Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polymer 46 (2005) 49–59

polymer

www.elsevier.com/locate/polymer

Photoinduced optical anisotropy in new poly(amide imide)s with azobenzene units

Ewa Schab-Balcerzak[a], Beate Sapich[b], Joachim Stumpe[b,c,*]

[a]Centre of Polymer Chemistry, Polish Academy of Sciences 34 M. Curie-SkŁodowska Str., 41-819 Zabrze, Poland
[b]Institute for Thin Film Technology and Microsensorics e.V., Kantstrasse 55, 14513 Teltow, Germany
[c]Fraunhofer Institute for Applied Polymer Research, Science Park Golm, 14476 Potsdam, Germany

Received 5 February 2004; received in revised form 15 July 2004; accepted 16 July 2004

Abstract

Two series of new photosensitive poly(amide imide)s (PAIs) containing photochromic azobenzene moieties as side groups have been synthesized. For this purpose the following diamines with azobenzene groups have been prepared: 2,4-diamino-4′-fluoroazobenzene, 2,4-diamino-4′-methylazobenzene, 2,4-diamino-4′-trifluoromethoxy-azobenzene and 2,4-diamino-4′-nitroazobenzene. The poly(amide imide)s have been obtained from diamidedianhydrides and diamino-chromophores using high-temperature polycondensation. The resulting polyimides are characterized by good solubility in some solvents, high glass transition temperatures (257–280 °C), high thermal decomposition temperatures and good film forming properties. The irradiation with linearly polarized light (488 nm, 100 mW/cm^2), causes a reorientation of the azobenzene groups by angular-selective *EZ* photoisomerization. In this way optical anisotropy is induced in the initially isotropic films casting from the amorphous polymers. The photoinduced dichroism in the films has been measured, and the results are discussed in relation to the structure of these polymers, whereas the substitution of the azobenzene moiety and the structure of the backbone are varied.

Keywords: Polyimides; Azobenzene-chromophores; Photoisomerization

1. Introduction

Photosensitivity and optical properties of polymers are extremely important in many fields of applications. Functional polymers containing photochromic groups have drawn much interest in the field of photonics-based technologies. Reversible changes of optical properties are achieved by molecular photoreactions and as a result of photo-induced effects changing the supramolecular structure of polymer films [1,2]. Among photochromic polymers, polymers with azobenzene groups are widely studied [3]. The exposure to linearly polarized light results in a directed reorientation of photochromic groups perpendicular to the electric field vector of the incident light [4]. The photoorientation process takes place via a number of angular selective *trans–cis* photoisomerization cycles combined with rotational diffusion in the steady state of the photoisomerization [5]. In this way optical anisotropy is generated in initially isotropic films. The possibility to generate optical anisotropy is very promising for optical data storage, orientation of polymers, photoalignment of liquid crystals (LCs) and the creation of anisotropic optical components.

Photosensitive polyimides (PI) are of special interest because of the opportunity of the photoinduced alignment of liquid crystals [6]. Macroscopic alignment of LCs is caused as a result of anisotropic interface interactions between the LC and the surface of polymer films. It allows photo-patterning of the LC alignment, so irradiation with polarized light can regulate alignment direction and tilt angle of nematic LCs [7]. In addition to the conventional rubbing technique there are many studies about the photoinduced alignment of LCs using different photochromic polymers

---

* Corresponding author. Address: Institute for Thin Film Technology and Microsensorics e.V., Kantstrasse 55, 14513 Teltow, Germany. Tel.: +49-331-568-1259; fax: +49-331-568-3259

E-mail address: joachim.stumpe@iap.fraunhofer.de (J. Stumpe).

0032-3861/$ - see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2004.07.053

[7–9]. Rubbing of polyimide films is the conventional method to produce LC displays, but it has a number of disadvantages especially due to dust and electrostatic effects. There is a strong interest to develop alternative technologies [10,11]. Photoalignment using polyimide would allow to combine the proper surface properties of PIs with photopatterning [12].

But in addition to photosensitivity, some other requirements must be fulfilled before such polymers can be applied as new aligning material. Some of these are thermal stability, especially high glass transition temperatures, solubility, film forming properties, and stability against solvents and LCs [6]. Polyimide meet these requirements; they are one of the most promising polymeric materials for various applications: nonlinear optics, optical data storage, optical information processing, or as aligning layers for LCs [6,13]. Surface properties, photochemical and optical properties of polymers depend on the polymer composition and the related processing. It is necessary to develop new functional polymers to find compromises in the polymer composition with respect to these requirements for specific applications. So it is necessary to find an optimal combination of easy preparation of thin transparent films, proper surface properties, and the high values of photo-induced anisotropy.

Bearing all this in mind a series of new PIs with the variation of the backbone as well as variation of the substitution of the azobenzene group [14–18] has been synthesized and studied.

2. Experimental

2.1. Materials

N-Methyl-2-pyrrolidinone (NMP) (Aldrich), 1,2-dichlorobenzene (Aldrich), *p*-toluidine (Aldrich), 4-(trifluoromethoxy)aniline (Aldrich), 4-nitroaniline (Aldrich), 4-fluoroaniline (Aldrich) and 1,3-phenylenediamine (Aldrich) have been used without purification.

2.2. Measurements

IR spectra have been recorded on a BIO-RAD FTS 40 A Spectrometer using KBr pellets. ^{1}H NMR spectra have been carried out on a Varian Inova 300 Spectrometer in DMSO-d$_6$ using TMS as the internal reference. Differential scanning calorimetry (DSC) measurements have been done using a TA DSC 2010 apparatus with a heating rate of 20 °C/min under nitrogen. Thermogravimetric analyses (TGA) have been performed on a Paulik–Erdey apparatus at a heating rate of 10 °C min^{-1} under nitrogen and air. The reduced viscosity has been measured in NMP at 25 °C using an Ubbelohde viscometer. Molecular weights of the synthesized polymers have been determined by size exclusion chromatography (SEC) using RI detector (Δn-1000, WGE Dr Bures). Measurements have been performed in *N*,*N*-dimethylformamide (DMF) with 5 mmol/l LiBr using a set of PSS Gram 10 μ columns: 10^3, 10^2 and 30A. All chromatograms have been obtained at 1 ml/min at 308 K. Molecular weights have been calculated according to polystyrene standards calibration using WINGPC software (PSS). The X-rays diffraction patterns have been recorded using Cu K$_\alpha$ radiation and powder samples on a wide-angle HZG-4 diffractometer working in the typical Bragg geometry. UV–Vis spectra have been recorded in NMP solution and in films on a Perkin-Elmer spectrometer Lambda 2S. The dichroism of the films has been induced irradiating with Ar$^+$ laser (Coherent Innova 90-4, 488 nm, 100 mW/cm^2). The photochemical conversion and induced dichroism have been measured using a Perkin–Elmer Lambda 19 spectrometer equipped with Glan-Thomson prism as polarizer measuring at each 10°. The dichroism has been calculated using Eq. (1).

$$D = (\mathrm{abs}_{\max} - \mathrm{abs}_{\min})/(\mathrm{abs}_{\max} + \mathrm{abs}_{\min}) \qquad (1)$$

Absorption has been measured at 488 nm.

