 1 % differences in the content of carbon.

Wide-angle X-ray diffraction measurements performed for azopolyimides showed the same diffraction patterns with one broad peak in the range of 16 – 40° of the diffusion type typical for perfectly amorphous materials ([Fig. S1](#) in [Supporting Information](#)) [25,28]. For **PI-AzPy-3** three broad diffusion peaks were observed, which could result from higher dispersity in comparison to the other polyimides ([Table 1](#)).

The SEC analysis in DMF was applied to estimate revealed average molar masses of the polymers. It should be stressed that the obtained values of molecular masses should be treated only indicatively. Absolute molar masses may differ from the calculated based on calibration if hydrodynamic values of the studied polymers differ from those of the polystyrene standards. The revealed number (M_n) and weight (M_w) average molar masses, and reduced viscosity (η_{red}) are collected in

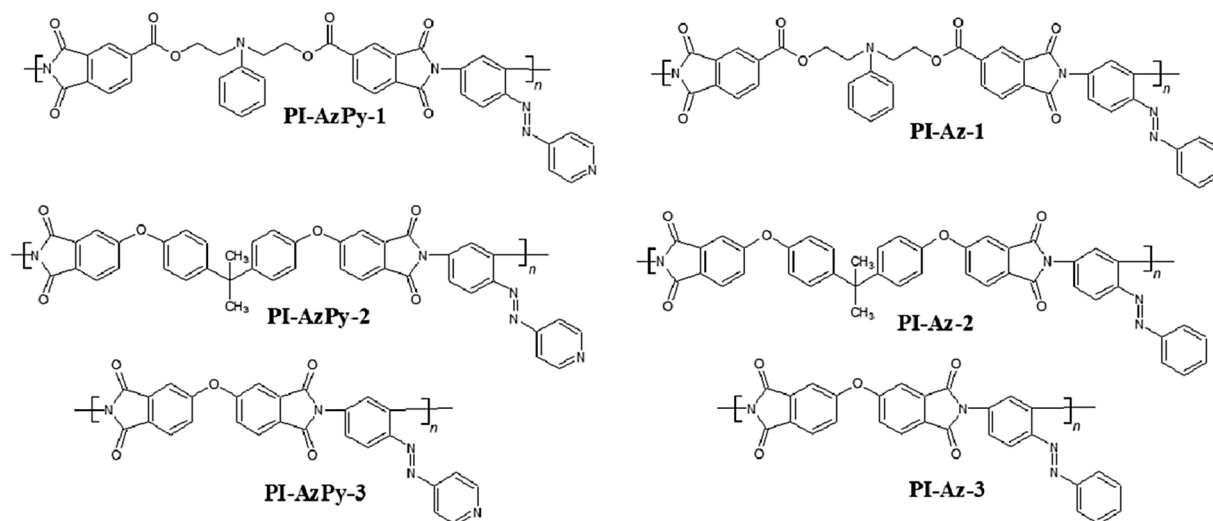


Fig. 1. Chemical structures of azopolyimides.

Table 1

Reduced viscosity (η_{red}), number-average (M_n) and weight average (M_w) molecular weights and the dispersity (M_w/M_n) of azopolyimides.

Polymer code	η_{red} (dL g ⁻¹)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
PI-AzPy-1	0.1 [25]	1 500	2 500	1.6
PI-AzPy-2	0.1 [25]	4 300	19 000	4.5
PI-AzPy-3	0.2	4 000	22 000	5.5
PI-Az-1	0.1 [25]	2 400	3 100	1.3
PI-Az-2	0.1 [25]	2 100	3 900	1.9
PI-Az-3	0.2	5 300	10 500	2.0

Table 1. Reduced viscosity was 0.1 or 0.2 (dL g⁻¹) for all polyimides. Values of M_w were in the range of 2500–22000 g/mol. Low values of M_w and η_{red} suggest the oligomeric nature of azopolyimides.

The solubility of polyimides was tested by the dissolution of 10 mg of the polymer in 1 ml of the organic solvent at room temperature. When the polymer was insoluble, the mixture was heated to the boiling point of the solvent. All azopolyimides were soluble in polar solvents, like NMP, DMSO and DMF and partially or non-insoluble in THF, cyclohexanone, and chloroform (Table S1 in Support. Inf.). Compare the polymers with similar molecular masses (PI-AzPy-1 and PI-Az-1) it can be noticed that the presence of azopyridine units limited the polymer solubility in low polar solvents.

