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-hydroxyxxyloxy-phenyl-4'-butoxyazobenzene) hexafluoropropane with hexafluorosopropylidene diphthalic diimide 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 nopolaredized 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 photoactive polymides, because they are highly thermal resistant [5-9] than azo compounds or vinylcynamate 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 polymides 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 hexafluorosopropylidene 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, dichloroanisiliane, chromic anhydride, p-bromotoluene, hexafluorosopropylidene 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-bromoanethoxy)-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-bromoanethoxy)-p'-butoxyazobenzene was obtained by reaction of 4-hydroxy-4'-butoxyazobenzene with 1,6-dibromohexane [15] and 4-hydroxy-4'-butoxyazo-benzene 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.

Elemental analysis for C₅₉H₆₈O₆N₆F₆; Calc. %: C: 66.15; H: 6.4; N: 7.84; F: 10.64; Found %: C: 67.28; H: 6.82; N: 7.58; F: 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 respectively O, on NH₂ protons at 4.84 ppm and aromatic protons in the domain 6.51-7.83 ppm.

Hexafluorosopropylidene 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) hexafluorosopropylidene-diphthalic diimide, was obtained by refluxing the corresponding dicarboxylic acid in thionyl chloride. The dicarboxylic acid was prepared by the reaction of hexafluorosopropylidene diphthalic anhydride with p-aminobenzoic acid. Melting point: 315-317°C [18].

Bis(p-chlorocarboxyphenyl) diphenylsilane, 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)
have been obtained by solution polycondensation reaction of 2,2-bis{3-amino-4-[(p-oxyhexyloxy-p'-butoxy)azo-
benzene]-phenylene}-hexafluoropropane with hexafluoro-
isoptylidene diphthalic anhydride or with the diacid 
chlorides N,N'-bis(p-chlorocarbonylphenyl) hexafluoroiso-
propylidene-diphthalic diimide or bis(p-chlorocarbonyl-
phenyl)diphenyl silane.

The polyimide was synthesized by a conventional two-
step procedure, including a solution polycondensation 
reaction between diamine containing azobenzene pendent 
groups and hexafluoroisopropyldiene diphthalic anhydride 
in NMP, to form poly(amic 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 poly-
condensation 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
have been recorded in solution and in films on a Perkin-Elmer spectrometer Lambda 2S. The UV irradiation (365 nm, 3.5 mW cm⁻²) 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, XDA V2.3) in combination with a computer controlled Glan-Thomson prism. Rotating the polarizer, the spectra were measured at five each to find the maximum and minimum of the orientational distribution. The dichroism has been calculated using (1).

\[ D = \frac{(abs_{\text{max}} - abs_{\text{min}})}{(abs_{\text{max}} + abs_{\text{min}})} \]  

(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 1385 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 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 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

![Fig. 1. Molecular models (four repeating units) of the polymers PI, PIA and PA](image)
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, $P = 3.4$ 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 365 nm 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.

The changes in absorbance at 360 nm upon nonpolarized 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 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 to the photoorientation process, the spin-coated films were firstly irradiated 1 min with nonpolarized UV light (Xe lamp, $\lambda = 365$ nm, $P = 3.5$ 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 ($\lambda = 488$ nm, $P = 100$ 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 (488 nm) 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. 2.** UV-VIS spectra of a film of PI upon nonpolarized UV irradiation and subsequent thermal relaxation

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

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

**Conclusions**

The behaviour upon irradiation with UV-Vis nonpolarized and polarized light of some new polymers which contain two pendant 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 pendant 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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