

Photosensitive Polymers Containing Pendent Azobenzene Groups

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Polymers with polyimide, polyamide or poly(amid-imide) structure have been obtained by polycondensation of 2,2-bis(3-amino-4-oxyhexyloxy-phenyl-4'-butoxyazobenzene) hexafluoropropane with hexafluoroisopropylidene diphthalic dianhydride or two different aromatic diacid dichlorides. These polymers have been characterized by FTIR and UV-VIS spectra, molecular mass determination, solubility and optical properties. The photochromic behaviour upon UV-Vis nonpolarized and polarized light was also investigated.

Keywords: pendent azobenzene groups, polyimide, polyamide, polyamid-imide, photoinduced optical properties

Functional polymers containing photochromic groups have generated much interest in the field of optical layer technologies. Among photochromic polymers the most studied ones are the polymers which contain azobenzene groups due to the fact that by exposure to linear polarized light, the photochromic groups get oriented perpendicular to electric field vector of the incident light [1-4]. Much efforts are focused on the development of photoreactive polyimides, because they are highly thermal resistant [5-9] than azo compounds or vinylcyanamate derivatives [10-12]. Much more, the photosensitive polyimides show a special interest due to the possibilities of photoinduced orientation in liquid crystals [13,14]. In this context the present study aims to synthesize and characterize new polymers with structure of polyimide, polyamide and polyamid-imide; they have been obtained by polycondensation reaction of an aromatic diamine which contains two pendent azobenzene groups with hexafluoroisopropylidene diphthalic anhydride or diacid dichlorides of different structure. The behaviour of the obtained polymers upon irradiation with UV-Vis linearly polarized light (488 nm) as well as by irradiation with nonpolarized light has been investigated.

Experimental part

Materials

p-butoxyaniline, *p*-diphenylaniline, phenol, 1,4-dibromobutane, 1,6-dibromohexane, *p*-aminobenzoic acid, dichlordiphenylsilane, chromic anhydride, *p*-bromotoluene, hexafluoroisopropylidene diphthalic anhydride, 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane, thionyl chloride, *N*-methylpyrrolidone (NMP), NaNO₂, K₂CO₃, KI, acetone were provided by different commercial sources and used as received.

Monomers

2,2-Bis{3-amino-4-[(*p*-oxyhexyloxy-*p*'-butoxy)azobenzene]-phenylene}-hexafluoropropane was synthesized by the reaction of 2,2-bis(3-amino-4-hydroxyphenyl)-hexafluoropropane with *p*-(6-bromohexyloxy)-*p*'-butoxyazobenzene in the presence of K₂CO₃/KI at reflux temperature in acetone for 45 h by using an adapted method reported in the literature [15].

p-(6-bromohexyloxy)-*p*'-butoxyazobenzene was obtained by reaction of 4-hydroxy-4'-butoxyazobenzene

with 1,6-dibromohexane [15] and 4-hydroxy-4'-butoxyazobenzene was synthesized by diazotized of butoxyaniline followed by coupling reaction with phenol [15, 16]. The detailed description of the reaction conditions was presented elsewhere [17].

In the scheme 1 is presented the synthesis of these compounds.

2,2-bis{3-amino-4-[(*p*-oxyhexyloxy-*p*'-butoxy)azobenzene]-phenylene}-hexafluoropropane, was purified by recrystallization from a mixture of toluene:ethanol 1:2.3. Melting point: 100-114°C (liquid crystalline). Yield: 63 %.

Elemental analysis for C₅₀H₈₈O₆N₆F₆; Calc. %: C: 66.15; H: 6.4; N: 7.84; F: 10.64 Found % C: 67.28; 67.41; H: 6.82; 6.88; N: 7.58; 7.56; F: 10.5; 10.6

The FTIR spectrum of the synthesized diamine shows the characteristic absorption bands of the amine group at 3460 and 3381 cm⁻¹ and of the methylene groups at 2938 cm⁻¹ and 2871 cm⁻¹. The azobenzene group is overlapping with benzene cycles at 1598 cm⁻¹ and the hexafluoroisopropylidene bridge is present at 1237 cm⁻¹.