The DFT method was used to get insight into a possible geometry of azopyridine functionalized polyimides (PI-AzPy-1 – PI-AzPy-3). The calculations were carried out for three repeating structural units. The optimized geometries of the polyimide chains together with some intramolecular hydrogen bonds are shown in Fig. 2.

The intramolecular hydrogen bonds between hydrogen from the aromatic ring and nitrogen in azo group N = N or oxygen of the carbonyl in the imide ring were observed for all azopyridine functionalized polyimides. Additionally, H-bonds between protons from phenyl ring and oxygen in ether or ester groups occur. The non-covalent connection of azo groups to the main chain of the polymer backbone can lead to the undesirable hindering of the *trans*-*cis* isomerization, which causes the lack of the photoinduced birefringence generation in the sample [29].

2.2. Thermal properties

Thermal properties including thermal stability and glass transition temperatures (T_g) of azopolyimides were evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Thermal properties for polymers denoted as PI-AzPy-1, PI-AzPy-2, PI-

Az-1, and PI-Az-2 were evaluated in our previous works [25,28]. The results of DSC and TGA measurements are collected in Table S2 in Supporting Information. The beginning of the thermal decomposition based on temperatures of 5% (T_5) and 10% (T_{10}) weight loss appeared in the range of 248–465 °C and 298–510 °C, respectively. All polymers characterized residual weight at 800 °C in the range of 37–60%. Considering the influence of the chemical structure of azopolyimides on thermal stability, it is seen that the incorporation of the pyridine ring to the azobenzene structure decreases the T_5 temperatures. Polyimides exhibited high values of T_g s in the range of 165–243 °C, despite their low molar masses (cf. Table 1). PI-Az-3 and PI-AzPy-3 showed higher T_g s than previously reported azopolymers [25,28]. It can be a result of their higher molar masses (cf. Table 1) and/or more rigid structure of the main chain. DTG curves for PI-Az-3 and PI-AzPy-3 are showed in Fig. S2 in Support. Inf..

2.3. Cis-trans isomerization reaction

The UV–Vis absorption properties of new azopolyimides (PI-AzPy-3, PI-Az-3) were investigated in the form of polymer films deposited on a glass substrate and in NMP solution (concentration 10⁻⁵ mol/L). Fig. S3 in Support. Inf. presents the UV–Vis absorption spectra measured for PI-AzPy-3 and PI-Az-3, which were compared with the spectra of polyimides described previously [25]. Table S3 in Support. Inf. compares the wavelengths (λ_{max}) corresponding to the maximum of the absorption bands observed for the six studied polyimides. As it is seen from Fig. S3, each spectrum recorded for PI-Az-3 showed two characteristic absorption bands attributed to the π - π^* and n - π^* electronic transitions of azo moieties, respectively. However, the bands were not present in the spectrum of PI-AzPy-3 (neither in solution nor in the film). PI-AzPy-2 and PI-Az-2 showed similar absorption spectra as PI-AzPy-3 and PI-Az-3, respectively, while for PI-AzPy-1 a slightly better-formed absorption bands were observed in the region (300–500) nm [25]. It is interesting to note that for structurally similar “T-type” azopolyimides containing azochromophores with pyridine ring being a part of the polymer main chain (i.e., unlike in the presented polymers which contain pyridine ring at the free end of the azo moiety) [25], the well-defined band maxima in the spectral region (300–500 nm) were not visible either. Taking the above into account we conclude that incorporation of a nitrogen atom in one of the phenyl rings of azobenzene chromophore results in large changes in the UV–vis absorption properties. Moreover, we postulate that for azopyridine-containing polyimides the lack of the absorption maxima typical for classical azobenzene polymers might be attributed to the presence of intramolecular H-bonds between the N = N group of

