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Cycloaliphatic–aromatic polyimides based on diamines with azobenzene unit

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Abstract

A new family of functionalized semiaromatic polyimides has been developed. Cycloaliphatic–aromatic polyimides, derived from the polycondensation of 1,2,3,4-cyclopentanetetracarboxylic dianhydride (CPDA) with various diamines bearing azobenzene group, have been prepared and characterized. Molecular structural characterization for the resulting polymers has been achieved by ^{13}C NMR, ^{1}H NMR, FTIR and UV–visible spectroscopies. Light-induced optical anisotropy, in novel azobenzene functionalized polyimides, has been studied by holographic polarization grating recording performed at 514.5 nm line of Ar^{+} laser. Two-wave mixing technique has been employed to inscribe the gratings in these polymers. Formation of gratings has been investigated with two s–s and s–p polarized writing beams. The kinetics of grating recording observed within the studied polymers is discussed in relation to their structure.

Keywords: Holographic grating recording; Azobenzene; Polyimides; Alicyclic dianhydride

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1. Introduction

Modern polyimide (PI) materials hardly need an introduction, being the subject of great interest all over the world. Over the past decade polymers have been involved in modern technologies to harness photons for a wide range of applications. Polyimides have generated considerable attention because of their possible applications in photonics-based technologies, for example as materials for holography [1–6]. An intensive research effort is being undertaken to use holographic techniques for optical information storage and optical information processing. Holographic storage is technologically very promising because information storage capacity, that can be reached with this technique, is much higher compared with other techniques [7] (the storage capacity of CD is 0.7 GB, of DVD is from 4.7 to 17 GB, of PAP DVD is about 40 GB, of HOLO CD could be 1 TB). The other advantage of holographic storage is parallelism, meaning that all the information contained

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in an object is recorded or read at the same time, in contrast to many present systems that write and read the stored information bitwise sequentially. This can yield high data transmission rate [8]. On the other hand, dynamic holography in which recording, reading out, and erasing of the optical information should be performed at the real time is also attracting much attention [9]. Development of holographic technology depends on the properties of recording materials. For such practical applications materials besides of specific requirements viz the principal the presence of photochromic moieties, the thermal stability of orientation alignment, the high optical non-linearity, high damage threshold, chemical resistance, mechanical endurance, they should exhibit the high optical quality ability and feasibility of device fabrication which are determined in wide range by their solubility. Significant efforts have been made to improve solubility of polyimides by designing their structure: (i) increasing flexibility along the polymer chain by employment of flexible links (e.g. –O–, –SO_2–, –CH_2–, NHCO–) or less symmetric, such as *meta*- or *ortho*-catenated aromatic units, (ii) introducing bulky pendant groups and biphenyl unit onto the backbone and (iii) utilizing fluorinated monomers [10–15]. Another approach is incorporation of the cycloaliphatic unit into the polyimide backbone which would facilitate less polymer–polymer interaction and enhance the solubility of the polymers [16–21], without sacrificing their excellent thermal stability due to that cycloaliphatic structure would foster less probability of main-chain scission because of the presence of multibonds and would increase main-chain rigidity [16,22,23]. Polyimides containing aliphatic groups are classified into three distinct categories based on the combination of monomers used in their synthesis. The first category would be comprised of PIs derived from aromatic dianhydrides and aliphatic diamines, the second one comprises PIs obtained from aliphatic dianhydrides and aromatic diamines, and the last type consists of PIs prepared form aliphatic dianhydrides and aliphatic diamines (i.e. fully aliphatic) [16,17]. Partially aliphatic polyimides are called semiaromatic PIs [19] and they occupy an intermediate position between aromatic and aliphatic derivatives, they combine the advantages of both. On the other hand alicyclic structures are also effective for the development of PIs with low dielectric constants and transparency in the visible [24,25].

As far as we know, no many reports on semiaromatic polymers with photochromic units appeared in the literature [18,26]. Studies in the synthesis and properties of photochromic polymers constitute a large area of research in contemporary polymer science. One of the central goal is the fundamental understanding of the structure-property relationship that might form the basis for a "molecular engineering" approach to photonic polymers. Among plenty of studied polymers, azobenzene containing polymeric systems have been the subject of intensive research due to their unique properties which allow various applications triggered by light [28–30]. In particular, special attention has been paid to the application of azopolymers as possible active materials in information storage devices [31]. Using a polarized laser beam, the information can be written, read, erased, and rewritten on the same spot by means of induced birefringence and dichroism. The mechanism of writing involves photochemical excitation of the azobenzene group which undergoes a reversible *trans–cis–trans* photoisomerization cycles [31,32]. It takes place via the repetition of angular-dependent excitation, photoisomerization cycles and rotational diffusion within the steady state [33]. In this way, the photochromic units become oriented perpendicularly to the electric field vector of the incident light and optical anisotropy is generated.

Extensive studies carried out in our laboratory involve the investigations of influence of polymer structure on their properties induced by polarized light such as dichroism and kinetics of grating inscription [1,2,27,34]. In the present article the cycloaliphatic–aromatic polyimides with identical main- and side-chain architecture but various substituents at the *para* position of the azobenzene part have been presented. It has been found that even the optically insensitive parts of the polymer molecule can lead to significant changes in photoinduced properties [27]. Survey of the literature reveals the dependency between the formation of the surface relief and azobenzene unit substitution for liquid-crystalline side-chain azobenzene polyesters [35] and polyazophenols [36]. Thus it seem to be interesting to investigate the influence of chromophore substituents in semiaromatic polyimides with stiff backbone and without flexible spacer between polymer chain and azobenzene group, such a structure may result in a significant increase in the stability of the optically induced anisotropy, and its kinetics.

2. Experimental section

2.1. Materials

1,3-Phenylenediamine, *N*-methyl-2-pyrrolidone (NMP), *N*,*N*-dimethylformamide (DMF), acetonitrile (AN) and others needed starting chemicals have been purchased from Aldrich Chemical Co. and have been used without purification. 1,2,3,4-Cyclopentanetetracarboxylic dianhydride (CPDA) as received has been recrystallized form acetic anhydride (Ac_2O).