The ¹H-NMR spectrum of this diamine presents the characteristic peaks of methyl CH₃ protons at 0.93-0.97 ppm, of methylene protons -CH₂ at 1.39-1.78 ppm and at 3.96-4.10 ppm depending on neighbours -CH₂ and respectively O, on NH₂ protons at 4.84 ppm and aromatic protons in the domain 6.51-7.83 ppm.

Hexafluoroisopropylidene diphthalic anhydride was provided from commercial source and used as received. Melting point: 245-247°C.

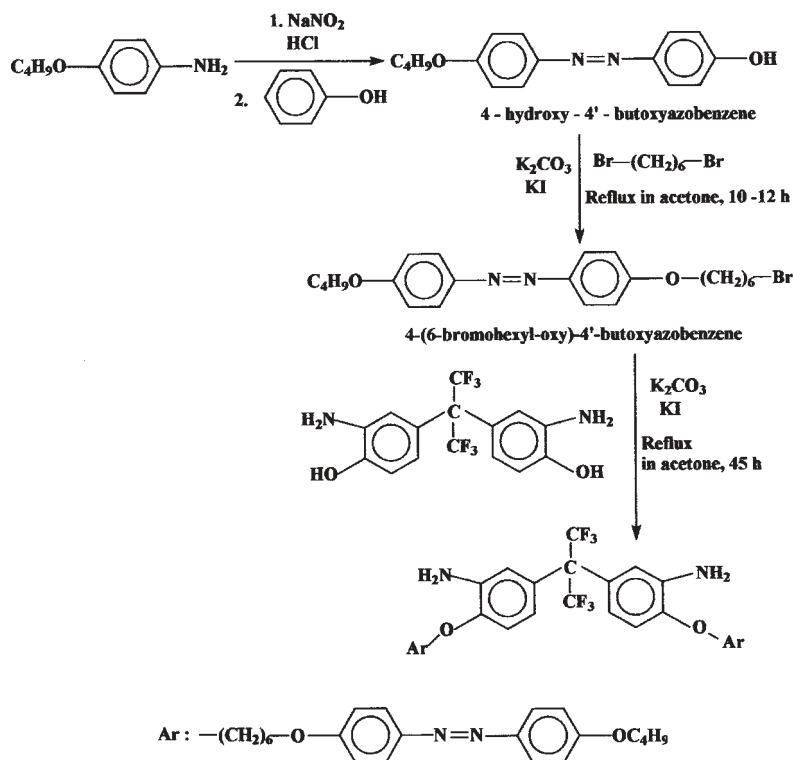
The diacid chloride containing preformed imide rings namely, *N,N'*-bis(*p*-chlorocarbonylphenyl) hexafluoroisopropylidene-diphthalic diimide, was obtained by refluxing the corresponding dicarboxylic acid in thionyl chloride. The dicarboxylic acid was prepared by the reaction of hexafluoroisopropylidene diphthalic anhydride with *p*-aminobenzoic acid. Melting point: 315-317°C [18].

Bis(*p*-chlorocarbonylphenyl)diphenyl silane, was synthesized according to a published method [19]. Melting point: 185-187°C.

Polymer synthesis

New polymers with structure of polyimide (PI), polyamid-imide (PIA) and respectively, polyamide (PA)

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Scheme 1. Diamine with two pendent azobenzene groups

