

# POLIMERY

CZASOPISMO POŚWIĘCONE CHEMII, TECHNOLOGII I PRZETWÓRSTWU POLIMERÓW

## Azopolyimides – influence of chemical structure on azochromophore photo-orientation efficiency<sup>\*)</sup>

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**Abstract:** This work is a summary of our previous investigations of polyimides containing derivatives of azobenzene or azopyridine. Here we discussed the relationship between the microstructure of azopolyimides and azochromophore photo-orientation efficiency determined in measurements of photo-induced birefringence as well as the relationship between the microstructure of azopolyimides and their selected physical properties. The designed architecture of azopolymers allowed to trace the effect of such structural elements as the structure of the polymer main chain and chromophore, its content, location including the method of dye assembling with the polymer matrix on thermal, optical and photoinduced properties. We also discussed the possibility of the intermolecular hydrogen bonds formation in functionalized azopolyimides, which hinder isomerization of the azobenzene molecules results the photoinduced birefringence is not observed in the material. Additionally, the possibility of potential applications of azopolyimides as layers for the liquid crystal alignment was presented.

**Keywords:** azobenzene derivatives, azopolymers, photoinduced birefringence, liquid crystal alignment.

## Azopoliimidy – elementy strukturalne a efektywność fotoorientacji azochromoforów

**Streszczenie:** Artykuł stanowi podsumowanie naszych badań dotyczących azopoliimidów zawierających pochodne azobenzenu lub azopirydyny. Przedstawiono zależność między budową azopolimerów a efektywnością fotoorientacji azochromoforów, określaną na podstawie mierzonej fotoindukowanej dwójłomności, z uwzględnieniem wpływu struktury na wybrane właściwości fizyczne. Przedmiotem rozważań były azopolimery o odpowiednio zaprojektowanej budowie chemicznej pozwalającej na określenie wpływu struktury łańcucha głównego polimeru, a także chromoforu, jego zawartości i sposobu przyłączenia oraz lokalizacji w merze polimeru na właściwości termiczne, optyczne i fotoindukowane

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światłem spolaryzowanym. Omówiono także możliwość tworzenia w polimerach funkcjonalizowanych międzycząsteczkowych wiązań wodorowych, które hamują izomeryzację grup azobenzenowych, w wyniku czego nie obserwuje się generowania fotoindukowanej dwójłomności w materiale. Przedstawiono ponadto badania aplikacyjne, które wykazały możliwość porządkowania mieszaniny ciekłokrystalicznej za pomocą warstw otrzymanych z wybranych azopoliimidów.

**Słowa kluczowe:** pochodne azobenzenu, azopolimery, fotoindukowana dwójłomność, porządkowanie ciekłych kryształów.

The dynamic development of optoelectronics and photonics has become a driving force in recent years to find new, recyclable, photoactive organic materials, in which light can cause changes in physicochemical parameters. The advantage of organic materials is the relatively easy modification of their chemical structures and consequently their properties for specific applications. In addition, the ease of integration in the devices resulting from the ability of organic compounds to create thin films on a variety of substrates using a variety of techniques should be stressed [1]. Among photoactive materials, photochromic polymers bearing optically bistable molecules called chromophores are the dominant [2]. Photochromic polymers can find a variety of uses, for example, in holographic optical memory, in dynamic information processing systems, for the production of diffractive optical elements, as light couplers in planar fibers or as liquid-crystal layering in liquid crystal displays [3–5]. In all applications, due to chromophore photo-orientation, changes in the refractive index and absorption coefficient occur in the polymer, which induces dichroism and optical birefringence. Particular attention is given to compounds containing N=N bond between aromatic rings in which the photochromic mechanism is photoinduced *trans-cis-trans* isomerization [2]. Polymers containing this type of bonding are called azopolymers [6]. Among the azopolymers, the attention of researchers is mainly concentrated on the macromolecular compounds containing the azobenzene derivatives [1, 6–8]. Azopyridine-based polymers are much less studied [9–14], therefore, such systems were also selected as a research object in the presented work. Taking into account the way of attaching the chromophore to the polymer backbone, functionalized polymers containing a covalently attached chromophore, ‘guest-host’ systems with non-covalently attached dye which can be molecularly dispersed in a polymer matrix (doped systems) or connected *via* hydrogen or ionic bonds,  $\pi$ - $\pi$  sticks *etc.* (supramolecular assemblies) can be distinguish [8, 15].