CPDA m.p. 212 °C. ^{13}C NMR (75 MHz, DMSO-d_6) 30.28 (C-2), 39.79 (C-1,3), 48.93 (C-4,5), 169.29 (CO), 173.34 (CO). ^1H NMR (300 MHz, DMSO-d_6) 2.6 (dd, 2H, H-2), 3.9 (m, 2H, H-1,3), 4.1 (m, 2H, H-4,5). FTIR (KBr) 1796 and 1864 cm^{-1} (C═O in anhydride ring).

Anal. Calcd. for $C_9H_6O_6$(210.14): C, 51.44%; H, 2.88%; found: C, 51.11%; H, 2.85%. Diamines have been prepared as described in Ref. [27].

2.2. Characterization techniques

The obtained polymers have been characterized by following techniques: elemental analysis (Vario EL III Elementar), ^{13}C NMR – 75 MHz, ^1H NMR – 300 MHz (Varian UNITY Inova 300 spectrometer, DMSO-d_6 solvent against TMS as an internal reference) and FTIR (BIO-RAD FTS 40 A spectrometer, KBr presses pellet technique). Differential scanning calorimetry (DSC) has been performed with a TA DSC 2010 apparatus under nitrogen using a heating/cooling rate of 20 °C min^{-1}. UV–vis spectra have been recorded in NMP and acetonitrile solution (concentration $= 1 \times 10^{-5}$mol/L) of polymers and as films casted on glass using a Jasco V570 UV–vis spectrometer. The holographic gratings have been recorded in standard degenerate two-wave mixing set-up using 514.5 nm Ar$^+$ laser light. The recording light powers of two intersecting beams were $P_{01} = P_{02} = 10.0$ mW ($I_1 = I_2 = 560$ mW/cm^2) and beam intersection angle was $\theta = 5.2°$, giving spatial period of the grating $\Lambda = 5.7$ μm. The power of the incident beams and one of the first-order diffracted beam have been measured by silicon detectors (LM-2 Silicon HD Smart Sensor, Coherent).

2.3. Polymer synthesis

All polymerization reactions have been carried out in nitrogen atmosphere with a mechanical stirrer. An equimolar amount of monomers have been used in all cases. The polymerization has been carried out by two different synthetic routes i.e. two-step and one-step method. The polymers have been precipitated and purified by methanol.

2.3.1. Two-step reaction

Polymerization has been conducted analogously to traditional poly(amic acid) synthesis with chemical cyclodehydration. After diamine (1 mmol) has been dissolved in 1.5 mL of dried DMF, dianhydride (1 mmol) has been added. The mixture has been stirred at room temperature for 4 h. Then, a mixture of Ac_2O and pyridine (Py) (volume ratio 2:1) has been added to the poly(amic acid) solution, and stirred in oil bath at 80 °C for 24 h to imidize.

2.3.2. One-step method

The method of high temperature polycondensation has been carried out in two variants viz. (i) in *m*-cresol with the presence of isoquinoline according to Ref. [18] and (ii) in mixture of NMP with 1,2-dichlorobenzene (80/20 (v/v), 20% total monomer concentration) for 3 h at 160 °C.

3. Results and discussion

In the present article, the physicochemical properties and kinetics of holographic gratings inscription in novel semiaromatic polyimides, derived form cycloaliphatic dianhydride and diamines with azobenzene unit, will be described.

3.1. Polymer synthesis and characterization

As cycloaliphatic dianhydride 1,2,3,4-cyclopentanetetracarboxylic dianhydride (CPDA) has been employed. On the other hand, aromatic diamines such as 2,4-diamino-4′-fluoroazobenzene, 2,4-diamino-4′-methylazobenzene, 2,4-diamino-4′-trifluoromethoxyazobenzene, 2,4-diamino-4′-nitroazobenzene and 2,4-diamino-4′-cyanoazobenzene have been prepared and condensed with CPDA. Additionally, the neutral polymer (**P6**) i.e. without azobenzene group, which is treated as a reference, from 1,3-phenylenediamine has been obtained. Chemical structures of the polyimides synthesized in this research are presented in Fig. 1.

Polycondensation of the dianhydride (CPDA) with diamines has been first carried out in two-step, low temperature method. However, the resulting materials have not form films on glass substrates

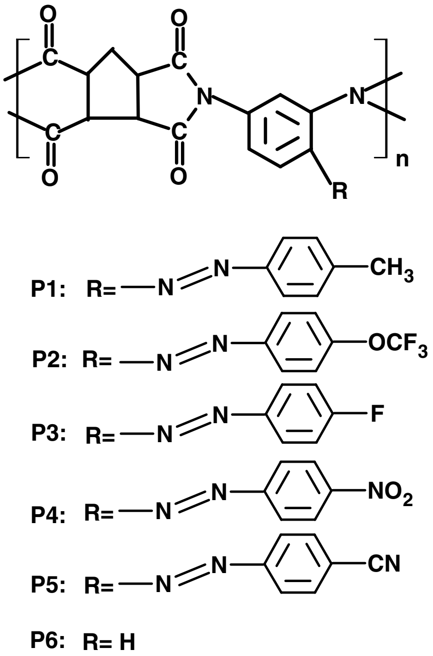


Fig. 1. Structure of the synthesized polyimides.

probably because of too low molecular weight (the reduced viscosity of these polymers has been in the range of 0.02–0.04 dl g^{-1}) and as a consequence of this are not useful for further investigations.

To achieve high-quality polymers, we adopted the high temperature one-step polycondensation in *m*-cresol solution as described in Ref. [18] for the same dianhydride. Unfortunately, elemental analysis of these polymers revealed that the values of nitrogen, carbon and hydrogen have been significantly lower than the ones calculated for the proposed structures which can indicate destruction of the polymers during reaction. However, in the FTIR spectra, bands resulting from the nitro, cyano group in the NLO chromophore in polymers **P1**, **P2** are observed, indicating that a part of the chromophores survived during reaction.