2.3. Synthesis of diamines

Concentrated hydrochloric acid (2.7 ml) and 10 ml of water have been added to 10 mmol of *p*-toluidine (4-(trifluoromethoxy)aniline, 4-nitroaniline and 4-fluoroaniline) to obtain salt solution. Then a solution of 10 mmol of sodium nitrite in 1.5 ml of water has been added drop-wise to the cooled salt solution (ice bath) and the mixture has been stirred at a temperature between 0 and 5 °C for 15 min. After that 10 mmol of 1,3-phenylenediamine in 8 ml of methanol has been poured slowly into the solution. The reaction has been carried out for 30 min in ice bath and neutralized with sodium acetate to pH 5–6. After raising the temperature to 20 °C the mixture has been stirred for 1 h. The product has been filtered, washed with water and dried in vacuum at 70 °C.

2.3.1. 2,4-Diamino-4′-methylazobenzene **1a** [18]

^{1}H NMR (DMSO-d_6, ppm): $\delta=2.41$ (d, CH$_3$, 3H), 5.58 (s, NH$_2$, 2H), 5.91 (d, ArH, 1H), 6.02 (d, d, ArH, 1H), 6.74 (s, NH$_2$, 2H), 7.23 (d, ArH, 2H), 7.38 (d, ArH, 1H), 7.57 (d, ArH, 2H). FTIR (KBr): 3496–3364 cm^{-1} (–NH$_2$), 2900 cm^{-1} (–CH$_3$). UV–Vis (NMP): $\lambda_{\max}=442$ nm. ($C_{13}H_{14}N_4$) (226.28): Calcd. C 69.00 H 6.24 N 24.76; Found C 68.92 H 6.27 N 24.70. Mp: 141 °C. Yield 96%.

2.3.2. 2,4-Diamino-4′-fluoroazobenzene **1b** [15]

^{1}H NMR (DMSO-d_6, ppm): $\delta=5.85$ (d, ArH, 1H), 5.91 (s, NH$_2$, 2H), 5.98 (dd, ArH, 1H), 6.99 (s, NH$_2$, 2H), 7.22 (d, ArH, 2H), 7.34 (d, ArH, 1H), 7.72 (d, ArH, 2H). FTIR (KBr): 3496-3364 cm^{-1} (–NH$_2$), 518 cm^{-1} (–F). UV–Vis (NMP): $\lambda_{\max}=444$ nm. ($C_{12}H_{11}N_4F$) (230.25): Calcd. C

62.60 H 4.82 N 24.33; Found C 63.43 H 4.77 N 25.65. Mp: 154 °C. Yield 90%.

2.3.3. 2,4-Diamino-4′-(trifluoromethoxy)azobenzene **1c**

^{1}H NMR (DMSO-d_6, ppm): $\delta = 5.85$ (s, NH$_2$, 2H), 5.90 (d, ArH, 1H), 6.02 (dd, ArH, 1H), 7.12 (s, NH$_2$, 2H), 7.35 (d, ArH, 2H), 7.46 (d, ArH, 1H), 7.75 (d, ArH, 2H). FTIR (KBr): 3496-3364 cm^{-1} (–NH$_2$), 1262 cm^{-1} (–O–C–), 517 cm^{-1} (–CF$_3$). UV–Vis (NMP): $\lambda_{max} = 450$ nm. ($C_{13}H_{11}N_4OF_3$) (296.26): Calcd. C 52.71 H 3.74 N 18.91; Found C 53.71 H 3.89 N 18.68. Mp: 131 °C. Yield 89%.

2.3.4. 2,4-Diamino-4′-nitroazobenzene **1d** [16,17]

^{1}H NMR (DMSO-d_6, ppm): $\delta = 5.84$ (d, ArH, 1H), 5.84 (s, –NH$_2$, 2H), 6.1 (dd, ArH, 1H), 6.44 (s, –NH$_2$, 2H), 7.38 (d, ArH, 1H), 7.80 (d, ArH, 2H), 8.23 (d, ArH, 2H). FTIR (KBr): 3496–3364 cm^{-1} (–NH$_2$), 1493 and 1336 cm^{-1} (–NO$_2$). UV–Vis (NMP): $\lambda_{max} = 521$ nm. ($C_{12}H_{11}N_5O_2$) (257.25): Calcd. C 56.03 H 4.31 N 27.22; Found C 55.95 H 4.31 N 27.31. Mp: 233 °C. Yield 80%.

2.4. Synthesis of dianhydrides **2**

The synthesis of the diamidedianhydrides has been carried out according to the procedure in the literature [19].

2.5. Polymer synthesis (**3**, **4**)

The method of one-step high-temperature polycondensation has been utilized for the preparation of the polyimides. The polymers have been synthesized starting from the diamidedianhydrides described in Ref. [19] and the diamine-chromophores (Fig. 2). A solution of equimolar amounts of diamidedianhydrides and diamines (1 mmol) in NMP and 1,2-dichlorobenzene (80/20 (v/v), 20% total monomer concentration) has been stirred at 175 °C for 3.5 h under argon. The polymers have been precipitated by methanol and further purified by Soxhlet extraction with methanol.

The ^{1}H NMR characteristics of the obtained PAIs are collected in Tables 1 and 2.

Fig. 1 presents the ^{1}H NMR spectrum of the polymer **4h** as an example.

3. Results and discussion

In this paper the relationship between the photoorientation process and the structure of a series of new poly(amide imide)s has been studied. Two series of novel polymers **3**, **4** (Fig. 2) with azobenzene units as side group have been prepared. The specific of the design is due to the fact that one of the aromatic cores of the azobenzene moiety is a part of the backbone connected in the 2 and 4 position with imide groups. The relationship between the structure of the amorphous polymers and the efficiency of the photoorientation process has been investigated considering two points of view: the type of the 4′-substituent of the azobenzene group (series **3**) and the structure of polymer main chain (series **4**).

3.1. Synthesis and characterization of poly(amide imide)s

Novel azobenzene containing poly(amide imide)s have been synthesized by high temperature polycondensation of monomers-diamines bearing azobenzene units (**1**) with diamidedianhydrides **2**. The structure of the monomers and polymers is presented in Fig. 2.

