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Characterization and photoinduced properties of photo chromic polymers. 1. Polyesterimides with 4-amino 4´-nitro azobenzene moieties

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Abstract: Novel photochromic polyesterimides (PEIs) with two different types of azobenzene units as side groups have been synthesized from 2,2’-{4-[(4-nitrophenyl)-azo} phenyl]iminobis(ethyl benzene-1,2-dicarboxylic acid anhydride-4-carboxylate) and diamines: 2,4-diamino-4’-methylazobenzene and 2,4-diamino-4’-(trifluoromethoxy)azobenzene. An analogous polyesterimide with one azobenzene group based on 1,3-phenylendiamine has been prepared to compare with these PEIs. Molecular structural characterization for these polymers has been achieved by FTIR, ^{1}H NMR and UV-Vis spectroscopy. These amorphous polyesterimides are thermally stable up to 260°C as follows from the thermogravimetric analysis (TGA). The glass transition temperatures (T_g) for the resulting polyimides have been determined from DSC thermograms and are in the range of 141-210°C. The irradiation with linearly polarized light of an Ar^+ laser results in the induction of optical anisotropy within the initially isotropic films. Light induced optical anisotropy in polymer films has been studied by examining the value of generated dichroism using Ar^+ laser (λ = 488 nm) and by holographic polarization grating recording performed at λ = 514.5 nm. The value of photoinduced dichroism is in the range of 0.15-0.26. The induction of dichroism and kinetics of grating inscription have been investigated in relation to the presence of the second type of azobenzene group in the polymer and its substitution.

Introduction

Aromatic polyimides (PI) are representative of high-performance polymers possessing cyclic imide and aromatic groups in the main chain. Polyimides, due to their outstanding properties have secured a permanent place in a variety of industrial applications [1-5]. The introduction of photochromic groups and chromophores with non-linear optical properties into polyimides offers opportunities for applications of PI in the field of photonics-based technologies. Aromatic polyimides have attained much attention for such applications mainly due to their high glass transition temperature (T_g). The employment of the polymers with high T_g is one of the approaches to overcome the serious problem of the temporal stability of chromophore alignment at elevated temperatures [6]. The achieved alignment of azobenzene groups is affected by the segmental and main chain motions [7]. High T_g polymers may show a more stable orientation, since the motions of the polymer chain are related to the difference between the operating temperature and T_g. It is preferable to investigate polymers with high T_g for the reversible optical storage process [7] and optical device applications in which polymers with high second-order nonlinear optical properties are required [8]. Fundamental studies to produce novel photo- and opto-functional polyimides are becoming increasingly indispensable [9-11]. Therefore, the development of polyimides with novel combination of properties continues to be an important research area.

Molecules of the chromophores can be introduced into polymer in different ways. Initially guest-host polymer system was studied, however, the current molecular design strategy is to synthesize fully functionalized polymers with chromophores covalently incorporated into an aromatic polyimide backbone [12, 13]. Incorporating photochromic molecules into materials leads to photoresponsive systems the properties of which can be manipulated by light. The interaction of linearly polarized light with photochromic moieties offers the opportunity for the photoinduced generation of optical anisotropy. The possibility to generate optical anisotropy is very promising for holography, photoalignment of liquid crystals (LCs) and other optic applications [14]. The phenomenon of photoinduced anisotropy produces optical dichroism and birefringence in various materials by generating an orientational order [15-17]. Azobenzene-containing polymers are known to be among the most effective materials for generating photoinduced anisotropy [18-21]. In such polymers the optically induced anisotropy is a consequence of the reversible E-Z (*trans-cis)* photoisomerization cycles of the azobenzene group upon irradiation with linearly polarized light, which induces an angular redistribution in the orientation of the photochromic entities.

Research on photochromic polyimides is aimed at three principal directions of potential applications: (i) as recording media for holographic data storage [9-11, 22-25], (ii) as alignment layers in LC devices [26-30] (because the photoalignment technique has the potential to replace the conventional rubbing method) and (iii) for second-order nonlinear optics i.e. electro-optical modulation, optical switching, and second harmonic generation [31-35].

One of the current challenges is to design photochromic polymers having optimized properties. In order to optimize the performance of materials for photonic applications, a fundamental understanding of the interrelationship between their chemical structure and photoinduced properties is required. The photoinduced order depends on many parameters: the substitution of the azobenzene moiety, the length of spacer between the polymer main chain and the azobenzene side group and their size, the structure of the photo-insensitive parts of the macromolecule, the molecular weight of the polymer as well as on the film preparation, the aging of the film, and the aggregation of the azobenzene moieties. Both the chemical structure of the chromophores and that of the polymer comprise the most important factors, which determine the photoorientation properties [36-39]. In our previous work [38, 40] we have studied the influence of the polyimides backbone structure and the kind of azobenzene group substituents on photoinduced anisotropy in polyimide films. It was found that even simple structural changes in the chromophore and in the polymer chain can lead to significant changes in optical properties (in value of photoinduced dichroism). This work is a part of a series of studies on the relation between polyimide structures and their photoinduced properties. Our previous results showed that the highest value of dichroism is exhibited by polyamideimides with $–NO_2$ and -

CH_3 groups in azobenzene moiety [38,40]. Thus such substituted azobenzene groups have been introduced into new polymers in order to investigate the influence of other structural elements on light induced properties. Photoinduced properties of polymer material can be significantly altered by varying the ratio of chromophore to polymer, thus concentration of chromophore moieties is another important parameter [41, 42]. In this article the correlation between concentration of chromophores in the polymer unit and photoinduced properties such as the value of photoinduced dichroism and ability of holographic gratings formation have been studied. Furthermore the influence of the kind of substituents on second azobenzene group (see Fig.1.) in polymer unit has been examined.