Therefore another variant of one-step polycondensation has been utilized. In this case the reaction has been conducted in the mixture of NMP and 1,2-dichlorobenzene, and the results are acceptable. Thus polyimides synthesized in this way are the subject of this work.

Instrumental techniques including FTIR and NMR spectroscopies have been performed for characterization of the polymer molecular structure.

Infrared spectroscopy. Fig. 2 shows the FTIR spectra of the dianhydride CPDA, the neutral polyimide **P6** and the exemplary polymer with azobenzene unit **P5** as KBr pellets (spectra (a)–(c), respectively).

In the spectrum (a), absorption bands at 1864 (medium intensity) and 1796 cm^{-1} (strong intensity) clearly indicate the existence of the anhydride carbonyl groups in the CPDA, while in the spectrum (b) and (c) they disappear. At the same time new absorption bands appear which are consistent with the formation of imides. The principal FTIR absorption bands observed in the polymers and their assignments are listed in Table 1.

The spectra of the polymers showed clearly the characteristic absorption bands at around 1780 cm^{-1} and 1720 cm^{-1} attributed to the symmetric stretching and asymmetric stretching of the carbonyl group of the five-membered cyclic imide rings, respectively, and the absorption band at approximately 1375 cm^{-1} related to the C–N stretching. The polymers revealed absorption band at around 2954 cm^{-1} characteristic for aliphatic C–H stretching vibration. The presence of absorption bands at 3470 cm^{-1} and 3371 cm^{-1} related to NH_2 stretching indicates the existence of amino terminated end groups. In FTIR spectra of polymers with azobenzene unit absorption peaks indicating the presence of the substituted chromophore are observed as well. The **P1** derived form diamine with methyl substituent exhibits $-CH_3$ vibration band at 2582 cm^{-1}. The peak at 1256 cm^{-1} in spectrum of **P2** is ascribed to the stretching vibration of $-OCF_3$ group. The characteristic absorption bands of the symmetrical and asymmetrical stretching of the nitro group are evidenced at approximately 1521 and 1342 cm^{-1}, respectively in the case of **P4**. The polymer **P5** revealed absorption band around 2228 cm^{-1}, due to the presence of the cyano group. The FTIR results support the chemical structure of the polyimides as proposed.

NMR spectroscopy. The ^{13}C NMR and ^{1}H NMR data of the polymers are listed in Tables 2 and 3.

In the ^{13}C NMR spectra the cycloaliphatic carbons (C1–C5) of the main chain resonated at about $\delta = 31.40–50.20$ ppm, carbon of the carboxyl groups (C6–C9) in the imide unit had an upfield resonance approximately at $\delta = 17.00–179.30$ ppm. The resonance lines at 20.98, 125.20 and 125.10 ppm are assigned to carbon of the methyl in **P1**, trifluorometoxy in **P2** and cyano group in **P5**. Polyimides with azobenzene units as compared to neutral polymer **P6** show resonance line of the carbon atoms C11–C15 shifted to the higher frequency.

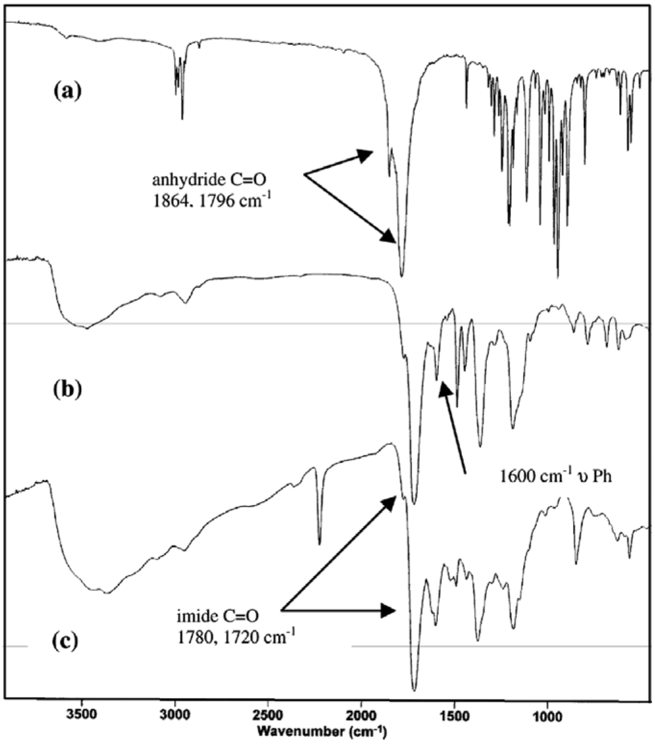


Fig. 2. FTIR transition spectra (KBr pellets) of (a) dianhydride CPDA, (b) neutral polyimide **P6**, and (c) polyimide **P5.**

Table 1
Assignment of FTIR absorption selected band positions (cm^{-1}) of the cycloaliphatic–aromatic polyimides

Polymer code	C=O stretching	υ Ph	C–N stretching	NH_2 stretching	Aliph C–H stretching
P1	1776, 1713	1647, 1602, 1495	1382	3449, 3364	2947
P2	1780, 1720	1620, 1604, 1497	1377	3441, 3365	2955
P3	1779, 1720	1621, 1594, 1499	1376	3466, 3372	2954
P4	1780, 1717	1620, 1606, 1499	1377	3450, 3371	2953
P5	1779, 1716	1621, 1604, 1494	1377	3439, 3364	2953
P6	1779, 1720	1607, 1551, 1495	1375	3471, 3366	2952

Considering the ^1H NMR spectra the peaks of the aromatic ring protons (H11–H13, H17 and H18) appeared in the region of 6.4–8.3 ppm and cycloaliphatic protons resonated at $\delta = 3.0$–4.2 ppm. The peak at 2.4 ppm in the case of **P1** is due to the protons in methyl group. Additionally, the value of chemical shifts of studied polyimides has been confirmed by using simulation program (G NMB Special Simulation).