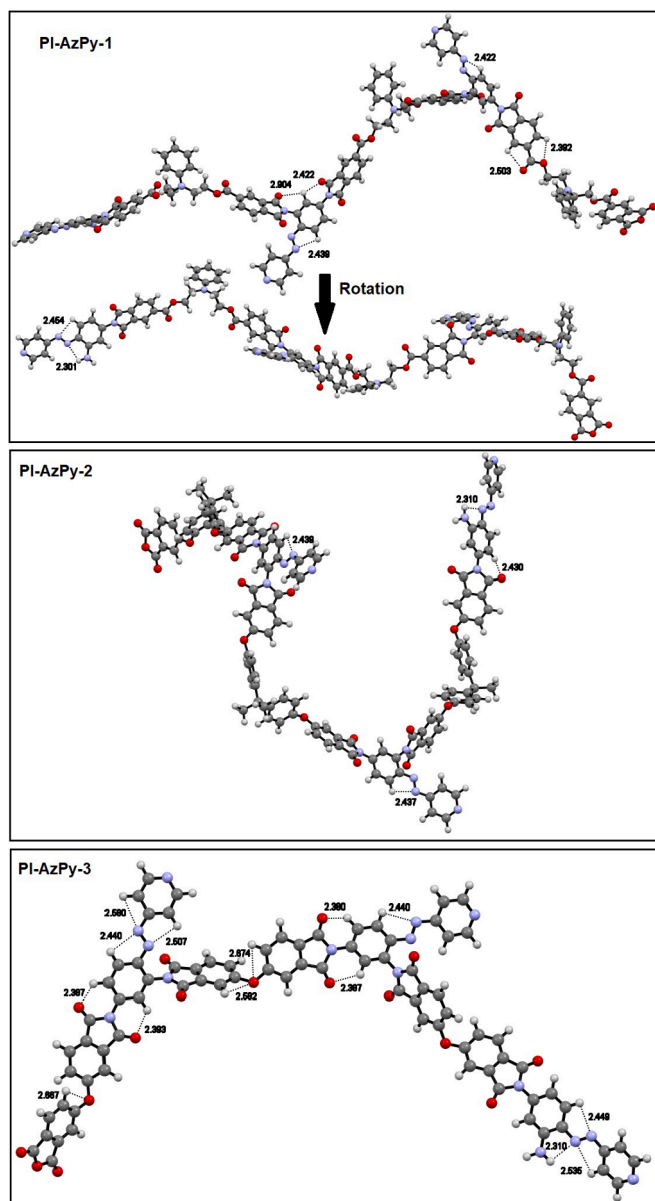


Fig. 2. Calculated geometries of azopyridine functionalized polyimides (trimers) PI-AzPy-1 – PI-AzPy-3 by DFT method with marked H-bonds with length in Å.

azopyridine and hydrogen in aromatic ring (cf. Fig. 2), which was revealed in DFT calculations.

The *cis*–*trans* isomerization upon diode light ($\lambda = 405$ nm; $P = 9$ W; irradiation time 3 min) was described previously for PI-Az-1, PI-Az-2, PI-AzPy-1, and PI-AzPy-2 [25]. In this work, the *cis*–*trans* isomerization process was studied after 5 min exposure to the 405 nm diode laser light ($P = 80$ mW). *Trans*–*cis* reaction was confirmed by the presence of isosbestic points, a reduction in band intensity and blue shift of λ_{\max} (Fig. 3). The *cis*-isomer content was calculated according to equation 1 (showed in the Supporting Information) directly after 5 min of laser irradiation and was collected in Table 2.

Turning off the excitation light resulted in the thermal *cis*–*trans* isomerization of azo groups observed as an increase in the intensity of λ_{\max} (Fig. 3). Changes in the absorption spectrum of azobenzene-functionalized polyimides were monitored for up to 6 days. The fastest recovery to the *trans* form was observed for PI-Az-2.