The subject of research in this paper is aromatic azopolyimides, *i.e.*, polymers containing in their structure imide rings and azobenzene or azopyridine derivatives covalently attached to the polymer chain or by other non-covalent interactions, mainly hydrogen bonds. Selection of this group of polymers, *i.e.*, polyimides, was dictated by their high glass transition temperatures and high thermal stabilities, providing stability of the photoinduced

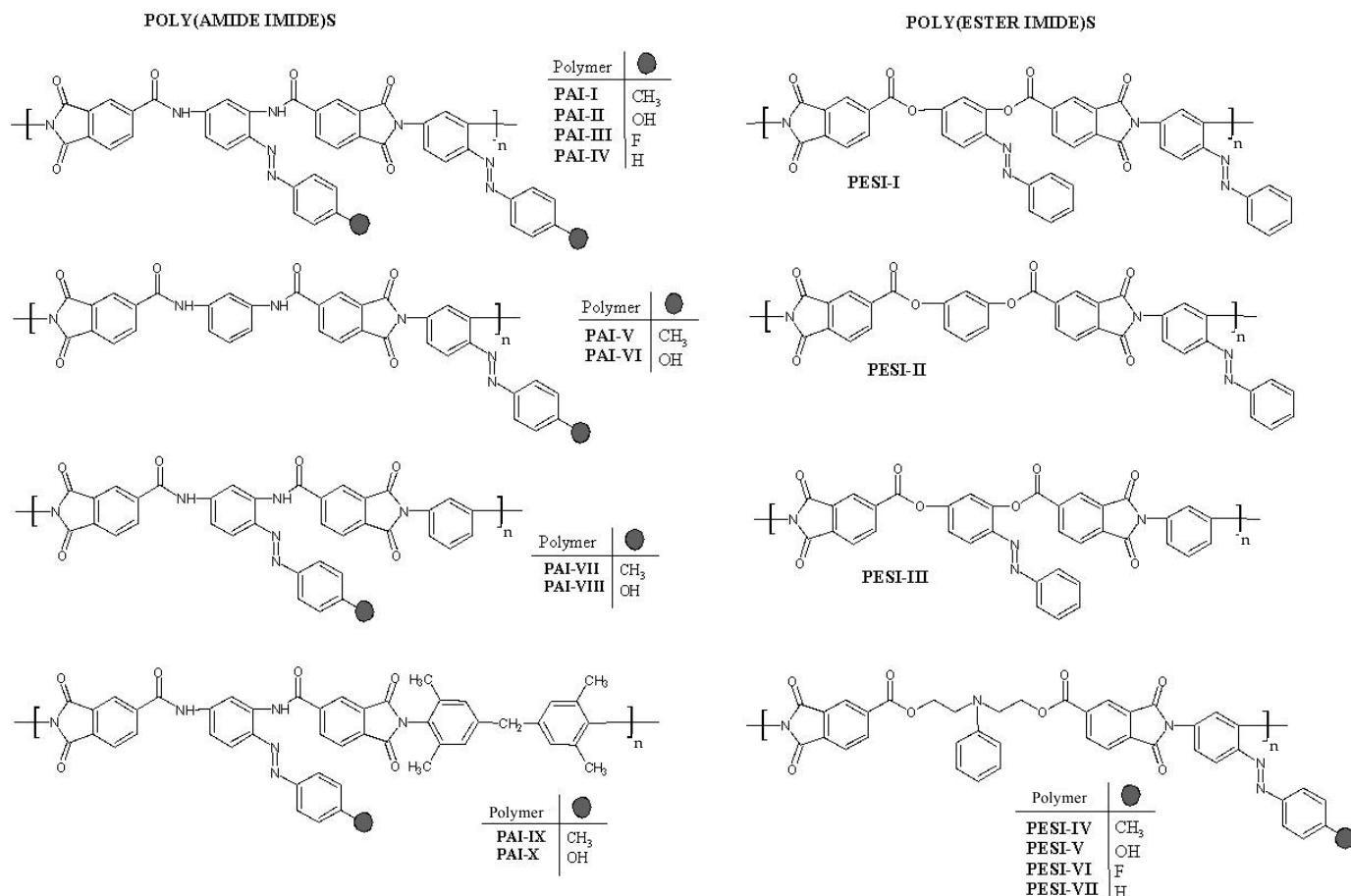
phenomena, low susceptibility to laser light damage and good chemical and mechanical resistance [16, 17]. The results described in numerous scientific papers show that polyimides containing covalently attached azobenzene derivatives easily form stable holographic diffraction gratings and surface relief gratings (SRGs) [9, 14, 18–20]. On the other hand, there is little literature on the effect of the chemical structure of functionalized and ‘guest-host’ azopolyimides on the photoinduced birefringence and its stability after ceasing the excitation beam [13, 21–25]. Due to the fact that photoinduced optical anisotropy is influenced by a number of factors referring to the chemical structure of azopolymers, detailed characterization of the relationship between azopolymer architecture and the photoinduced effects may allow optimization of the properties of the synthesized azopolymers to their intended uses. The research was conducted in “feedback”, *i.e.*, the results of investigations of certain properties, including photoinduced optical birefringence, were the inspiration for further chemical modification of the obtained compounds.