The monomers **1** and **2** have been characterized by elemental analysis, FTIR spectroscopy, ^{1}H NMR and UV–Vis spectroscopy. The results are in accordance with the planed structures. The polymers of the series **3** and **4** have been characterized by FTIR and ^{1}H NMR spectroscopy. The FTIR spectra of all polymers show characteristic absorption bands for: the carbonyl group of the imide ring at about 1780 and 1727 cm^{-1}, the corresponding carbonyl group in the amide group at 1666 cm^{-1} and the band characteristic for the stretching vibration of the N–H groups in the region of 3350–3050 cm^{-1}. The band of the N=N linkage overlaps with that of C=C vibration of the benzene rings at around 1600 cm^{-1}. Other characteristic absorption bands have been found for the following groups: –NO$_2$ for polymer **3d** at 1510 and 1340 cm^{-1}, –O– for the polymer **3c** at 1256 cm^{-1} and –CF$_3$ for the polymer **3c** and –F for the polymer **3b** at about 518 cm^{-1}.

The ^{1}H NMR spectra of the polymers in DMSO have exhibited signals of methylbenzene, fluorobenzene, fluoromethoxybenzene, nitrobenzene and the aromatic rings at 7.30–8.6 ppm. Signals have been found for =NH at 9.90–10.1 ppm, –CH$_3$ in the main chain in the case of polymers: **3** at about 2.10–2.18 ppm, –CH$_2$– at 3.83 ppm (**3**) and 3.93 ppm (**4f**), –CH$_3$ substituted on the azobenzene group at 2.38, 2.42 ppm (isomer *cis* and *trans*) (**3a**) and –C$_2$H$_5$ at about 1.1 and 2.53 ppm (**4h**) (Tables 1 and 2).

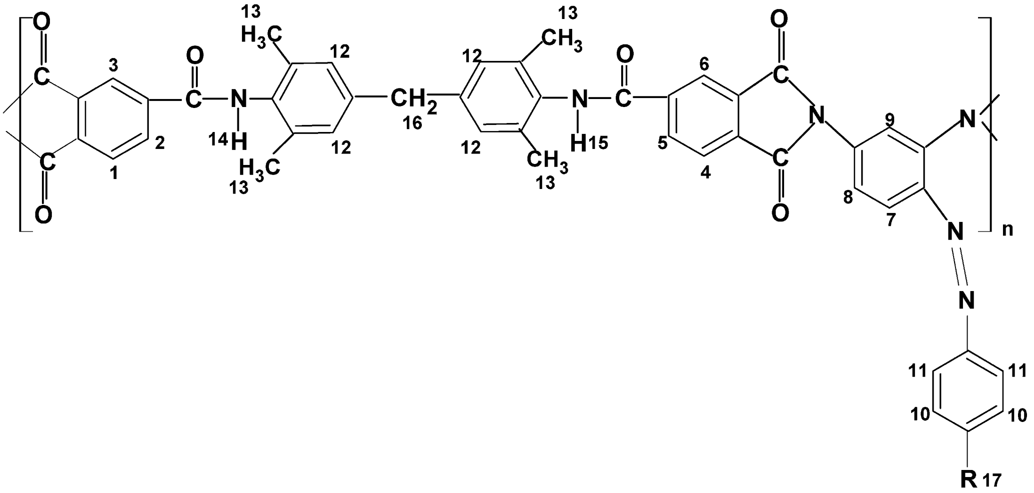
Wide-angle X-ray diffractometry indicates that there is not any crystallinity in the PAIs. (Fig. 3).

Further properties of the synthesized PAIs polymers have been investigated. The reduced viscosity and solubility of the PAIs are summarized in Table 3.

The reduced viscosity of the poly(amide imide)s is in the range between 0.16 and 0.30 dl g^{-1}. Molecular weights of some synthesized polymers (**3a**–**3d**) have been determined using size exclusion chromatography (SEC). All poly(amide imide)s have exhibited good solubility in a variety of aprotic polar solvents such as: NMP, DMA, DMF, DMSO, pyridine and 4-chlorophenol. The polymers have been insoluble in chloroform even after heating and some of them (**3a**–**3d**) have been partially soluble in THF after heating (Table 3). The ability of these polymers to form films has been examined as well. They do not form free-standing films but they give coatings of good quality on glass substrates.

The thermal behavior of the polymers is evaluated by DSC and by thermogravimetric analysis (TGA) in a

Table 1
^{1}H NMR spectra of PAIs-series **3**



Polymer code	^{1}H NMR (ppm)						
	1, **2**, **3**, **4**, **5**, **6**, **7**, **8 9**, **10**, **11**	**12**	**13**	**14**	**15**	**16**	**17**
3a(**4e**)	7.30–8.60 (m)	7.03 (s)	2.10 (s)	9.98 (s)	10.15 (s)	3.85 (s)	2.38, 2.42 (2s, *cis*, *trans*)
3b	7.38–8.58 (m)	7.03 (s)	2.19 (s)	9.90 (s)	10.14 (s)	3.84 (s)	–
3c	7.50–8.60 (m)	7.03 (s)	2.18 (s)	9.90 (s)	10.13 (s)	3.83 (s)	–
3d	7.50–8.60 (m)	7.03 (s)	2.18 (s)	10.00 (s)	10.14 (s)	3.84 (s)	–