2.4. Photoinduced birefringence and surface relief grating inscription

The process of photoinduced birefringence generation was studied using a 405 nm excitation beam. The film absorption coefficients at 405 nm were 2.2×10^4 , 1.9×10^4 or 1.0×10^4 cm^{-1} for PI-Az-1, PI-Az-2 or PI-Az-3, respectively. The absorption coefficients of the azopyridine analogues were slightly larger and equal to 4.1×10^4 , 3.4×10^4 , or 5.7×10^4 cm^{-1} for PI-AzPy-1, PI-AzPy-2 or PI-AzPy-3, respectively. For three azobenzene polyimides, turning on the writing light resulted in a systematic growth of optical birefringence with irradiation time (Fig. 4a). After turning off the excitation light, a gradual decrease in the induced birefringence was observed due to *cis*–*trans* back-reactions and angular disordering of the *trans* azo moieties (Fig. 4b). On the other hand, sample irradiation with a 405 nm beam caused no birefringence generation in PI-AzPy-1, PI-AzPy-2 and PI-AzPy-3. The lack of photoresponsive behaviour indicated highly inefficient *trans*–*cis* isomerization reactions under blue light illumination and correlated with the results of *cis*–*trans* isomerization studies demonstrating no changes in the UV–vis absorption spectra of azopyridine polyimides upon irradiation (see Table 2). Thus, functionalization of polyimides by incorporation of pyridine structure from azopyridine derivative, into polymer as side group gives no photoresponsive azo material.

As it can be seen from Fig. 4a the measured values of final birefringence of the three azobenzene polyimides were similar and equal to ca. 0.015, which is rather a low birefringence level, when compared to the values obtained for other “T-type” azopolymers with one azo moiety in a polymer repeating unit. [9,29,30]. Saturation of birefringence generation process was found for PI-Az-1 but was not observed for PI-Az-3, which possessed the largest molecular weight among the studied azobenzene materials. Moreover, a relatively slow birefringence decrease after irradiation (by only 6% during ca. 8 min in the dark) was found for PI-Az-1 and PI-Az-3, while an evidently less stable birefringence exhibited PI-Az-2. The latter observation correlates with the results of thermal *cis*–*trans* isomerization studies (par. 2.3) revealing the least stable *cis* isomers for PI-Az-2.

The experiments on SRG inscription were carried out for the azobenzene polyimides using two coherent 442 nm beams with opposite circular polarizations. Since the angle between the recording beams was relatively small (i.e., 7°), it could be assumed that the resulting interference pattern was characterized by almost constant intensity distribution in the interference region and the resulting polarization state being linear with an azimuth that continuously rotates along a transverse direction [31,32]. The 442 nm irradiation excited the n – π^* electronic transitions of the *trans* isomer in the case of the PI-Az-2 and PI-Az-3 polymer layers, while both of the π – π^* and n – π^* transitions were induced in the case of PI-Az-1 (see Fig. 3).

For each of the studied material layer, the irradiation process was accompanied by the formation of a diffraction grating. The +1st and –1st order diffracted probe beams (690 nm) were observed behind the samples at the angles of ca. $\pm 10^\circ$ as expected for gratings with a designed spacing of 3.6 μm . Fig. 5 presents the temporal evolution of the +1st order diffraction efficiency (please note that the +1st order diffraction efficiency is defined as the ratio between the intensity of the probe beam diffracted into this order and the intensity of the incident probe beam).

After 90 min of irradiation, the +1st order diffraction efficiency reached a very large value of ca. 20% for PI-Az-2. Simultaneously, the presence of higher-order diffracted beams (up to the fifth-order) was detected behind this sample. It should be noticed, that the maximum theoretical value of the diffraction efficiency of phase grating predicted from the first-order Bessel function is 33.9% [33]. The +1st order diffracted signal was relatively strong (ca. 6.5%) for PI-Az-3, while low diffraction efficiency was observed for PI-Az-1 (ca. 1%). Examination of surface topography after irradiation confirmed the presence of regular relief structures on the surfaces of all the studied azobenzene polyimides. The period of the structures was 3.8 μm , equal within the