The ^1H and ^{13}C NMR spectra of the polymers have been consistent with their assigned structures.

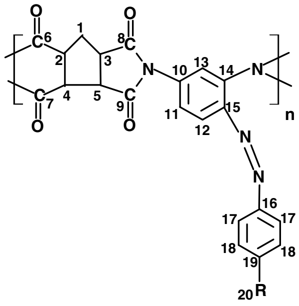
3.2. Polymer properties

The results of the elemental analyses of the polyimides are collected in Table 4.

Compared to the calculated content of carbon and nitrogen in the proposed structures, the elemental analyses show a deficiency in carbon content of about 0.8–4.9% and differences in nitrogen in the range of 0.24–1.54%. The significant difference in carbon content is likely a result of the difficulties in burning these polymers [37]. The presence of end amine groups may influence on the not excellent agreement of the calculated and found values of elemental composition of the synthesized polyimides, as well.

The solubility of synthesized polyimides has been determined (by visual observation) for the powdery samples in excess of solvents. Tested solubility and reduced viscosity of the polyimides are listed in Table 5.

Table 2
Examination of polyimides by ^{13}C NMR in DMSO-d_6



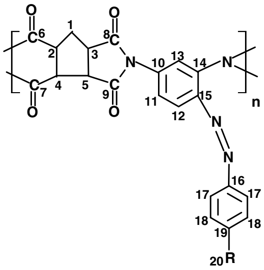
^{13}C NMR [ppm]										
P1	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
	31.42	47.60	44.65	49.95	48.41	173.76	177.13	174.88	178.01	135.78
	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20
	150.45	145.39	129.80	134.85	150.45	124.02	114.96	113.95	122.26	20.98
P2	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
	32.00	48.20	44.60	49.90	48.50	170.00	175.00	172.60	178.00	134.00
	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20
	149.00	161.00	127.20	146.00	154.60	126.80	116.80	114.60	111.90	125.20
P3	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
	31.80	48.00	44.40	50.20	47.60	171.80	175.60	172.20	179.90	133.80
	C11	C12	C13	C14	C15	C16	C17	C18	C19	–
	149.20	161.50	126.90	145.70	155.00	126.20	116.00	115.20	112.90	
P4	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
	31.49	47.80	44.70	48.64	48.38	173.82	177.45	174.78	178.00	136.71
	C11	C12	C13	C14	C15	C16	C17	C18	C19	–
	147.42	155.17	124.94	146.09	155.17	124.04	114.83	113.62	123.05	
P5	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
	31.40	47.50	44.10	49.60	48.20	172.90	176.80	172.10	177.80	126.80
	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20
	148.60	152.30	128.10	145.20	157.20	125.90	118.20	115.60	113.40	125.10
P6	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10
	31.49	46.32	44.57	49.35	48.53	177.45	177.77	173.87	177.53	127.39
	C11	C12	C13	C14	C15	–	–	–	–	–
	132.31	132.41	126.55	129.07	149.24					

The polymers are soluble not only in amide polar solvents but also in less polar *m*-cresol and even in conventional solvents such as pyridine and THF (**P4** and **P5** partially soluble in THF) at room temperature. The resultant polyimides exhibited very similar, not high value of the reduced viscosity which can suggest not high molecular weight of prepared polymers. Moreover, despite their rather low molecular weight, polyimides show film forming properties. Good optical quality films can be obtained by casting from solution on glass substrates.

The glass transition temperatures of all polymers have not been observed by differential scanning calorimetry (DSC) up to 300 °C.

In this part of article we would like to compare chosen properties of our polyimides with similar ones described in literature. However, semiaromatic polyimides with photochromic groups are study very rarely. Actually, we have found only one paper concerning such polymers. Kim et al. [18] reported the semiaromatic polyimides obtained also from CPDA dianhydride and containing photochromic units and these polymers were partially soluble in such sol-