#### EFFECT OF THE POLYMER STRUCTURE ON THE SELECTED PHYSICAL PROPERTIES

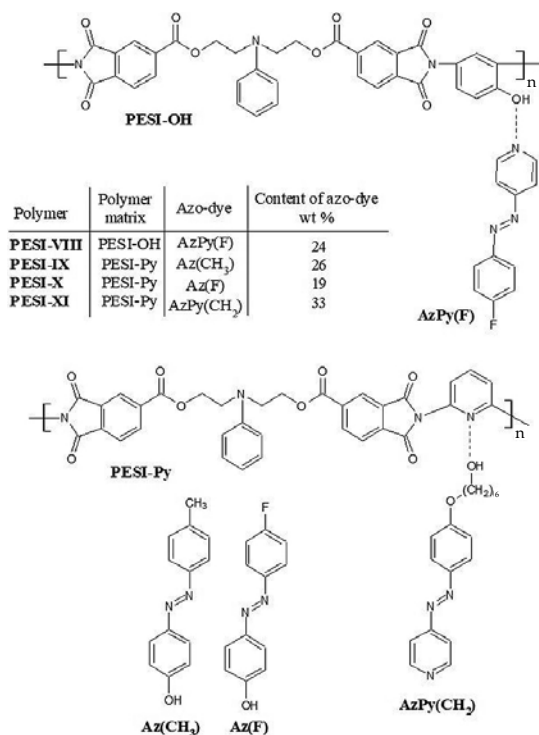
In this work two kinds of azopolymers, that is functionalized azopolyimides containing covalently bonded derivatives of azobenzene (Scheme A) and the ‘guest-host’ assemblies with the non-covalent attachment of azo-dyes (Scheme B) are discussed. Synthesis and characterization of functionalized poly(amide imide)s (PAI) were reported in our previous works [23, 24], while poly(ester imide)s (PESI-I – PESI-VII) were described in [21, 22]. Poly(amide imide)s denoted as PAI-VII and PAI-VIII have not been described in the literature yet.

Our previous reported studies [13] revealed that PESI-VIII and PESI-XI are supramolecular systems based on hydrogen bonds between polymer matrix and chromophore, while PESI-IX and PESI-X can be treated as doped polymers.

The presented polymers differing in structural element allowed for description the effect of the microstructure of the polymer main chain and chromophore structure, its content, location including the method of dye assembling with polymer matrix, and also influence of the intermolecular hydrogen bonds formation in functionalized azopoly(amide imide)s on the photoinduced bire-



Scheme A. Functionalized azopolyimides



Scheme B. 'Guest-host' assemblies containing derivatives of azobenzene or azopyridine

fringence and its stability. All of the polymers exhibited an amorphous structure and good film-forming properties. Their basic important physical properties together with a photoinduced birefringence ( $\Delta n$ ) and its stability as the percentage of  $\Delta n$  are conserved in the polymer film after switching off the excitation beam ( $\Delta n_{\text{norm}}$ ) [23]. Film thickness ( $d$ ) measured with a Dektak XT stylus profiler are collected in Table 1.