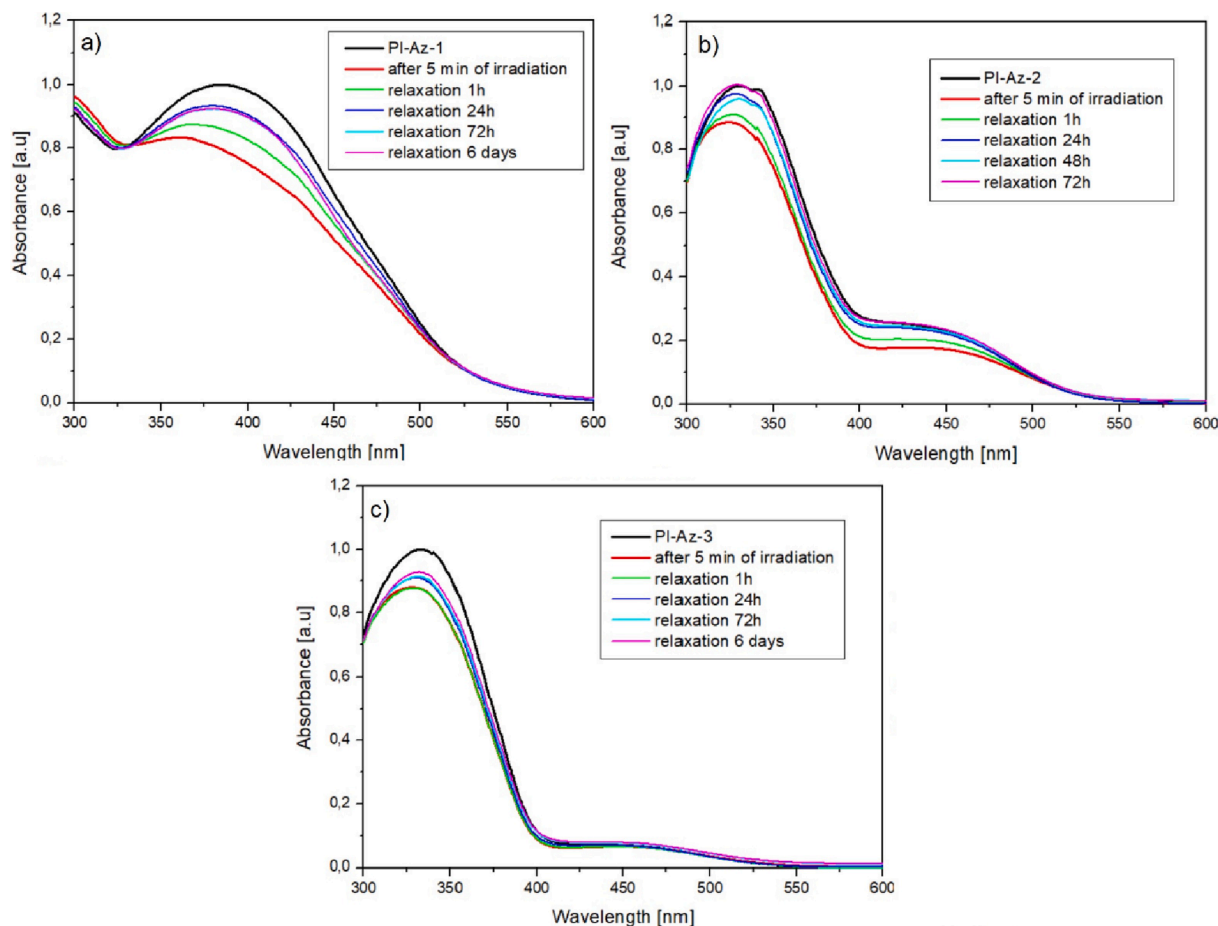


Fig. 3. UV-Vis spectra in the solid-state for (a) **PI-Az-1**, (b) **PI-Az-2**, (c) **PI-Az-3**; before irradiation (black curve); after 5 min of irradiation with 405 nm light (red curve); after 1 h to 6 days from switching off 405 nm light (green, blue, or cyan curve, respectively). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2

Maximum absorption wavelength (λ_{\max}) of the *trans*- and *cis*-isomers in the solid-state, location of the isobestic points and content of *cis*-isomer obtained directly after 5 min of irradiation for azopolyimides.

Polymer code	λ_{\max} of the <i>trans</i> -form [nm]	λ_{\max} of the <i>cis</i> -form [nm]	Isobestic points [nm]	Content of <i>cis</i> -isomer (%)
PI-AzPy-1	301; 383*	–	–	–
PI-AzPy-2	301	–	–	–
PI-AzPy-3	302	–	–	–
PI-Az-1	384	361	331; 533	17
PI-Az-2	330; 437*	325	521	12
PI-Az-3	333; 450	329	491	12

experimental errors to the period of the arranged light interference pattern. In the case of **PI-Az-2**, the sinusoidal modulations were as deep as 260 nm (Fig. 6). The amplitudes of the two other relief gratings were lower and equal to ca. 17 nm or 30 nm for **PI-Az-1** or **PI-Az-3**, respectively. For **PI-Az-2** the stability of the SRG was checked. Poly(ether imide) characterized high stability of the sinusoidal deformation. Two years after the generation of the surface relief grating we did not observe any decrease in the modulation.