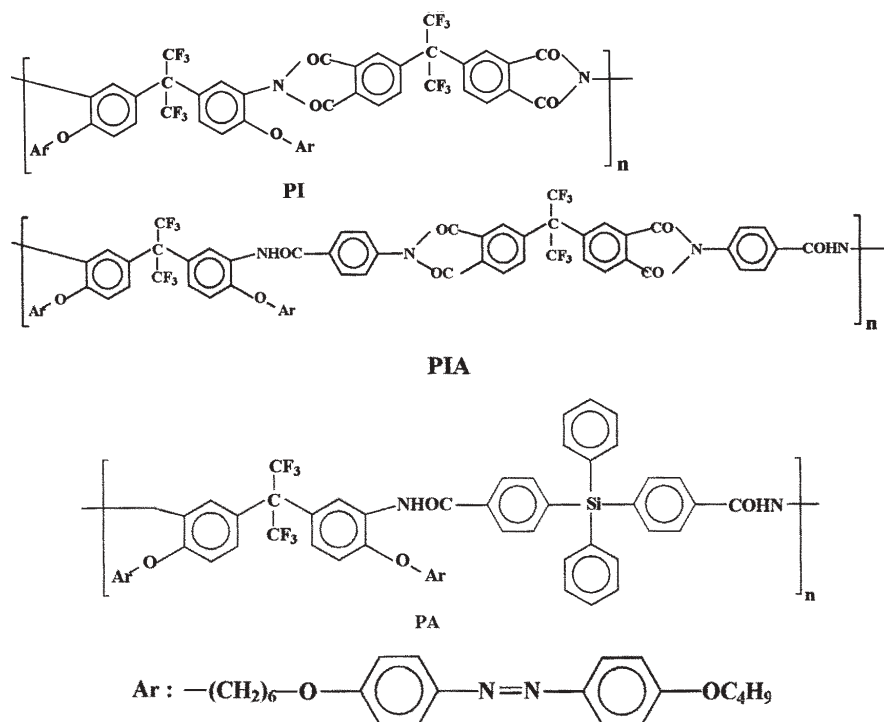
have been obtained by solution polycondensation reaction of 2,2-bis{3-amino-4-[(p-oxyhexyloxy-p'-butoxy) azobenzene]-phenylene}-hexafluoroisopropylidene diphthalic anhydride or with the diacid chlorides *N,N'*-bis(p-chlorocarbonylphenyl) hexafluoroisopropylidene-diphthalic diimide or bis(p-chlorocarbonylphenyl)diphenyl silane.

The polyimide was synthesized by a conventional two-step procedure, including a solution polycondensation reaction between diamine containing azobenzene pendent groups and hexafluoroisopropylidene diphthalic anhydride in NMP, to form poly(amid acid), followed by the chemical imidization at 100 °C in the presence of pyridine and acetic anhydride for 4 h. The imidization process was monitored by IR spectra of the precipitated polymer samples. The complete disappearance of the absorption bands characteristic for amide groups at 3450 cm⁻¹ and

1680 cm⁻¹ meant that the polymer was fully imidized. The poly(amide-imide) and the polyamide containing pendent azobenzene units have been prepared by polycondensation reaction of equimolar amounts of diamine and the corresponding diacid chlorides in NMP as a solvent, at low temperature, by using pyridine as acid acceptor. The structures of these polymers are presented in scheme 2.

Measurements

FTIR spectra were recorded with a FTS 3000 Exalibur spectrometer (Digilab). The molecular weights were determined by gel permeation chromatography (GPC) using a Waters GPC apparatus provided with refraction and UV detectors and PL Mixed C Column. Measurements were carried out with polymer solutions of 0.2% concentration in DMF containing 0.1 M NaNO₃ and by using DMF with 0.1 M NaNO₃ as eluent. Polystyrene standards of known molecular weight were used for calibration. UV-VIS spectra



Scheme 2. The structure of the polymers (PI, PIA and PA)

have been recorded in solution and in films on a Perkin-Elmer spectrometer Lambda 2S. The UV irradiation (365 nm, 3.5 mW/cm²) was carried out in a set-up consisting of a HBO lamp (100 W Osram), a metal interference filter and a water filled cuvette suppressing the IR irradiation. The dichroism of the films has been induced by irradiating with Ar⁺ laser (Coherent Innova 90-4, 488 nm, 100 mW/cm²). The angular dependence of absorbance was detected using a photodiode array UV-VIS spectrometer (Polytech, XDAP V.2.3) in combination with a computer controlled Glan-Thomson prism. Rotating the polarizer, the spectra were measured at 5° each to find the maximum and minimum of the orientational distribution. The dichroism has been calculated using (1).

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

Model molecules for a polymer fragment were obtained by molecular mechanics (MM+) by means of the Hyperchem program, Version 7.5 [20]. The same program was used to visualize the structures obtained after energy minimization. The calculations were carried out with full geometry optimization (bond lengths, bond angles and dihedral angles).