### Microstructure of the polymer backbone

Taking into account the microstructure of the main chain of the polymers, three pairs of functionalized azopolymers, *i.e.*, PAI-IV with PESI-I, PESI-II with PESI-VII, PAI-VII (PAI-VIII) with PAI-IX (PAI-X), are considered. The microstructure of the main chain greatly influences the solubility of polymers. In general replacement of amide linkages with ester groups improved solubility of polyimides. Poly(amide imide)s PAI-VII and PAI-VIII with chromophore between amide linkages and phenyl between imide rings were insoluble and were excluded from further investigations. Modification of the poly(amide imide)s backbone by incorporation of diphenyl methane derivative (PAI-IX and PAI-X) instead of phenyl rings (PAI-VII) gave soluble polymers. PAI-IX and PAI-X were soluble in NMP (*N*-methylpyrrolidone) and partially soluble in THF (tetrahydrofuran) and CHCl<sub>3</sub>. The presence of amide linkages raises the glass transitions temperatures ( $T_g$ ) that can be seen con-

**Table 1.** Molecular weight ( $M_w$ ) and the dispersity ( $D$ ), reduced viscosity ( $\eta_{red}$ ), glass transition temperature ( $T_g$ ), temperature of 5 % weight loss ( $T_{5\%}$ ), value of the photoinduced birefringence ( $\Delta n$ ) and its stability ( $\Delta n_{norm}$ ), absorption coefficient at 405 nm ( $\alpha_{405}$ ) and layer thickness ( $d$ )

Polymer	$M_w \cdot 10^{3[1]}$ , g/mol or $\eta_{red}^a$ , dl/g	$T_g^{[2]}$ , °C	$T_{5\%}^{[3]}$ , °C	$\Delta n^{[4]}$	$\Delta n_{norm}$ , %	$\alpha_{405}$ , cm <sup>-1</sup>	$d$ , μm
PAI-I	41.2 ( $D = 2.1$ )	nd	258	0.06	95	$1.0 \cdot 10^5$	0.13
PAI-II	14.0 ( $D = 1.7$ )	281	335	0.055	98.5	$1.0 \cdot 10^5$	0.12
PAI-III	2.8 ( $D = 1.9$ )	247	361	0.06	98.5	$2.5 \cdot 10^5$	0.06
PAI-IV	6.8 ( $D = 1.6$ )	254	371	0.055	98.5	$1.0 \cdot 10^5$	0.19
PAI-V	1.9 ( $D = 1.7$ )	247	290	nd	–	$3.5 \cdot 10^4$	0.38
PAI-VI	1.9 ( $D = 1.7$ )	240	352	nd	–	$3.0 \cdot 10^4$	0.22
PAI-IX	31.0 ( $D = 1.7$ )	333	380	0.025	82	$7.0 \cdot 10^4$	0.41
PAI-X	11.4 ( $D = 2.0$ )	207	333	0.03	92	$6.0 \cdot 10^4$	0.19
PESI-I	0.3 <sup>a</sup>	195	310	0.035	93	$2.2 \cdot 10^4$	0.45
PESI-II	0.1 <sup>a</sup>	174	246	0.03	96	$1.2 \cdot 10^4$	0.84
PESI-III	0.4 <sup>a</sup>	206	245	0.017	92	$2.1 \cdot 10^4$	0.66
PESI-IV	3.9 ( $D = 2.0$ )	146	295	0.025	95	$2.5 \cdot 10^4$	0.40
PESI-V	3.2 ( $D = 1.6$ )	170	294	0.025	88	$3.8 \cdot 10^4$	0.70
PESI-VI	3.9 ( $D = 2.0$ )	143	307	0.017	93	$2.0 \cdot 10^4$	0.56
PESI-VII	3.1 ( $D = 1.7$ )	145	303	0.015	93	$2.2 \cdot 10^4$	0.42
PESI-VIII	5.7 ( $D = 1.7$ )	167	nm	0.003	82	$2.7 \cdot 10^4$	0.45
PESI-IX	5.7 ( $D = 1.7$ )	93	nm	0.009	73	$1.1 \cdot 10^4$	2.00
PESI-X	5.7 ( $D = 1.7$ )	90	187	0.008	68	$0.6 \cdot 10^4$	0.90
PESI-XI	5.7 ( $D = 1.7$ )	122	nm	0.018	85	$2.4 \cdot 10^4$	0.45