Results and discussion

Novel polyesterimides containing two different kinds of azobenzene unit as pendant functional groups have been synthesized (Fig. 1).

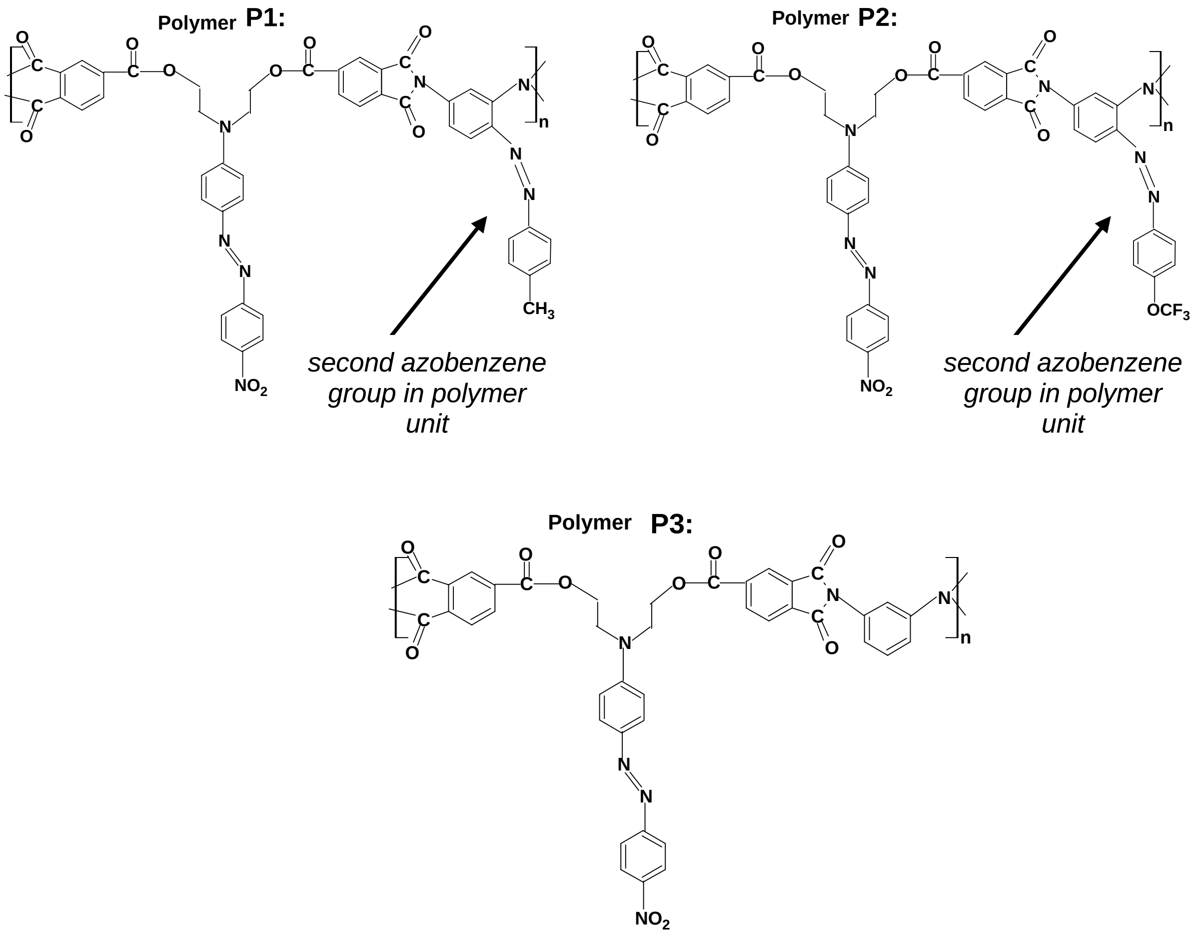


Fig. 1. Structure of the synthesized polyesterimides.