Results and discussion

The structure of synthesized polymers was confirmed by FTIR spectra which show characteristic absorption bands for the carbonyl group of the imide ring at about 1785 and 1725 cm⁻¹; the absorption band at 1365 cm⁻¹ is due to C-N stretching of the imide ring and the absorption peak at 720 cm⁻¹ is possibly due to imide ring deformation. The absorption band for carbonyl in amide group was found at 1680 cm⁻¹ and the band characteristic for the stretching vibration of NH in amide groups was found in the domain of around 3450 cm⁻¹. The band of the N = N linkage overlaps with that of C = C vibration of the benzene ring at about 1600 cm⁻¹; absorption peaks at 1200 cm⁻¹ and 1240 cm⁻¹ are characteristic to hexafluoroisopropylidene groups and absorption peak at 2940 cm⁻¹ and 2870 cm⁻¹ are characteristic of alkyl groups. Other characteristic absorption bands have been found for the phenyl-silane bonds in polymers **PA** at 1430 cm⁻¹, 1110 cm⁻¹ and 700 cm⁻¹.

All polymers exhibited IDTs (initial decomposition temperature at 5 % weight loss) above 370 °C.

The molecular weight of polymers was determined by gel permeation chromatography (GPC). The values of number-average molecular weight Mn are in the range of

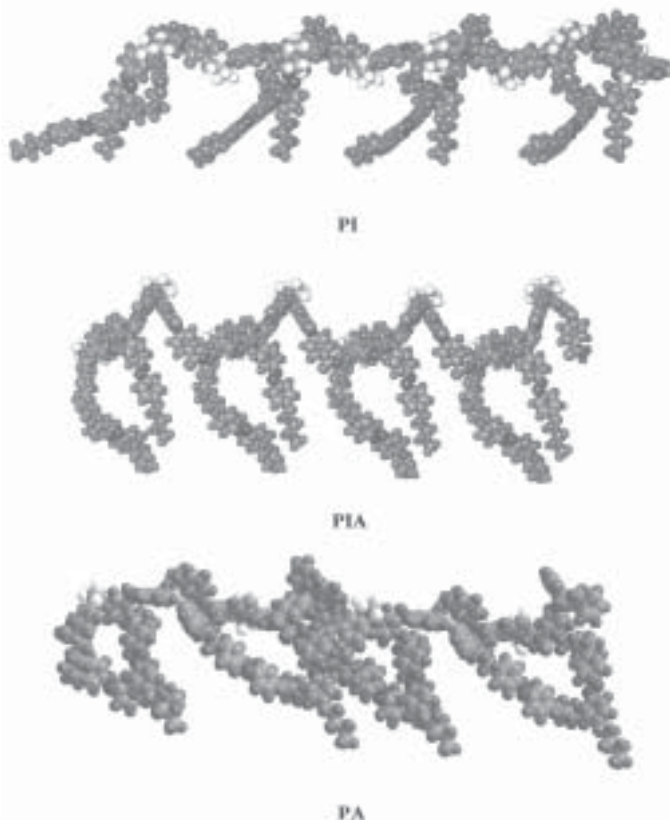


Fig. 1. Molecular models (four repeating units) of the polymers **PI**, **PIA** and **PA**

3000-42000, the weight-average molecular weight Mw is in the range of 14000-74000 and the polydispersity Mw/Mn is in the range of 1.7-4.5 (table 1). The relatively low values of molecular weight could be due to the impurity of the diamines, as shown by elemental analysis.

All polymer solutions exhibited the same position of absorption maxima in the UV-VIS spectra. Thin polymer films with a thickness of 110 nm to 180 nm were prepared from polymer solutions in THF (20 mg/mL) by spin-coating technique at room temperature in air. The polymer films were examined by UV-VIS spectroscopy and showed the same absorption maxima as the polymer solutions (Table 2). This indicates that the azobenzene moieties do not aggregate in the film.