nd – not detected, nm – not measured, <sup>[1]</sup> the molar mass and dispersity were determined by size exclusion chromatography (SEC) in DMF, <sup>[2]</sup> determined by DSC from the second heating cycle at 20 °C/min, <sup>[3]</sup> at a heating rate of 20 °C/min under controlled flux of nitrogen, <sup>[4]</sup> diode laser,  $\lambda_{prob.} = 690$  nm,  $\lambda_{exc.} = 405$  nm,  $I = 75$  mW/cm<sup>2</sup>,  $t = 1000$  s.

sidering polymer pair PAI-IV and PESI-I. Poly(ester imide) with aliphatic groups in the backbone (PESI-VII) is characterized by lower  $T_g$  than fully aromatic poly(ester imide) (PESI-II), because of the more flexible main chain. The investigations showed that structure of the polymers main chain significantly influences on the photoinduced birefringence. Large (0.055) and extraordinary stable (98.5 %) birefringence was generated in poly(amide imide)s PAI-IV. Its analogue with ester linkages (PESI-I) showed lower an  $\Delta n = 0.035$ . Reduction of polymer backbone flexibility by replacement of *N,N*-diethylaniline derivative between ester linkages (PESI-VII) by phenyl ring (PESI-II) increases twice birefringence value from 0.015 to 0.03 and slightly raises its stability, as well. Although, PESI-VII exhibited almost twice higher value of absorption coefficient at 405 nm ( $\alpha_{405}$ ) corresponding applied laser wavelength for  $\Delta n$  induction. It can be concluded that the presence of amide linkages in polymer backbone (PAI-IV with respect to PESI-I) and its rigidity (PESI-II with respect to PESI-VII) are responsible for a higher both induced birefringence and its stability. Stability of the photoinduced  $\Delta n$  depends on many material parameters, but mainly on  $T_g$  of azopolymer, if it is high then generally the stability is high if low it is low [12]. However, in the case of presented polymers which exhibited high  $T_g$ , it can be observed that this parameter did not decide about  $\Delta n_{norm}$  (cf. Table 1).

### Chemical structure of azochromophores

Considering the influence of azochromophore chemical structure, it means a kind of substituent in azobenzene group (-OH, -CH<sub>3</sub>, -F and -H), the following polymers are discussed: PAI-I – PAI-IV, PAI-IX, PAI-X, PESI-IV – PESI-VII (Scheme A) and PESI-IX with PESI-X and PESI-VIII with PESI-XI (Scheme B). Kind of azobenzene substituent does not effect on the solubility of the functionalized polyimides.  $T_g$ s were the highest for polyimides with OH substituent, which was 281 °C, 170 °C and 122 °C for PAI-II, PESI-V and PESI-XI, respectively, compared to polymers with other substituents. It should be stressed that a series of PESI-IV – PESI-VII exhibited similar weight average molar masses (cf. Table 1), thus its influence on  $T_g$  it is of no importance and kind of substituent is crucial. In comparing polyimides with four different substituents in azobenzene groups PAI-I – PAI-IV and PESI-IV – PESI-VII, the highest thermal stability by means of 5 % weight loss temperature ( $T_{5\%}$ ) was observed for polyimides with F and H atom, which were above 360 °C for poly(amide imide)s and 300 °C for poly(ester imide)s (Table 1). The highest differences in reached  $\Delta n$  value were observed in a series of poly(ester imide)s PESI-IV – PESI-VII. It was found that poly(ester imide)s with azobenzene moieties containing CH<sub>3</sub> and