Table 3
Examination of polyimides by ^{1}H NMR in DMSO-d_6



	^{1}H NMR [ppm] J [Hz]					
P1	H1	H2, H3		H4, H5		H11
	3.3 (2H, dd, J_{H1-H2}=6.0, $J_{H1-H3} = 6.4$)	3.4–3.6 (2H, m, $J_{H2-H1} = 6.0$, $J_{H2-H4} = 6.3$, $J_{H3-H1} = 6.4$, $J_{H3-H5} = 6.8$)		3.7–4.0 (2H, m, $J_{H4-H2} = 6.3$, $J_{H4-H5} = 5.2$, $J_{H5-H3} = 6.8$, $J_{H5-H4} = 5.2$)		7.7 (1H, dd, $J_{H11-H12} = 7.3$)
	H12	H13	H17	H18	H20	
	6.5 (1H, d, $J_{H12-H11} = 7.3$)	6.9 (1H, d)	7.8 (2H, d, $J_{H17-H18} = 7.0$)	7.3 (2H, d, $J_{H1-H3} = 7.0$)	2.4 (3H, s)	
P2	H1	H2, H3		H4, H5		H11
	3.2 (2H, dd, $J_{H1-H2} = 6.2$, $J_{H1-H3} = 6.5$)	3.5–3.7 (2H, m, $J_{H2-H1} = 6.2$, $J_{H2-H4} = 6.6$, $J_{H3-H1} = 6.5$, $J_{H3-H5} = 6.8$)		3.8–4.0 (2H, m, $J_{H4-H2} = 6.6$, $J_{H4-H5} = 5.7$, $J_{H5-H3} = 6.8$, $J_{H5-H4} = 5.7$)		7.5 (1H, dd, $J_{H11-H12} = 7.5$)
	H12	H13	H17	H18		
	6.4 (1H, d, $J_{H12-H11} = 7.5$)	6.9 (1H, d)	8.0 (2H, d, $J_{H17-H18} = 7.3$)	7.4 (2H, d, $J_{H1-H3} = 7.3$)		
P3	H1	H2, H3		H4, H5		H11
	3.3 (2H, dd, $J_{H1-H2} = 6.2$, $J_{H1-H3} = 6.7$)	3.4–3.6 (2H, m, $J_{H2-H1} = 6.2$, $J_{H2-H4} = 6.0$, $J_{H3-H1} = 6.7$, $J_{H3-H5} = 7.2$)		3.2–3.9 (2H, m, $J_{H4-H2} = 6.0$, $J_{H4-H5} = 5.1$, $J_{H5-H3} = 7.2$, $J_{H5-H4} = 5.1$)		7.6 (1H, dd, $J_{H11-H12} = 7.8$)
	H12	H13	H17	H18		
	6.5 (1H, d, $J_{H12-H11} = 7.8$)	7.0 (1H, d)	7.7 (2H, d, $J_{H17-H18} = 7.1$)	7.6 (2H, d, $J_{H1-H3} = 7.1$)		
P4	H1	H2, H3		H4, H5		H11
	3.0 (2H, dd, $J_{H1-H2} = 6.3$, $J_{H1-H3} = 6.5$)	3.6–3.8 (2H, m, $J_{H2-H1} = 6.3$, $J_{H2-H4} = 6.2$, $J_{H3-H1} = 6.5$, $J_{H3-H5} = 7.0$)		3.3–3.5 (2H, m, $J_{H4-H2} = 6.2$, $J_{H4-H5} = 5.2$, $J_{H5-H3} = 7.0$, $J_{H5-H4} = 5.2$)		7.8 (1H, dd, $J_{H11-H12} = 7.6$)
	H12	H13	H17	H18		
	6.6 (1H, d, $J_{H12-H11} = 7.6$)	7.2 (1H, d)	8.3 (2H, d, $J_{H17-H18} = 7.1$)	7.8 (2H, d, $J_{H1-H3} = 7.1$)		
P5	H1	H2, H3		H4, H5		H11
	3.1 (2H, dd, $J_{H1-H2} = 6.3$, $J_{H1-H3} = 6.7$)	3.3–3.5 (2H, m, $J_{H2-H1} = 6.37$ $J_{H2-H4} = 6.6$, $J_{H3-H1} = 6.5$, $J_{H3-H5} = 7.0$)		3.7–3.9 (2H, m, $J_{H4-H2} = 6.6$, $J_{H4-H5} = 5.3$, $J_{H5-H3} = 7.0$, $J_{H5-H4} = 5.3$)		7.7 (1H, dd, $J_{H11-H12} = 7.5$)
	H12	H13	H17	H18		
	6.7 (1H, d, $J_{H12-H11} = 7.5$)	7.4 (1H, d)	8.1 (2H, d, $J_{H17-H18} = 7.4$)	7.6 (2H, d, $J_{H1-H3} = 7.4$)		
P6	H1	H2, H3		H4, H5		H11
	3.4 (2H, dd, $J_{H1-H2} = 6.4$, $J_{H1-H3} = 6.5$)	3.7–3.9 (2H, m, $J_{H2-H1} = 6.4$, $J_{H2-H4} = 6.0$, $J_{H3-H1} = 6.5$, $J_{H3-H5} = 7.6$)		4.0–4.2 (2H, m, $J_{H4-H2} = 6.0$, $J_{H4-H5} = 5.0$, $J_{H5-H3} = 7.6$, $J_{H5-H4} = 5.0$)		8.1 (1H, dd, $J_{H11-H12} = 7.8$ $J_{H12-H15} = 6.8$)
	H12	H13	H15			
	6.9 (1H, d, $J_{H12-H11} = 7.8$)	7.6 (1H, d)	7.3 (1H, dd, $J_{H15-H12} = 6.8$)			

vents in which our polymers have been soluble completely. Inherent viscosity values of these polyimides indicate that the molecular weight of obtained polyimides was not very high similar as in the case of our polyimides. Partially solubility of described polymers limits their processing. Utilization, by the same authors, another dianhydride with metyl-3-cyclohexane-1 unit for the preparation of polyimides with chromophore resulted in soluble PI (in DMF, NMP, *m*-cresol, THF, $CHCl_3$, and cyclohexanone), however, holographic grating recording was not investigated in these polymers [18].

Absorption spectra of the polyimides. The UV–vis spectra of the polymers synthesized in this study have been acquired both in solutions and in films. The UV–vis solution spectra of the polyimides have been recorded using their NMP and AN solutions. The polymers (**P1**–**P5**) give orange solutions and colorless solutions in the case of the neutral **P6.** The color of the polymers is governed by the presence of two types of chromophore groups in their macromolecules, namely the aromatic rings and the azobenzene units. Fig. 3 shows in acetonitrile solution spectra of the exemplary polymer **P5** along with that of the neutral polyimide **P6** for comparison.

In spectrum of polymer **P6,** which does not contain azobenzene group, intense absorption band at around 190 nm and slight, weak band below 300 nm are found which are described to polymer backbone. Thus appearance of the peaks above 300 nm in polyimides containing chromophore could be attributed to the azobenzene group. In

Table 4
Elemental analysis of the polyimides obtained in one-step method (NMP, 1,2-dichlorobenzene, 3 h, 160 °C)

Polymer code	Repeating units formulae (Formula weight)	Elemental analysis Calc. (Found)		
		C%	H%	N%
P1	$(C_{22}H_{16}N_4O_4)_n$ $(400.39)_n$	66.00 (63.32)	4.03 (4.66)	14.00 (15.54)
P2	$(C_{22}H_{13}N_4O_5F_3)_n$ $(470.36)_n$	56.18 (54.22)	2.79 (3.66)	11.91 (13.85)
P3	$(C_{21}H_{13}N_4O_4F)_n$ $(404.35)_n$	62.38 (57.40)	3.24 (3.98)	13.86 (12.80)
P4	$(C_{21}H_{13}N_5O_6)_n$ $(431.33)_n$	58.48 (57.64)	3.04 (4.00)	16.23 (16.63)
P5	$(C_{22}H_{13}N_5O_4)_n$ $(411.37)_n$	64.23 (59.67)	3.19 (4.06)	17.02 (15.57)
P6	$(C_{15}H_{10}N_2O_4)_n$ $(282.25)_n$	63.83 (59.04)	3.57 (4.38)	9.93 (9.42)

Table 5
Solubility[a] in some solvents and the reduced viscosity of the polyimides

Polymer code	THF	DMA	DMSO	NMP	*m*-cresol	Py	η_{red}[b] [dl g^{-1}]
P1	+	+	+	+	+	+	0.13
P2	+	+	+	+	+	+	0.10
P3	+	+	+	+	+	+	0.10
P4	±	+	+	+	+	+	0.10
P5	±	+	+	+	+	+	0.10
P6	–	+	+	+	+	+	–

[a] Key: "+", soluble; " ± ", partially soluble; "–", insoluble.