Photoorientation in polymer films

The UV-VIS absorption spectrum of polymer **PI** upon irradiation with nonpolarized light and subsequent thermal

Table 1
THE PROPERTIES OF THE POLYMERS

Polymer	Fotoorientation ¹⁾		Spectroscopic characterization		Mw (g/mol)	Mn (g/mol)	Mw/Mn
	Dicroism Indus ²⁾		Solution (THF) λ _{max} (nm)	Film λ _{max} (nm)			
	D ₁ After irradiation	D ₂ (%D ₁) 14 days thermal relaxation ³⁾					
PI	0.16	0.10 (63%)	359	361	14000	3000	4.5
PIA	0.19	0.13 (68%)	359	361	74000	42000	1.7
PA	0.14	0.09 (64%)	359	362	27000	11000	2.4

¹⁾ irradiation conditions: 1 min nonpolarized UV light (365 nm, P= 3,5 mW/cm²); 30 min linearly polarized VIS light (488 nm, P= 100 mW/cm²); ²⁾ dichroism at 360 nm (π-π* band of azochromophore); D = (abs_{max}-abs_{min}) / (abs_{max}+abs_{min}); ³⁾ at room temperature in the dark

relaxation are shown in figure 2. The initial spectrum is characterized by the strong $\pi-\pi^*$ transition of the azobenzene chromophore at 360 nm and its weak $n-\pi^*$ transition at 450 nm (fig. 2). Upon UV irradiation (365 nm, $P = 3.4 \text{ mW/cm}^2$) of the polymer film the $\pi-\pi^*$ absorption band decreases while the absorbance of the $n-\pi^*$ transition is increased due to the photoisomerization *trans-cis*. A steady state is established upon irradiation with 365nm characterized by a high ratio of the *trans* isomer to *cis* isomer. This steady state is comparable to that observed in solution and indicates that a high percentage of the azobenzene groups can undergo the isomerization reaction and there is no restriction in non-reactive sites. The subsequent thermal *trans-cis* isomerization (thermal relaxation) regenerates the *trans* isomer in the dark.

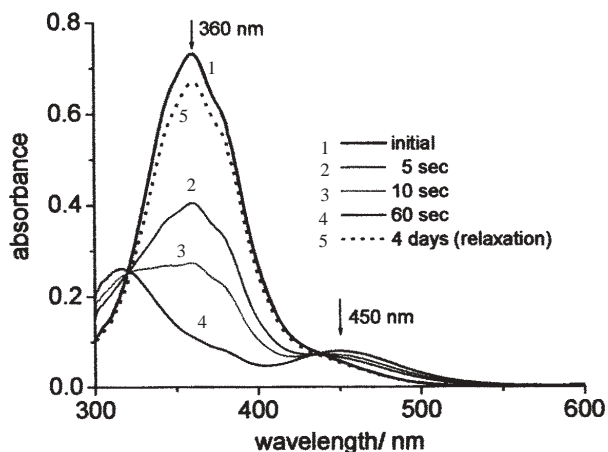


Fig. 2. UV-VIS spectra of a film of PI upon nonpolarized UV irradiation and subsequent thermal relaxation

The changes in absorbance at 360 nm upon non-polarized exposure (365 nm) and subsequent linearly polarized (488 nm) irradiation and thermal relaxation are shown in figure 3. The photostationary state is reached after 1 min nonpolarized UV irradiation. The initial absorption at 360 nm is declined by ca. 85%. After linearly polarized VIS irradiation ca. 60-75% of the initial absorption is regenerated by *trans-cis* photoisomerization. By subsequent thermal *trans-cis* isomerization at room temperature in the dark over a period of up to 18 days, the initial state is regenerated in 90 to 95%. The loss of absorbance compared to the initial film is caused by