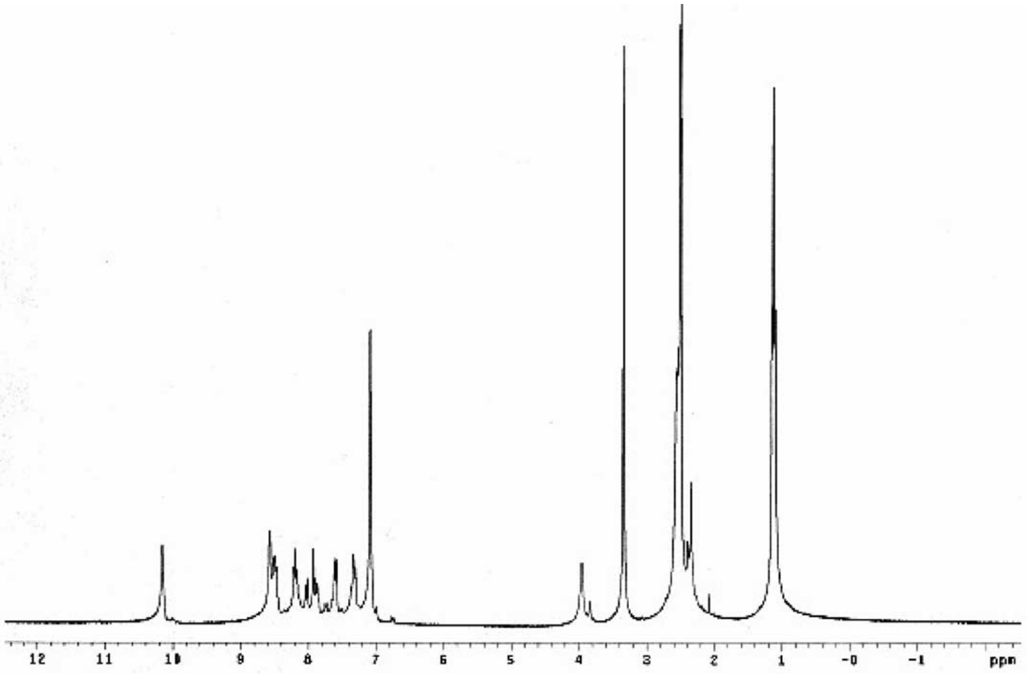
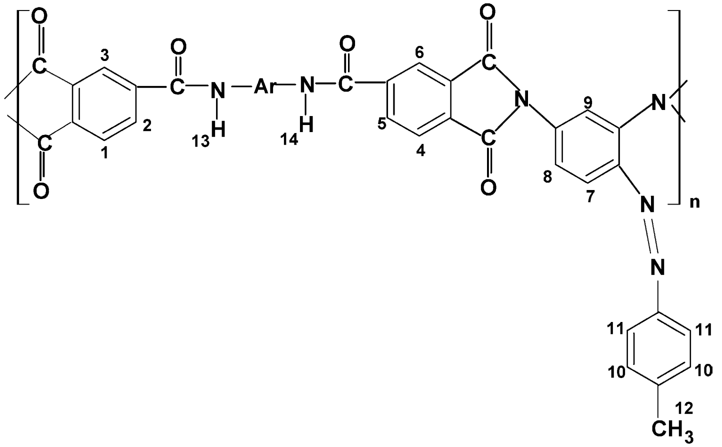
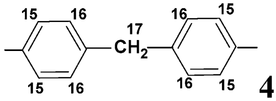
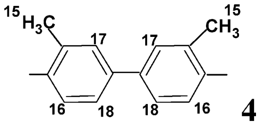
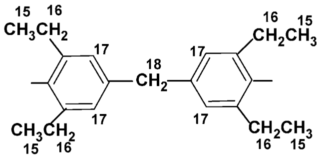


Fig. 1. ^{1}H NMR spectrum of the polymer **4h**.

Table 2
^{1}H NMR spectra of PAIs-series **4**



Polymer code Ar	^{1}H NMR [ppm]							
	1, **2**, **3**, **4**, **5**, **6**, **7**, **8**, **9**, **10**, **11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**
 **4f**	6.73–8.58 (m)	2.33, 2.38 (2s, *cis*, *trans*)	10.60 (s)		7.24 (d)	6.74 (d)	3.93 (s)	–
 **4g**	7.30–8.60 (m)	2.36, 2.39 (2s, *cis*, *trans*)	10.19 (s)	10.39 (s)	2.32 (s)	7.0 (d)	7.06 9s)	6.77 (d)
 **4h**	7.30–8.56 (m)	2.34, 2.38 (2s, *cis*, *trans*)	10.15 (s)		1.11 (t)	2.53 (q)	7.07 (s)	3.95 (s)

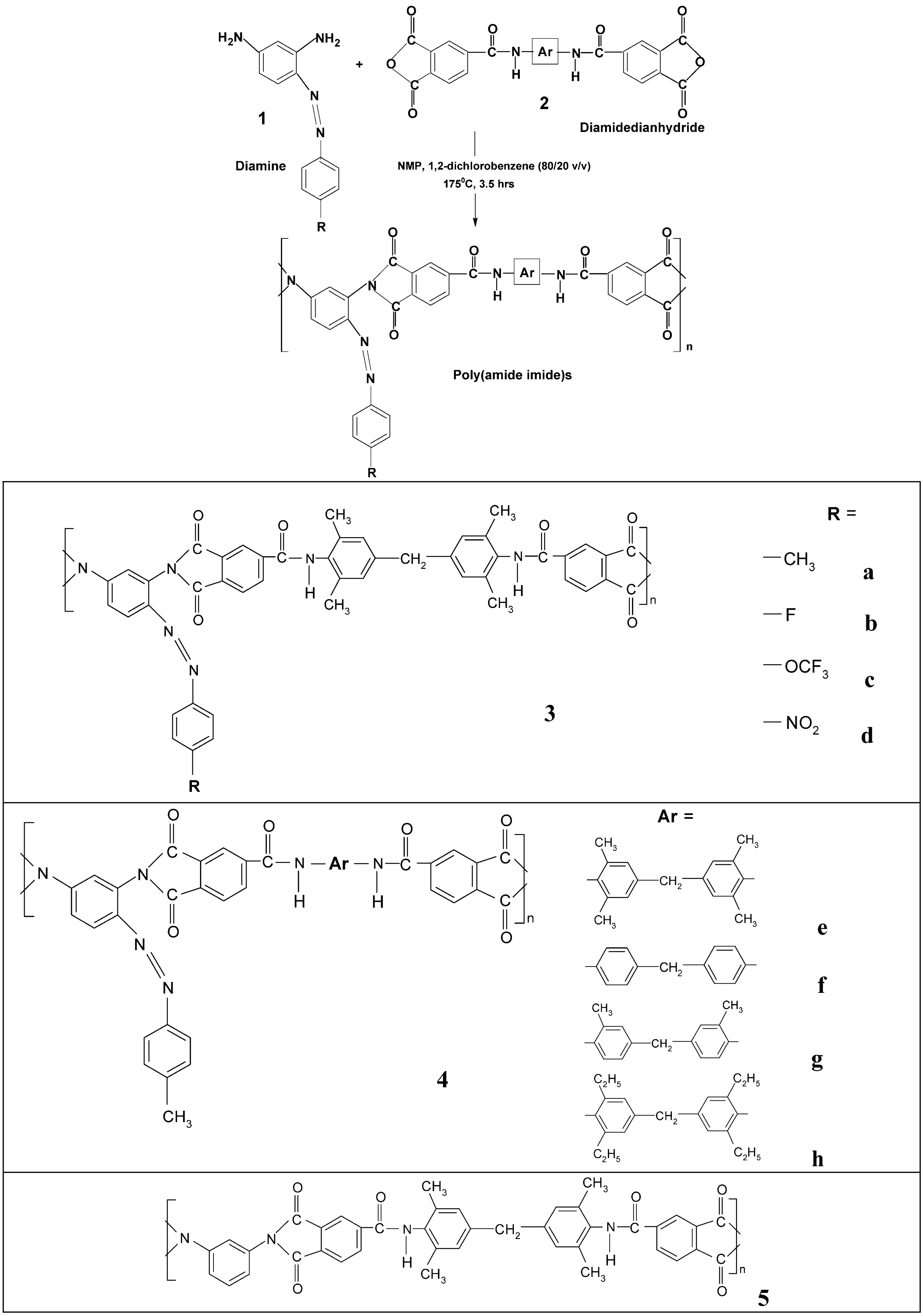


Fig. 2. Scheme of polycondensation and polymers structure.