[b] Reduced viscosity of polyimides measured in NMP, concentration = 0.2 g/100 ml at a temperature 25 °C.

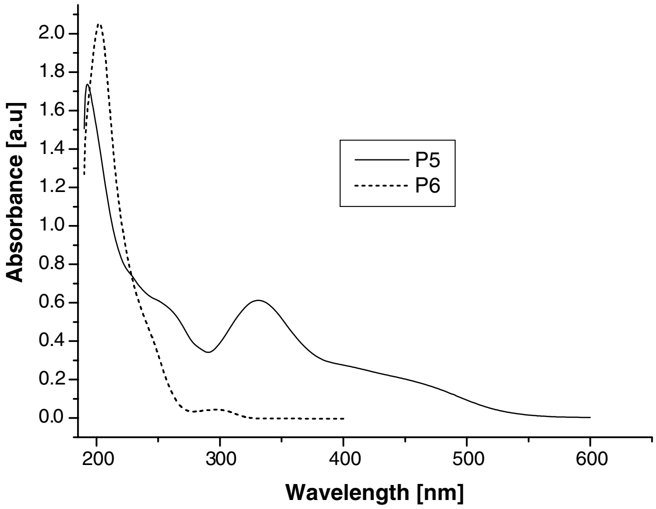


Fig. 3. Optical absorption spectra of the polyimide in solution without (**P6**) and with azobenzene moiety (**P5**).

the case of polyimide **P5** and also other investigated polymers in acetonitrile three absorption peaks are observed. The absorption band centered at 327–339 nm in acetonitrile assigned to the π–π* transition moment of *trans-p*-substituted azobenzene chromophore which is separated clearly from the absorption of polyimide backbone existing in the region of 180–190 nm is observed. Additionally, the weak, broad absorption peak above 400 nm due to n–π transition of *trans*-azobenzene isomer is detected [36]. The absorption spectra i.e. position of azobenzene absorption band of the polyimides are changed compared to that of the diamines. The maximum absorption band (λ_{max}) of the monomers – diamines is in the range of 442–521 nm (in NMP solution). The kind of substituent in azobenzene group influences the wavelength of λ_{max} in diamines. Namely, in dependence of substituent absorption maxima are at 442, 444, 450, 521 and 485 nm for diamine with $-CH_3$, –F, $-OCF_3$, $-NO_2$ and –CN, respectively. The peak assigned to the π–π* transition of azobenzene moiety in the studied polyimides is significantly blue-shifted (337–339 nm in NMP) as compared to diamines.

The data obtained form optical absorption spectra in NMP and AN solutions of polyimides are reported in Table 6.

Table 6
π–π* transition of azobenzene group in the polyimides both in acetonitrile and NMP solution

Polymer code	AN		NMP	
	λ_{max} [nm] (eV)	E_g [eV]	λ_{max} [nm] (eV)	E_g [eV]
P1	327 (3.79)	2.41	337 (3.68)	2.35
P2	328 (3.78)	2.29	333 (3.72)	2.10
P3	329 (3.77)	2.32	332 (3.73)	2.20
P4	339 (3.66)	2.21	348 (3.56)	2.09
P5	331 (3.75)	2.30	339 (3.66)	2.14

As can be seen the absorption λ_{max} of the π–π* transition of azobenzene moiety in the nitro-substituted polyimide (**P4)** is batochromically shifted about 10 nm in both NMP and AN solutions, in comparison with the position in λ_{max} of others investigated polymers. Furthermore the optical gap ($E_g = 2.21$ eV) of **P4** is the smallest. The polyimide **P1** exhibited the highest value of band gap ($E_g = 2.41$ eV with the λ_{max} at 327 nm). This effect is attributed to the lack of delocalized π-electrons in methyl substituent on azobenzene unit [38]. In general, the solution absorption spectra of polyimides in acetonitrile show the slightly lowest energy of λ_{max} of the azobenzene group compared to that in NMP solution (see Table 6). The differences are in the range of 3–10 nm thus in this case the polyimides display weak solvatochromic effect.

The polyimide films have been examined by UV–vis spectroscopy as well. Polymer films have been prepared by casting their solutions in NMP on glass substrates. Fig. 4 illustrates the position of λ_{max} of polyimides in the NMP solution and in film.

As can be seen the solution and film absorption maxima of polyimides are the same, indicating that the conformations in solution and the solid state are identical.

3.3. Holographic grating formation

For evaluation of a material's fundamental holographic properties i.e. diffraction efficiency and recording time constants the standard degenerate two-wave mixing technique (DTWM) with 514.5 nm line of Ar^+ laser has been utilized. The writing beams, with equal intensities, intersect in the sample film at an incident angle of $\theta/2 = 2.6°$, leading to the formation of the grating with spatial periodicity $\Lambda = 5.7$ μm. Polarization states of the

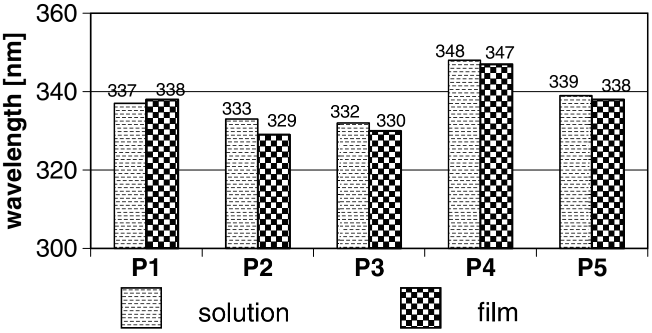


Fig. 4. Comparison of absorption maximum peak position in the polyimides in NMP solution and film.