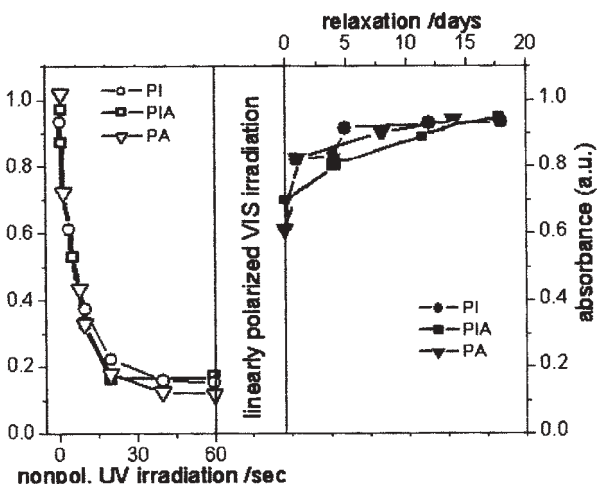


Fig. 3. Changes in absorbance at 360 nm upon nonpolarized (365 nm) irradiation, linearly polarized irradiation (488 nm) and subsequent thermal relaxation.

azobenzene groups which are aligned in the propagation direction of the laser beam preferably oriented in a plane perpendicular to the electric field vector of the incident light [21].

To prevent any aggregation of azobenzene chromophores prior the photoorientation process, the spin-coated films were firstly irradiated 1 min with nonpolarized UV light (Xe lamp, $\lambda = 365 \text{ nm}$, $P = 3.5 \text{ mW/cm}^2$). By this pre-treatment the photostationary state of the *trans-cis* photoisomerization is reached (fig. 2) and there is no anisotropy observed (fig. 3). In order to induce optical anisotropy due to photoorientation the polymer films were subsequently irradiated with linearly polarized light of an Ar^+ laser ($\lambda = 488 \text{ nm}$, $P = 100 \text{ mW/cm}^2$) at room temperature. The irradiation causes the *trans-cis* photoisomerization of the azobenzene group establishing a wavelength dependent steady state between both isomers. The films were irradiated up to 30 min and the orientational distribution of the azobenzene moieties was monitored by polarized UV-VIS spectroscopy. The polymers reach their maximum value of dichroism after 30 min of irradiation. Due to the thermal *trans-cis* isomerization and structural relaxation at room temperature the value of dichroism slightly decreases retaining the photoinduced orientation of the azobenzene groups. A practical example, the polymer film **PI** shows no anisotropy before irradiation as well as after nonpolarized UV exposure. Linearly polarized irradiation (488nm) results in an angle-dependent absorption of the $\pi-\pi^*$ band of the azochromophore with a dichroism of 0.03 after 5 s and a maximum value of 0.16 after 30 min. After 14 days of thermal relaxation in the dark a dichroism of 0.10 was detected (fig. 4).

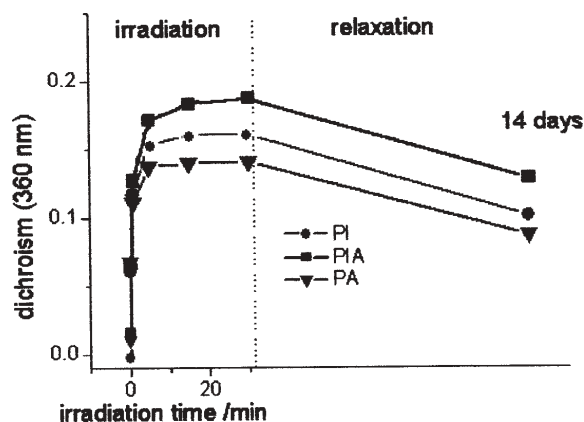


Fig. 4. Changes in photochemically induced dichroism at 360 nm upon linearly polarized irradiation (488nm) and subsequent thermal relaxation

Conclusions

The behaviour upon irradiation with UV-Vis nonpolarized and polarized light of some new polymers which contain two pendent groups per repeating unit have been studied. Readily processable films with interesting optical properties were obtained. Anisotropic optical films with long term stability were fabricated by irradiation with linearly polarized light (488 nm). Induced dichroism data were obtained in the range of 0.16 (**PI**) 0.19 (**PIA**) and 0.14 (**PA**) with slightly higher values for polymers containing phenyl-substituted azobenzene pendent groups. Thermal relaxation at room temperature caused a decrease of the initial values of dichroism by approx. 30-40 % within 14 days.

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