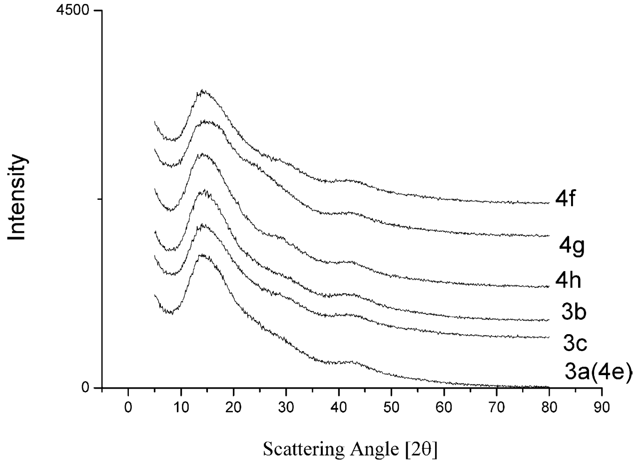


Fig. 3. X-ray diffraction patterns of the prepared PAIs.

nitrogen atmosphere and in air; the results are presented in Table 4. The DSC data does not indicate any melting peaks or phase transitions. These findings support the amorphous character of the polymers.

The DSC thermograms of the PAIs obtained from the second heating trace have showed T_g's in the range from 257 to 280 °C except for polymer **3a**(**4e**) where T_g was not detected by DSC. The polymers with 4′-methyl substitution of the azobenzene unit show in general a little lower values of the glass transition temperature (**4**) compared to polymers with other substituents. The polymer **3d** with $-NO_2$ substitution exhibits the highest T_g value. The high T_g of the polymers is mainly attributed to the imide linkages in the main chain therefore all polymers exhibit a good thermal stability. The polymers lose 10% of their weight at temperatures in the range between 400 and 470 °C in nitrogen and at 410–490 °C in air atmosphere, respectively. The residue at 800 °C is in the range of 53-70% in a nitrogen atmosphere. The highest thermal stability has been found for polymer **4g**, which should be caused by the higher rigidity of the *p*-phenylene linkages compared to the $-CH_2$-linkages in the other polymers. It is interesting that the T_{d5} and T_{d10} values in air are higher then in nitrogen. The gain of the polymer weight in air can be explained by the oxidation of the $-CH_3$ groups, which form carbonyl (C=O) and hydroxyl (O–H) groups [20]. Only in the case of polymer **3d** the values of T_{d5} and T_{d10} in air are smaller then in a nitrogen atmosphere, which probably results from the decomposition of the $-NO_2$ group at about 250 °C [21].

The influence of the substitution of polymers and diamines has been investigated by UV–Vis spectroscopy in NMP solution. Fig. 4 presents the UV–Vis absorption spectra of the diamines **1**. The weak absorption band at 280 nm corresponds probably with the benzene rings, the strong transition at a wavelength above 400 nm is connected with the π–π^* transition of azobenzene group. The influence of the kind of substitution in azobenzene group on the wavelenght of absorption maximum characteristic for π–π^* transition is observed. The absorption maximum of

Table 3
Reduced viscosity, solubility and SEC characterizations of some poly(amide imide)s studied

Polymer code	SEC (kDa eq. PS)			η_{red}^{a} (dl g^{-1})	Solubility						
	Mn	Mw	I		NMP	DMA	DMF	DMSO	Pyridine	THF	
3a (**4e**)	5.05	9.98	1.9	0.18	+	+	+	+	+	-	-+^{c}
3b	6.83	12.6	1.8	0.16	+	+	+	+	+	-	+^{c}
3c	9.14	32.2	3.5	0.22	+	+	+	+	+	-	-+^{c}
3d	6.91	15.0	2.1	0.19	+	+	+	+	+	-+	-+^{c}
4f	[b]	[b]	[b]	0.16	+	+	+	+	+	-	-^{c}
4g	[b]	[b]	[b]	0.30	+	+	+	+	+	-	-^{c}
4h	[b]	[b]	[b]	0.26	+	+	+	+	+	+	

+, soluble at room temperature; -+, partially soluble at room temperature; +^{c}, soluble after heating; -+^{c}, partially soluble after heating; -^{c}, insoluble after heating.

[a] Reduced viscosity of poly(amide imide)s measurement in NMP, concentration = 0.2 g/100 ml at a temperature 25 °C.

[b] Not measured.

Table 4
Thermal properties of poly(amide imide)s

Polymer code	T_g (°C)[a]	TGA[b]				Residue at 800 °C (%)[c]
		T_{d5} (°C)		T_{d10} (°C)		
		In N_2	In air	In N_2	In air	
3a (**4e**)	–	360	380	430	430	60
3b	279	340	400	430	430	61
3c	278	350	360	400	410	57
3d	280	340	300	430	380	58
4f	268	350	430	460	460	59
4g	257	405	430	470	390	70
4h	269	330	380	420	420	53

[a] Detected by DSC method, II run (second run) after rapid cooling at a heating rate of 20 °C/min.

[b] Recorded via TGA at a heating rate of 10 °C/min.

[c] Residual weight percentage at 800 °C in nitrogen.

the 4-nitro group (diamine **1d**) is bathochromically shifted in comparison to the other derivatives. The diamnie **1a** with methyl substitution shows the maximum at the shortest wavelength.

The same dependency from the substitution is detected for polymers obtained from these diamines-series **3** as showed in Fig. 5.

Two absorption bands in UV–Vis spectra are seen. The first absorption band is observed at about 340 nm and the second one at above 440 nm, the latter being much weaker. Taking into account the UV-Vis spectra of chromophores **1** it can suppose that the first absorption band corresponds the polymer main chain and the second one is characteristic for azobenzene group. In order to confirm this assumption the additional polymer **5** without the azobenzene group has been synthesized (Fig. 2). This polymer is obtained from 1,3-phenylenediamine and the same diamidedianhydride which is utilized for the polymer **3a**(**4e**). Both UV–Vis spectra of **5** and **3a**(**4e**) are compared in Fig. 6.