incoming beams were either perpendicular to the incidence plane i.e. s–s configuration or one of them has been rotated by 90° to obtain s–p polarization. The interference of the incident s–s beams produces dark and bright fringes whereas for s–p configuration film is uniformly illuminated. In both cases of polarization geometries a periodic birefringence and/or dichroism is induced. This is evidenced by an appearance of a light self-diffraction. Measurements of the temporal evolution of the first-order diffracted beam's power enabled study of the kinetics of its build-up process. Holographic gratings have been recorded for both configurations at a light intensity of 560 mW/cm^2 and exposure times up to 20 min. Examples of grating inscription for s–s and s–p polarization for polyimide **P3** are shown in Fig. 5.

Grating inscription and erasure is qualitatively similar for all tested polymers. In the case of s–s polarization the grating inscription (Fig. 5a) process can be divided into three stages according to the slope of the first-order diffracted power versus exposure time i.e. (i) rapid growth (on the order of 0.1 s) of the diffraction signal at the initial stage, (ii) decrease of the signal to smaller value, and (iii) monotonic increase up to the saturation level (cf. Fig. 5a). Over a 1400 s inscription period is insufficient to observe a plateau. The polyimides need much longer time to obtain saturation, for example in the case of polyimide **P2** approximately 2000 s. Initially, the dynamics of the s–s type grating build-up is faster than the s–p. Investigations of the short time diffraction signals evolution (s–s polarization) for the polyimides have been made using oscilloscope and a fast responding photodiode. The exemplary result is presented in Fig. 5b for polyimide **P3**.

An example of typical writing-erasing cycles, obtained in the case of s–p polarization geometry, is shown in Fig. 5c for polyimide **P3**. The inscription

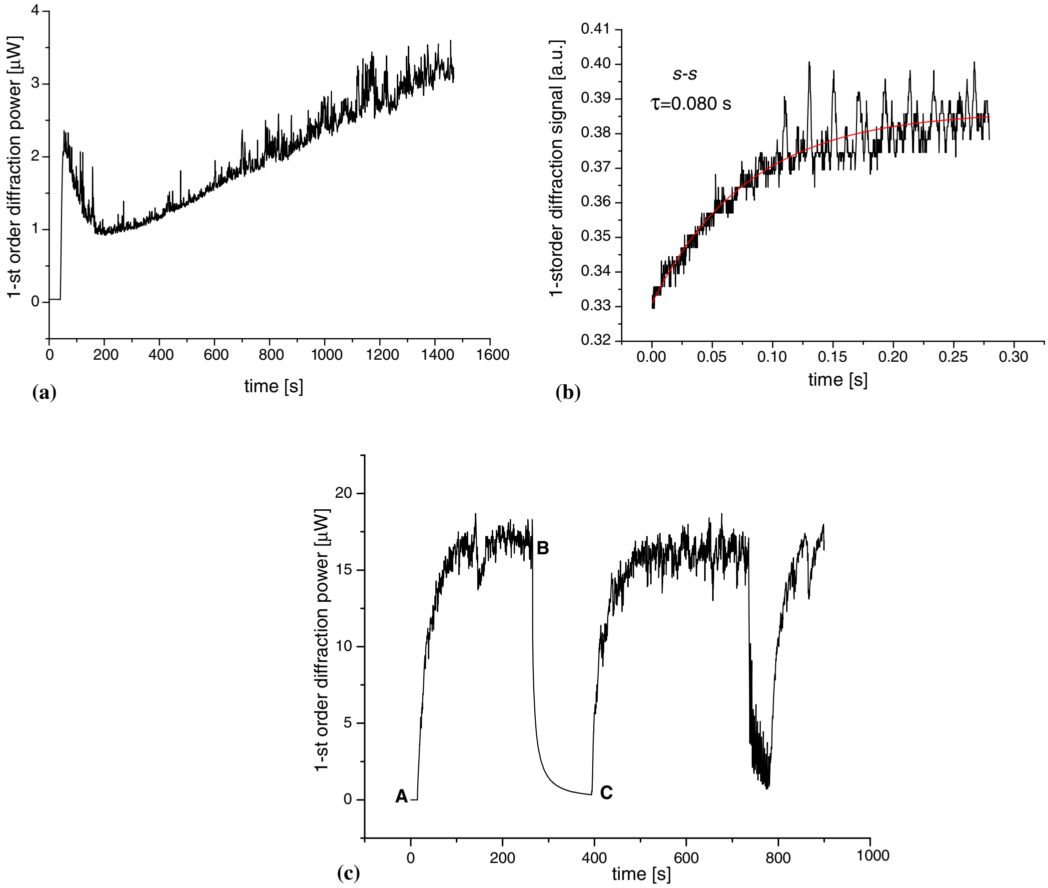


Fig. 5. Examples of grating recording kinetics in polyimide **P3** (a) for s–s polarization, (b) oscilloscope trace of first-order diffraction signal fast grating build-up process for s–s configuration, and (c) repetitive writing-erasing cycles for s–p polarization.

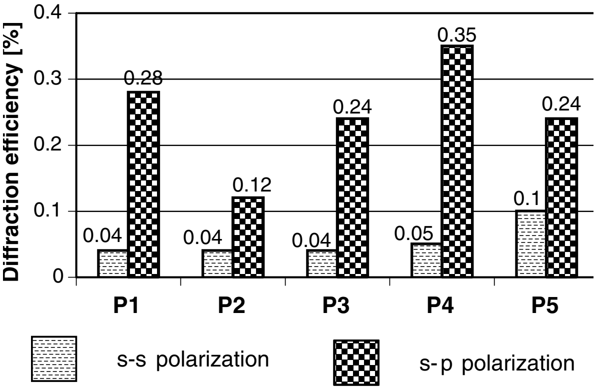


Fig. 6. Diffraction efficiency according to different polarization configurations (s–s and s–p) of the writing beams for investigated polymers.

process is turned on at point A, the diffraction signal appears and reaches the saturation level. At point B one of the writing beam is blocked and the light induced grating erasure is observed. The diffraction signal drops almost to zero within several seconds. After opening the blocked writing beam at point C, the diffraction signal returns to its previous value and the process of erasure can be applied again.