The obtained results indicate that the chemical structure of the **PI-Az-2** and **PI-Az-3** materials is advantageous for the holographic recording of efficient diffraction gratings. A lower amplitude of surface grating in **PI-Az-3** in comparison to that in **PI-Az-2** might be attributed to its larger molecular weight and/or more rigid chemical structure. The result observed for **PI-Az-2** is surprising, comparing to other poly(ether

imide)s similar in the structure to **PI-Az-2** i.e. synthesized from 4,4'-(4,4'-isopropylidenediphenoxy)-bis(phthalic anhydride) dianhydride and azochromophore with CN or CH₃ substituents [34]. These polymers exhibited significantly lower diffraction gratings efficiency (0.01–0.33%) and modulations of SRGs (up to 10 nm). The surface modulation depth generated in **PI-Az-2** is remarkably high, and interestingly, is equal to the modulation depth of the relief fabricated in functionalized azopoly(amide imide)s containing much larger azobenzene concentration, i.e., mono- and bis-azobenzene groups in the repeating unit [26]. However, taking into account the economical point of view production of previously reported poly(amide imide)s is highly expensive, because of a multi-step synthesis, which includes preparation of two different azochromophores, dianhydride, and in the final step – an azopolyimide. The advances of **PI-Az-2** are attractive photoinduced properties and much cheaper synthesis than previously reported. For the preparation of **PI-Az-2**, we used a commercially available dianhydride and easy in synthesis azochromophore, which was prepared from cheap substrates in an environmentally safe aqueous solvent. Moreover, **PI-Az-2** exhibited very good solubility in low-boiling solvents as THF or CHCl₃, which is an additional advantage of this material.

The modulation of the SRG in **PI-Az-2** was measured two years after the inscription. We did not observe any decrease in the surface modulation depth. It should be mentioned that the polymer sample was not extra protected from the environmental factors i.e. humidity, temperature, light. The sample spent two years wrapped in aluminium foil. For a better understanding of the large and stable photoresponse of **PI-Az-2** additional investigations are necessary, which are in progress and will be presented in our future work.

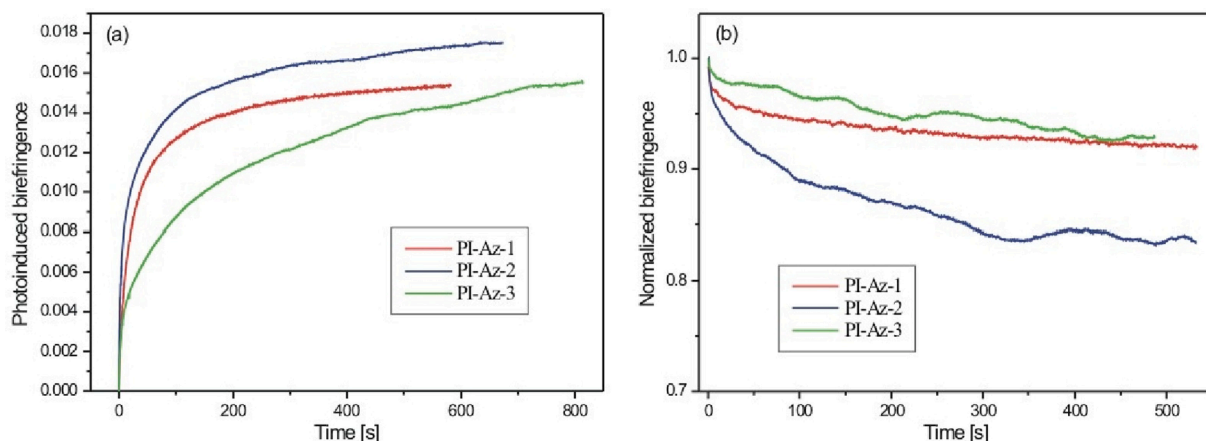


Fig. 4. (a) Birefringence growths, (b) decays, after switching on and off 405 nm 100 mW/cm² excitation beam, respectively. Data for PI-Az-1 taken from [28].