OH groups showed the highest  $\Delta n$  comparing to polymers with F and H atoms. Poly(amide imide)s bearing methyl group as chromophore substituent (PAI-I and PAI-IX) exhibited lower  $\Delta n$  stability *ca.* 95 and 82 % comparing to others. Even though their molar masses and  $T_g$  are higher than polymers with others substituents and could be expected higher  $\Delta n_{\text{norm}}$ . The influence of -F, -OH and -H in chromophores in PAI-II – PAI-IV is not clearly pronounced. In ‘guest-host’ systems, PESI-IX and PESI-X exhibited a similar photoinduced birefringence of *ca.* 0.008 and stability, irrespectively of a kind of substituent. In the case of supramolecular PESI-VIII and PESI-XI with azopyridine compounds connected with hydrogen bonds with polymers, a significant difference in the value of  $\Delta n$  was observed. However, such differences are a result of kind of atoms between H-bonds are formed. PESI-VIII exhibited six times lower birefringence than PESI-XI. In PESI-VIII hydrogen bonds form between OH group of matrix and pyridine ring in the chromophore, what can hinder isomerization of the azopyridine and result in a low level of the photoinduced birefringence as was reported [13]. In the case of PESI-XI, the hydrogen bonds form far away from pyridine ring, what in our opinion may increase the efficiency of isomerization of the azopyridine chromophore and lead to a large value of  $\Delta n$ . Stability of  $\Delta n$  was similar for both azopolyimide assemblies.

### Azochromophore content and its localization in polymer backbone

Effect of chromophore content can be discussed in three pairs of functionalized polymers, that is, PESI-I with PESI-II, PAI-I with PAI-V and PAI-II with PAI-VI. Chromophore content, it means a number of azobenzene moieties in the polymer repeating units, does not impact on the solubility of the poly(ester imide)s and poly(amide imide)s [21–25]. Similarly, the increasing number of azobenzene as side units in the backbone does not clearly effect on the  $T_g$  and  $T_{5\%}$ . The presence of two chromospheres in the repeating units significantly raises their absorption coefficient. It is expected that together with increasing of chromophores content increase of the photoinduced  $\Delta n$  should be observed [12]. Surprisingly, in the case of poly(ester imide)s, with two (PESI-I) or one (PESI-II) chromophores per repeating unit, similar photoinduced birefringence was generated, although their  $\alpha_{405}$  differing almost twice. Moreover, the stability of the birefringence was higher for PESI-II. In poly(amide imide)s definitely different relationship between a number of chromophores and  $\Delta n$  was detected. Namely, in PAI-V and PAI-VI bearing one azo-dye in the polymer repeating unit the birefringence was not induced, despite the fact that PAI-V and PAI-VI exhibited lower molar masses than PAI-I and PAI-II, which should be conducive to the inscription of higher birefringence [26]. Whereas, in PAI-I and PAI-II a relatively high value of  $\Delta n$  (0.06) was registered. Therefore, other polymers also with one azobenzene but localized between amide linkages (PAI-IX and PAI-X) were pre-

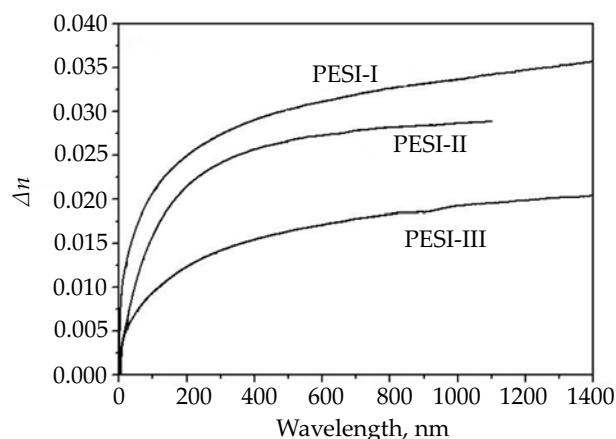


Fig. 1. The photoinduced birefringence of fully aromatic poly(ester imide)s

pared. In these polymers birefringence *ca.* 0.03 was successfully generated. Thus, it can be concluded that in poly(amide imide)s except for a number of azo-dye units, chromophore location in polymer backbone plays the crucial role due to intermolecular hydrogen bonds formation. In our previous work [24], it was proved that formation of the hydrogen bonds in poly(amide imide)s mostly depends on the position of the azobenzene group in the main chain. Strong intermolecular hydrogen bonds between amide groups in poly(amide imide)s (PAI-V and PAI-VI) limited chromophore photo-orientation resulted in a lack of birefringence. The impact of chromophore localization can be also observed in poly(ester imide)s (PESI-I, PESI-II and PESI-III). It seems that more beneficial is the location of the azo unit between imide rings (PESI-II) than between ester linkages (PESI-III) (Fig. 1). However, in this case, the influence of molar masses on  $\Delta n$  cannot be excluded because PAI-III, considering reduced viscosity value  $\eta_{\text{red}}$  showed higher molar masses, which may reduce the efficiency of chromophore orientation and lower  $\Delta n$  can be obtained.