Measurements of the beam power diffracted into first order during grating recording process enable estimation of the diffraction efficiency η. The diffraction efficiency defined as the intensity ratio of the first diffracted beam to the incident one ($\eta = (I_{1\mathrm{diff}}/I_1) \times 100$) has been calculated. The diffraction efficiencies, for two polarization geometries of the writing beams, for all investigated polyimides, are compared in Fig. 6.

The value of diffraction efficiency for s–s polarization is calculated after 1400 s of irradiation. The grating of the s–p type gives stronger diffraction than the s–s one. The inscribed diffraction gratings show low diffraction efficiencies (the highest one $\eta = 0.35\%$ was measured for polyimide **P4**) which is probably due to the restricted motion in the polyimides. The kinetics of grating recording depends on the polymer properties as well as on external parameters like an intensity of recording light [39,40]. The preliminary investigation of grating recording rate in function of writing beam power has been carried out for polyimide **P1**. The kinetics of grating inscription in **P1** for two intensities of incident beams i.e. 10 mW and 30 mW is shown in Fig. 7.

As a result, the higher the intensity of pump beam, the faster the recording rate of grating inscription.

The shape of square root of diffracted power signal versus time can be well described by a mono- or double-exponential function of the form:

$$\sqrt{P_1(t)} = A_1\left[1-\exp\left(-\frac{t}{\tau_1}\right)\right] + A_2\left[1-\exp\left(-\frac{t}{\tau_2}\right)\right] \tag{1}$$

here τ_1 and τ_2 describe time constants of two different grating build-up processes fast and slow, respectively [41]. The fast process in connected with the *trans–cis–trans* isomerization rates and the local

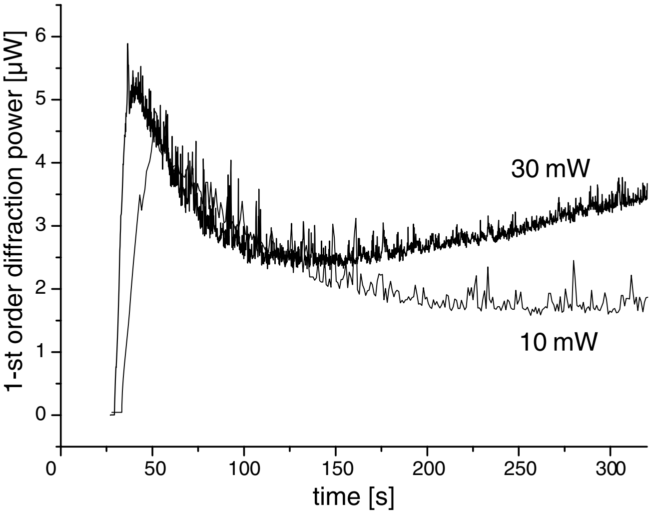


Fig. 7. Dependence of writing beam intensity on the first-order diffracted power in polyimide **P1**.

Table 7
Parameters estimated by fitting the diffracted power signal versus time for s–p and s–s polarization configurations

Polymer code	Polarization s–p				Polarization s–s	
	τ_1 [s]	A_1	τ_2 [s]	A_2	τ [s]	A
P1	3.0	1.67	23.2	3.66	0.07	0.074
P2	0.9	1.04	14.6	2.04	–	–
P3	3.1	2.26	25.2	2.60	0.08	0.055
P4	9.9	3.50	61.7	2.19	0.06	0.041
P5	3.1	1.87	42.4	1.99	–	–

mobility of azobenzene groups, which is determined by the size of azobenzene groups, the free volume around them, the strength of the coupling interaction between the azobenzene group and the polymer backbone. The slow one would depend on the coupling interaction between the azobenzene groups and the polymer segments, and the mobility of the polymer chains. Parameters A_1 and A_2 describe the contribution of these processes to diffraction. The build-up process of grating inscription in exemplary polyimide **P3** together with the fitting curve is shown in Fig. 6. The fitted parameters, obtained according to Eq. (1) for all studied polyimides, for both polarization geometries s–p and s–s (only for first stage), are summarized in Table 7.

Monoexponential function can be utilized for estimating time constant of grating recording for the first stage in case of s–s polarization. In this polarization geometry all polyimides exhibit fast recording ($\tau \sim 0.07$ s). As can be seen from Table 7 the kind of substituents on azobenzene unit in the polyimides influences the kinetics of grating inscription. Taking into account s–p configuration the fastest grating formation, is observed for polyimide **P2** with trifluorometoxy group. The relatively slower recording is found for polyimide **P4** containing nitro substituent. Other polyimides i.e. **P1** and **P3** exhibit the similar value of time constants. Polyimide **P5** needs longer time to achieve saturation as compared to **P1** and **P3**.

The relatively fast grating inscription at low light intensities in these polymers is promising for dynamic holography purposes.

4. Conclusion

Semiaromatic polyimides differing only in the nature of the substituent on azobenzene group have been synthesized and characterized. The azobenzene side groups undergo the *trans–cis–trans* isomerization induced by laser light. This causes the changes of the optical material properties which could be exploited in applications. The DTWM experiment showed the formation of diffraction gratings with small diffraction efficiencies up to 0.35%. Polyimides exhibit fast rate of grating recording for s–s polarization (about 0.07 s). The diffraction grating could be optically erased and recorded multiple times for s–p geometry. It is observed that the formation of grating in polyimide films depends on the polarization of the recording beams and the kind of azobenzene substituent. Studied polyimides form a class of materials with a potential for dynamic holography purposes due to fast grating inscription.

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