In the case of polymer **5**, which does not contain any azobenzene group, only the absorption band at 300 nm is found. It confirms that the absorption band above 440 nm is connected with the π–π^* transition of *E* azobenzene isomer. The blue shift of absorption band characteristic for polymer main chain in polymer **3a**(**4e**) in comparison with polymer **5** can be caused by the presence of additional benzene rings coming from the chromophore [6].

Fig. 7 presents a comparison of the UV–Vis absorption spectra of the polymers with the same kind of chromophore but with different structure of the PAIs main chain **4**.

One can expect that all polymers **4** exhibit the same position of absorption maximums. The polymer films have been examined by UV-Vis spectroscopy as well. They have been prepared by casting from polymer solutions in NMP on glass substrate and heating at 100 °C for a few hours. The spectra of polymer films are compared with spectra obtained in solution. No differences between the position of absorption maximum in film and in solution are observed (**3b**–**d**, **4f**–**h**) in the case of all polymers except for polymer **3a**(**4e**). The π–π^* transition of the azobenzene in the film is 18 nm hypsochromically shifted with respect to the solution which indicates the formation of H aggregates [22].

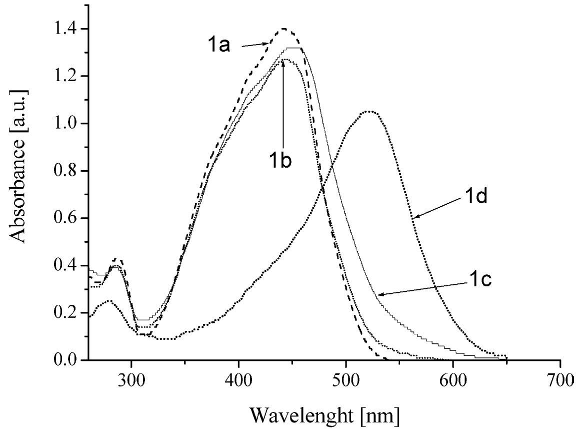


Fig. 4. UV–Vis absorption spectra of diamines in NMP solution (conc. 1×10^{-5} mol/l).

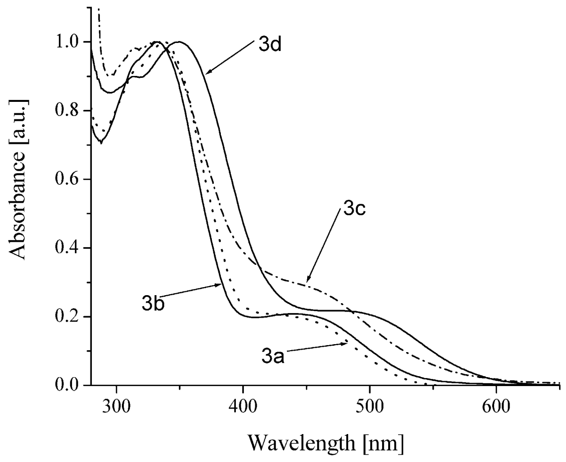


Fig. 5. UV–Vis absorption spectra of polymers **3** in NMP solution (conc. 1×10^{-5} mol/l) PAIs with different substituents on azobenzene group.

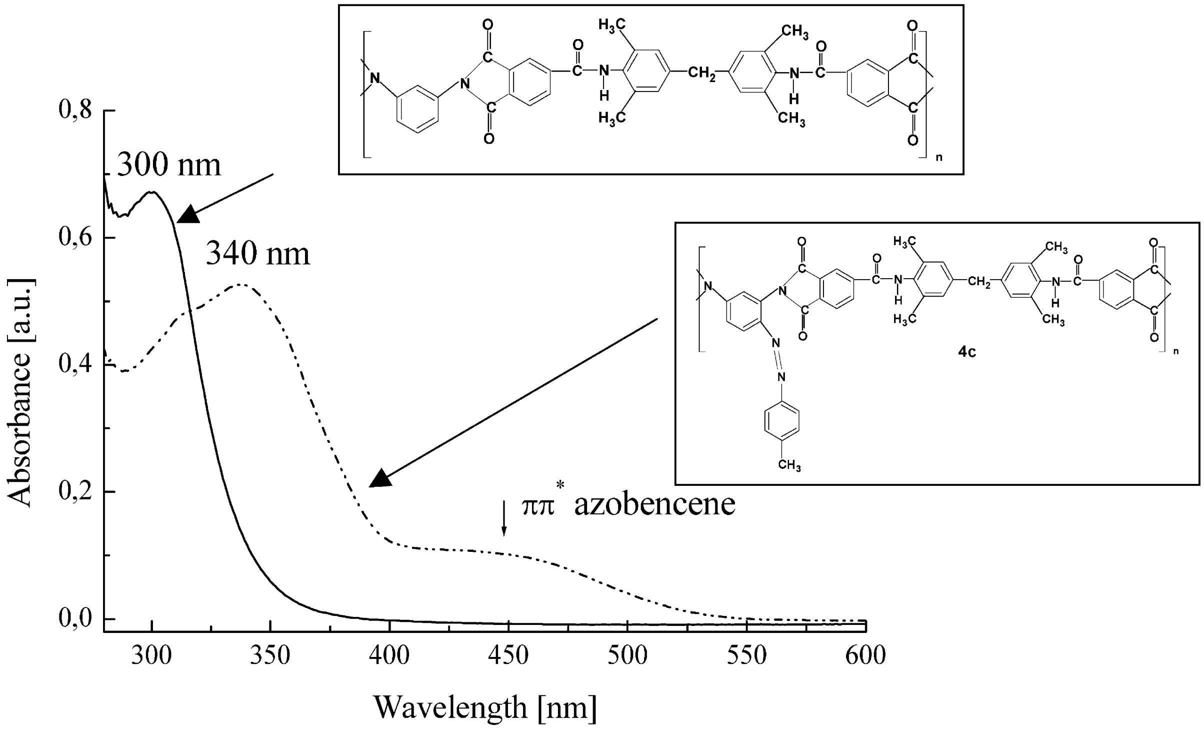


Fig. 6. Comparison the UV–Vis absorption spectrum of polymer without azobenzene group **5** with polymer containing such unit **3a**(**4e**) (in NMP solution (conc. 1×10^{-5} mol/l).

3.2. Photoorientation in polymer films

The polymer films have been irradiated with linearly polarized light of an Ar^+ laser ($\lambda=488$ nm, $P=100$ mW/cm^2) at room temperature. The irradiation causes the *EZ* photoisomerization of the azobenzene group establishing a wavelength dependent steady state between both isomers.