### The way of azo-dye attachment to the polymer backbone

Polymers PESI-IX and PESI-X may be treated as the non-covalent analogues of the functionalized side chain poly(ester imide)s PESI-IV and PESI-VI (Scheme A). Covalent attachment of azobenzene significantly affects thermal properties ( $T_g$ ,  $T_{5\%}$ ), the photoinduced birefringence and its stability in the dark. Functionalized polyimides exhibited *ca.* 50 °C higher  $T_g$  than their non-covalent analogues. Covalent attachment of azochromophore favorably affected on  $T_{5\%}$ , which was 120 °C higher for functionalized PESI-VI than non-covalent PESI-X (Table 1). The photoinduced birefringence was also higher and more stable in the dark for PESI-IV and PESI-VI. Functionalized azopolyimides exhibited  $\Delta n$  *ca.* 0.02, while the birefringence of non-covalent PESI-IX and PESI-X did not exceed 0.009 (Table 1). In this case contrary to the most of the functionalized polymers, lower final birefringence

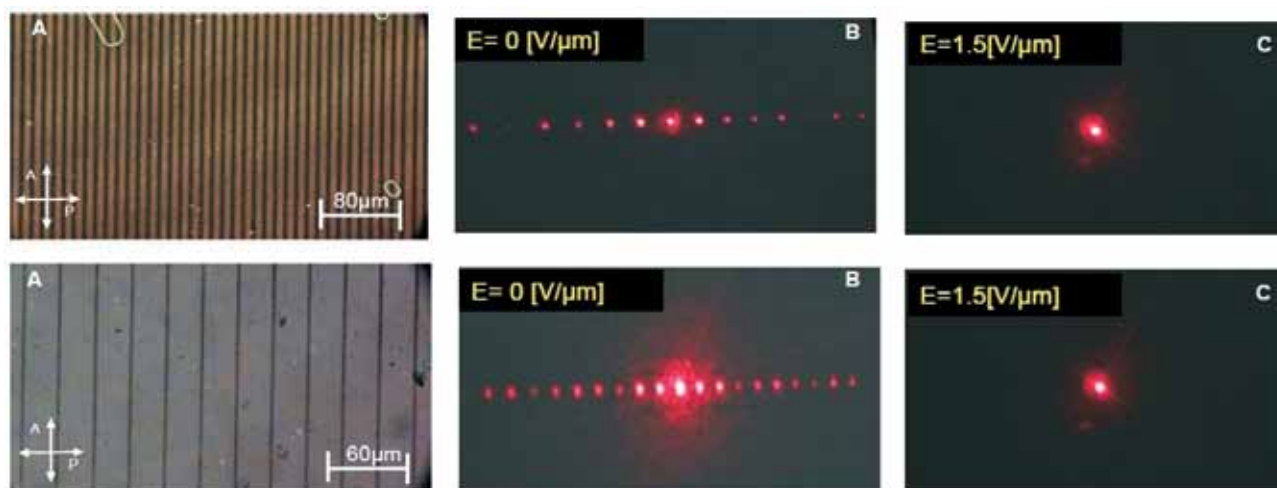


Fig. 2. A) Optical polarizing microscopy images of one-dimensional 1D gratings, visible diffraction patterns created from one-dimensional polarization gratings at: B) 0 V/μm, C) 1.5 V/μm applied electric field (1 kHz square wave)