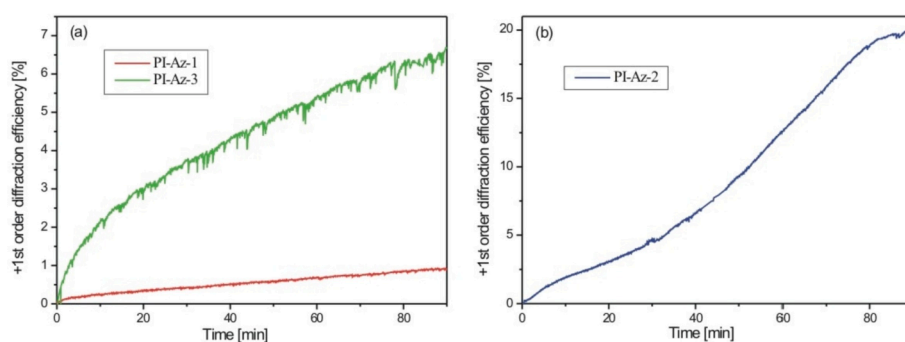


Fig. 5. Temporal evolution of the +1st order diffraction efficiencies of the gratings generated in (a) PI-Az-1 and PI-Az-3, (b) PI-Az-2.

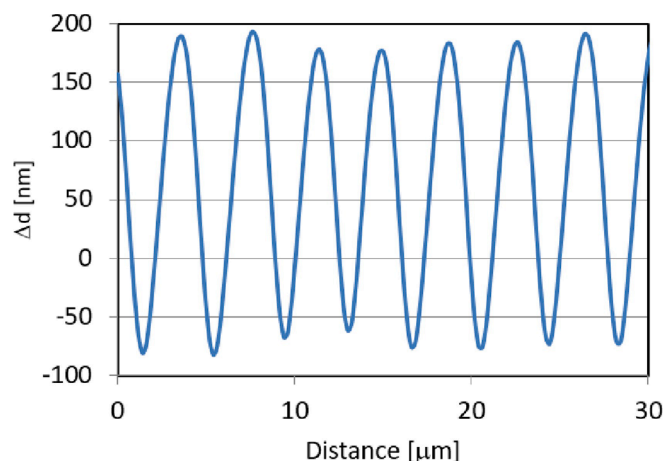


Fig. 6. Surface profile measured after irradiation for PI-Az-2.

3. Conclusions

The photoresponsive behaviour of functionalized azobenzene and azopyridine T-type polyimides was investigated upon irradiation with a single 405 nm light beam or 442 nm light interference pattern. The studies included UV-vis spectroscopy measurements of *cis-trans* isomerization reaction, efficiency of photoinduced birefringence generation and surface relief grating formation. The obtained results showed that incorporation of a nitrogen atom to the azobenzene structure had a disadvantageous effect on light-induced processes, as reduces significantly the efficiency of *trans-cis* conversion of the azo group. In

consequence, neither birefringence generation nor surface relief grating fabrication was observed. The possible structural feature leading to inefficient isomerization reactions in azopyridine polyimides is a formation of intramolecular hydrogen bonding between the nitrogen of the azo group N = N and hydrogen from the aromatic ring of the azo moiety, which was revealed in DFT calculations. The experiments on holographic grating recording demonstrated that in two azobenzene materials, i.e., PI-Az-2 and PI-Az-3, surface relief gratings may be quite easily formed upon irradiation with light interference pattern and exciting the $n-\pi^*$ electronic transitions of the *trans* isomer. The surface grating inscribed particularly in PI-Az-2 possessed a remarkably high modulation depth, equal to 260 nm, and thus the fabricated grating was characterized by a very high diffraction efficiency of 20% for the +1st order. The large amplitude of relief structure inscribed in PI-Az-2 despite its rather low azo moiety concentration indicates a beneficial role of its polymer backbone structure in the macroscopic mass transport phenomenon. PI-Az-2 characterized the high stability of the formed relief grating. Two years after SRG inscription the modulation was still observed with no decrease, which proves its great application potential.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was funded by the National Science Centre, Poland, grant number UMO-2019/35/D/ST5/00533.