Films have been irradiated up to 3 h. The orientational distribution of the azobenzene moieties has been monitored after: 20 s, 1, 5, 30, 60, 120 and 180 min by polarized UV–Vis spectroscopy. The thermal *ZE* isomerization has been investigated after 1 and 7 days. The cast polymer films are optically isotropic before the irradiation process as shown for polymer **4h** as an example in Fig. 8(a).

As visualized in Fig. 8(b), the polarized exposure results in an anisotropic absorbance indicating the preferred orientation of the azobenzene groups towards a direction perpendicular to the electric field vector of the actinic light.

The value of the photoinduced dichroism for all investigated PAIs under identical experimental conditions is summarized in Table 5.

The PAIs reach their maximum value of dichroism after 120 min of irradiation. Due to the thermal *ZE* isomerization and structural relaxation at room temperature the value of dichroism slightly decreases. The value of dichroism in the case of polymer **4h** decreased from 0.20 (after irradiation) to 0.16 after 7 days. Similar drop in dichroism value is characteristic for others studied polymers.

As an example the changes in the UV–Vis absorption spectra of polymer **4h** after the thermal back reaction are present in Fig. 9.

In some of the polymer films a dichroism value up to 0.23 has been generated as shown in Fig. 8(b), whereas no dichroism has been generated in films of the polymers **3b**, **3c** and **4f**. Under standard conditions the saturation values of the dichroism, *D*, develop in the follow line:

$$-F(0) = -OCF_3(0) < -NO_2(0.18) < -CH_3(0.23)$$

Thus, quite high values of dichroism are found in the case of

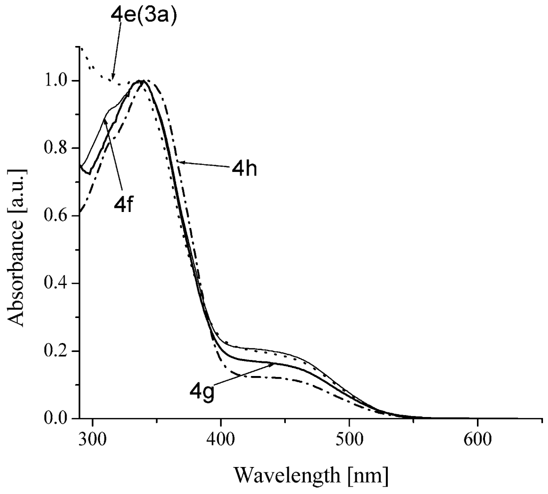
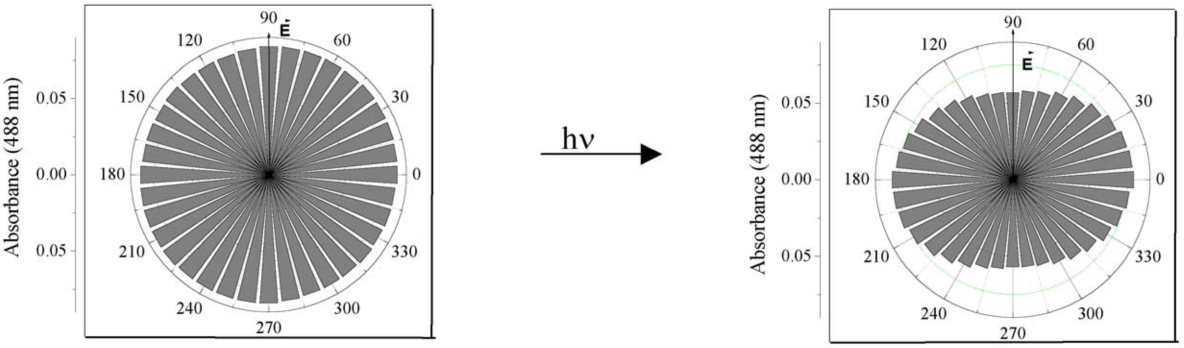


Fig. 7. UV–Vis absorption spectra of polymers **4** in NMP solution (conc. 1×10^{-5} mol/l) PAIs with different part of main chain.



(a) (b)

Fig. 8. Angular dependence of the absorbance (at 488 nm) of polymer **4h** in the initial state (a) and after polarized irradiation (b) (180 min); *E* is the direction of the electric vector of actinic light.

Table 5
The value of the photoinduced dichroism for PAIs under identical experimental conditions

	3a(**4e**)	**3b**	**3c**	**3d**	**4f**	**4g**	**4h**
Dichroism after 180 min	0.23	0	0	0.18	0	0.17	0.20

PI with donor–donor alkoxy substitution as well as with donor–acceptor alkoxy/nitro substitution. Surprisingly, the photoorientation process does not occur in the case of the polymers with the –F and –OCF$_3$ substitution of the azobenzene moiety, whereas all the polymers of the series have the same backbone. As shown by other studies, all azobenzene groups under investigation are in principle able to undergo photoorientation. The result has to be explained by the changed intermolecular interactions of the differently substituted azobenzene groups. They differ in the polarity, required free volume for the photoisomerisation, number of isomerization cycles, and the lifetimes of the *Z* isomers. The combination of substitution and matrix effects seem to influence the azobenzene-azobenzene interactions and the ability of photoorientation significantly in the case of –F containing polymers where segregation and aggregation tendency seems to increase.

In order to destroy these restrictions, polymer **3c** has been exposed to non polarized UV light before the linearly polarized irradiation. Such a photochemical pretreatment has been successfully applied in ordered and/or aggregated films to overcome supramolecular restrictions and to improve the photoorientational behavior in this way. In the case of polymer **3c** such a treatment causes an increase of the value of photo-induced dichroism from ~0 to 0.10 as shown in Fig. 10.

Moreover, the polymer of series **4** demonstrates strong influence of the polymer backbone on the photoorientational behavior, whereas all polymers have the same photochromic group with 4-CH$_3$ substitution. Therefore, the structure of the polymer main chain influences the value of the photoinduced dichroism, *D*, in a dramatic way in the line:

$$\mathbf{4f}(0) \ll \mathbf{4g}(0.17) < \mathbf{4h}(0.20) < \mathbf{4e}(\mathbf{3a})(0.23) \qquad (1)$$

Taking into account the relationship between the value of photo-induced dichroism and the polymer structure a few dependencies have been found. The highest value of dichroism is generated in the polymer which contains four methyl groups in the aromatic amid part of main chain **3a**(**4e**). The lateral methyl and ethyl groups, respectively, may increase the distance between chains, subsequently causing a decrease of inter- and intramolecular forces such as hydrogen bonding and ππ stacking between the polymer

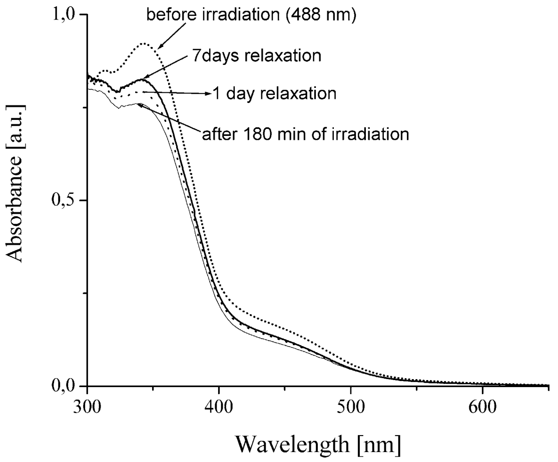


Fig. 9. Change of the absorbance of a polymer film **4h** before and after irradiation with linearly polarized light at 488 nm (180 min) and thermal back reaction.