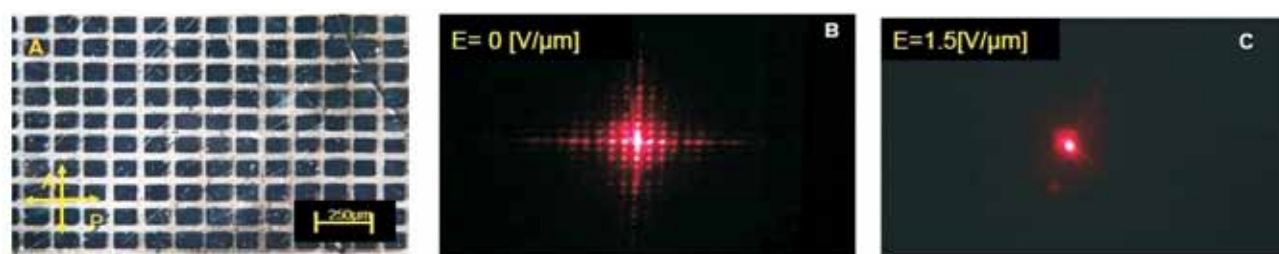


Fig. 3. A) Optical polarizing microscopy images of two-dimensional 2D gratings, visible diffraction patterns created from two-dimensional polarization gratings at: B) 0 V/μm, C) 1.5 V/μm applied electric field (1 kHz square wave)

correlates with a twice-lower value of absorption coefficient (of *ca.*  $10^4 \text{ cm}^{-1}$ ) for PESI-IX and PESI-X *versus ca.*  $2 \cdot 10^4 \text{ cm}^{-1}$  for PESI-IV and PESI-VI. After turning off the excitation beam, the photoinduced birefringence was more stable for functionalized azopolyimides,  $\Delta n_{\text{norm}}$  was *ca.* 94 % for PESI-IV and PESI-VI and in the range 68–82 % for non-covalent polyimides (Table 1).

### Applications of selected azopolyimides

Poly(ester imide) PESI-VI and poly(amide imide) PAI-I were selected for examination of them as an ordering layer for liquid crystal (LC), because of good film-forming properties, high and stable photoinduced birefringence. However, the quality of prepared film form PESI-VI was much better and their ability for LC photoalignment was reported [27]. The ability of the PESI-VI polymer to align LC was verified using nematic liquid crystal mixture for assembling of the twisted nematic (TN) testing cell. The anisotropy of the polyimide thin film was induced by UV linearly polarized light. It has been proved that the TN arrangement of the liquid crystal layer has not been changed for at least six months. This result suggests that anisotropic properties of the azopolymer induced under UV irradiation remains permanent. Furthermore, the stable photoinduced birefringence 0.02 is sufficient for permanent ordering the LC mixture, which is an essential is-

sue for the alignment of LCs applied at LCD and photonic technologies. Detail of the LC cells preparation, mechanism of the ordering of the liquid crystal and the information about verification of the TN arrangement were presented in our previous work [27].

The positive attempts to orient the LC mixture allow applied poly(ester imide) to the simple fabrication of one- and two-dimensional diffraction gratings based on a patterned nematic liquid crystals photoalignment involving periodically alternating planar-twisted nematic domains [28]. Figures 2 and 3 showed the prepared one-dimensional 1D and two-dimensional 2D gratings. It was found that the 1st order diffraction efficiency of this kind of gratings is relatively high (about of 29 % for 1D and 12 % for 2D, respectively).

### CONCLUSIONS

Presented results showed a complex effect of various structural factors including the hydrogen bonds on photoinduced phenomena. They are typical for particular groups of polyimides, that is, poly(ester imide)s or poly(amide imide)s, however, some of them can be generalized. To summarize, the following conclusions can be drawn from our work:

- structure of polymer backbone, it means the presence of amide or ester linkages, determined their photoinduced birefringence reached value, its stability

and polymer solubility together with their thermal properties;

- in the case of poly(amide imide)s crucial role of the intermolecular hydrogen bonds in the isomerization of the azobenzene moieties was found. Formation of intermolecular H-bonds depends on localization of the azochromophore in polymer repeating units;

- optical properties, expressed by absorption coefficient  $\alpha$  value, do not play a crucial role considering reached birefringence value in functionalized polymers;

- considering high glass transition temperature of polymers from polyimide family,  $T_g$  value does not decide about photoinduced birefringence stability;

- covalent bonds between azochromophore and polymer backbone are responsible for birefringence stability;

- in the case of poly(amide imide)s with two azobenzene derivatives in polymer repeating units the influence of kind of chromophore substituents on reached  $\Delta n$  is of no importance;

- it was proved that stable photoinduced birefringence equal to 0.02 is sufficient for order the LC mixture for potential applications.

In conclusion, azopolyimides constitute a prospective group of polymers as layers for LC alignment. The results could lead to further developments of azopolyimides to obtain polymers with properties adapted to the particular optical process.

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