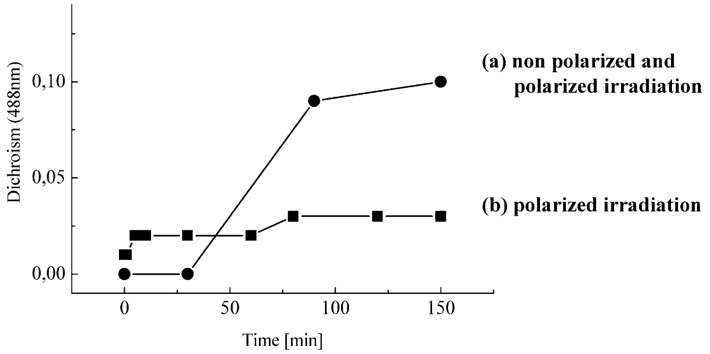


Fig. 10. Photoinduced dichroism for polymer **3c** obtained by: (a) combined irradiation (first non polarized light and then polarized light (488 nm, 100 mW/cm^2, 150 min); (b) polarized irradiation (488 nm, 100 mW/cm^2, 150 min).

chains. The polymer **4h** shows the same trend. It is less pronounced in the case of **4g** with only two methyl groups. In contrast to this, the value of dichroism in the case of polymer **4f** without any methyl group in the main chain is 0.

The anisotropic films of the synthesized PAIs have been tested concerning their ability to align liquid crystals. For this purpose polymer film of **3a**(**4e**) has been irradiated with linearly polarized light (488 nm, 100 mW/cm^2, 3 h). The polarization plane of the incident light has been tilted to 45° direction of the LC filling. The LC cell consists of a substrate with irradiated polymer **3a** film, and a substrate with rubbed polyimide. The cell has been filled with LC by capillary forces. However, homogenous LC alignment is not achieved by such aligning layer.

4. Conclusions

The new soluble poly(amide imides)s with photosensitive azobenzene groups, of which one aromatic core is a part of the stiff main chain, have been synthesized and characterized. The PAIs exhibit high glass transition temperature and high thermal stability. The molecular orientation in PAIs films induced by the irradiation with linearly polarized light causes the orientation of the azobenzene groups. However, the photoorientation process is strongly influenced by the 4′-substitution of the azobenzene group and depends on the polymer backbone, thus polymers with 4′-F and 4′-OCF$_3$ do not show any orientational effect, where azobenzenes such as the donor substitutent 4′-CH$_3$ or the strong acceptor 4′-NO$_2$ allow the induction of anisotropy. However, anisotropy can induced in all polymers by pre-irradiation with non polarized UV light and subsequent linearly polarized Vis irradiation.

Lateral methyl or ethyl substituents in the aromatic amids moiety increase the light-induced orientation effect. The generation of optical anisotropy depends on the power and on the wavelength of the incident light and each polymer needs well-chosen condition of irradiation. Polymers show pronounced long-term stability of optical anisotropy. However, the ability of such anisotropic film to align LCs is not well pronounced.

References

[1] Fisher T, Läsker L, Rutloh M, Czapla S, Stumpe J. Mol Cryst Liq Cryst 1997;299:293.
[2] Eckard T, Rutloh M, Stumpe J, Krüger H. J Inf Record 1998;24:369.
[3] Iftime G, Natansohn A, Rochon P. Macromolecules 2002;25:365.
[4] Läsker L, Fisher T, Stumpe J, Kostromin S, Ivanov S, Shibaev V, Ruhmann R. Mol Cryst Liq Cryst 1994;253:1.
[5] Yager KG, Barret ChJ. Curr Opin Solid State and Mater Sci 2001;5: 487.
[6] Kim H-T, Lee J-W, Sung Sh-J, Park J-K. Liq Cryst 2000;27:1343.
[7] Matsunaga D, Tamaki T, Akiyama H, Ichimura K. Adv Mater 2002; 20:14.
[8] Ibn-Elhaj M, Schadt M. Nature 2001;410:796.
[9] Schadt M. Mol Cryst Liq Cryst 2001;365:151.
[10] Neill MO, Kelly SM. J Phys D: Appl Phys 2000;33:R67.
[11] Lee SW, Kim SI, Lee B, Choi W, Chae B, Kim SB, Ree M. Macromolecules 2003;36:6527.
[12] Sakamoto K, Usami K, Kikegawa M, Ushioda S. J Appl Phys 2003; 39:1039.
[13] Viswanathan NK, Kim DY, Bian S, Williams J, Liu W, Li L, Samuelson I, Kumar J, Tripathy SK. J Mater Chem 1999;9:1941.
[14] Helgert M, Wenke L, Hvilsted S, Ramanujam PS. Appl Phys B 2001; 72:429.
[15] Soluka J, Bekarek V. Collect Czech Chem Commun 1980;45:1379.
[16] Sęk D, Grabiec E, Miniewicz A. Scientific Papers of the Institute of Organic and Polymer Technology of the Wroclaw University of Technology No.52, Conferences 2003, 25, 346.
[17] Grabiec E, Sęk D, Sobolewska A, Miniewicz A. Thin Solid Films 2004;453:367.
[18] Schab-Balcerzak E, Janeczek H, Kaczmarczyk B, Bednarski H, Sęk D, Miniewicz A. Polymer 2004;45:2483.
[19] Schab-Balcerzak E, Sęk D. High Perform Polym 2001;13:45.
[20] Liaw D-J, liaw B-Y, Chen J-J. J Polym Sci Part A: Polym Chem 2000; 38:797.
[21] Meng X, Natansohn A, Rochon P. J Polym Sci Part B: polym Phys 1996;34:1461.
[22] Date RW, Fawcett AH, Geue T, Haferkorn J, Malcolm RK, Stumpe J. Macromolecules 1998;31:4935.