The polyesterimides have been obtained from dianhydride which contains amino-4'-nitroazobenzene group as photoactive moiety as well as ester and aliphatic units. Such dianhydride has been selected because the presence of amino-4'-nitroazobenzene group constitutes more flexible connection with the polymer backbone than in polyimides described in our previous work [38]. Furthermore the presence of alkyl groups and ester linkages in polymer backbone should enhance the solubility of polyimides and as a consequence of this improve the processability. The aromatic core of the second azobenzene group (**P1** and **P2**) is a part of the polymer backbone, which connects two imide groups by substitution in the 2 and 4 positions. This azobenzene unit is substituted in the 4´ position with methyl or trifluoromethoxy group. The relationship between structure of the new polymers and the efficiency of the photoorientation process has been investigated. Properties of these polyesterimides (**P1** and **P2**) have been compared with properties of polyesterimide with lower concentration of azobenzene groups in polymer unit that means, containing only amino-4'-nitroazobenzene group (**P3**) which is partially described in our previous work [40]. After confirming the structure of the resulting polymers their properties such as T_g, thermal stability, solubility, and photoinduced properties i.e. value of dichroism and kinetics of grating recording in polymer films have been investigated.

Polymer characterization

The structure of the polymers has been confirmed by conventional techniques such as elemental analyses (Tab. 1), FTIR (Tab. 2) spectroscopy and ^{1}H NMR (Tab. 3) spectroscopy. The results of the elemental analyses of PEIs are collected in Tab. 1.

Tab. 1. Elemental analysis of the polyesterimides

Polymer code	**Repeating units formulae (Formula weight)**	**Elemental analysis; Calc. (Found)**		
		C%	**H%**	**N%**
P1	$(C_{47}H_{32}N_8O_{10})_n$ $(868.80)_n$	64.98 (62.10)	3.71 (4.39)	12.89 (11.59)
P2	$(C_{47}H_{29}N_8O_{11}F_3)_n$ $(938.74)_n$	60.13 (61.99)	3.11 (3.46)	11.94 (12.57)
P3	$(C_{40}H_{26}N_6O_{10})_n$ $(750.68)_n$	64.01 (62.28)	3.49 (3.52)	11.20 (10.10)

Compared to the calculated content of nitrogen and hydrogen in the proposed structures, the elemental analysis shows good agreement. However, some differences in the calculated and found values of carbon may be due to the difficulties in burning these high-temperature polymers.

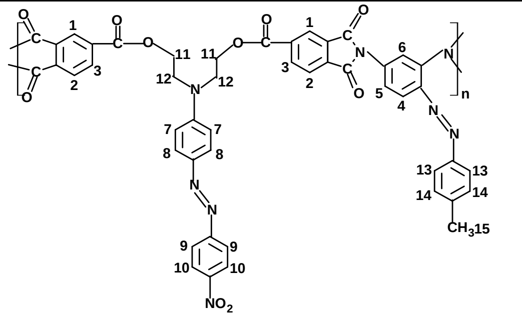
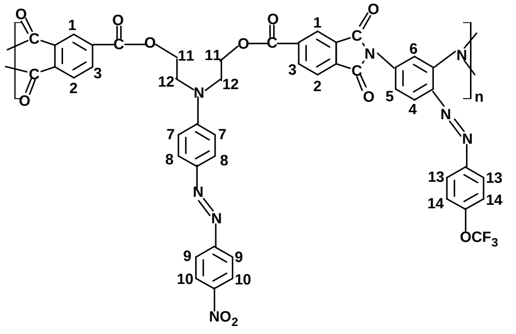
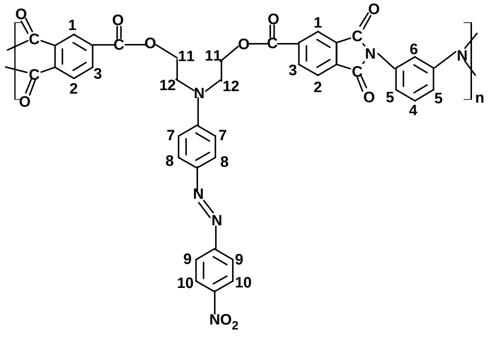
Tab. 2. Characteristic IR absorption selective bands (cm^{-1}) of the polyesterimides

Polymer code	**P1**	**P2**	**P3**
-C=O stretching	1782, 1727	1784, 1727	1782, 1724
-C-N stretching	1365	1365	1365
-N=O	1516, 1340	1515, 1341	1516, 1340
-C-O	1250	1252	1249
C= O bending	727	727	726

The FTIR spectra of the polyesterimides show clearly the characteristic imide absorption bands at approximately 1782 and 1724 cm^{-1} attributed to the symmetric stretching and asymmetric stretching vibration of the carbonyl group of the fivemembered ring, the absorption band at about 1365 cm^{-1} corresponding to the C-N stretch and the absorption band at 727 cm^{-1} to the C=O bending vibration, respectively. The absorption bands at about 1516 and 1340 cm^{-1} indicate the existence of the nitro groups in the structure of the polymers. Characteristic IR absorption selective bands of the polyesterimides are summarized in Tab. 2.

Additional characterization of the molecular structure of the polymers has been done by ^{1}H NMR spectroscopy. The ^{1}H NMR characteristics of the polymers are collected in Tab. 3.

Tab. 3. Examination of polyesterimides by ^{1}H NMR in DMSO

Structure	**^{1}H NMR [ppm]**			
	**H1**	**H2-H5**	**H6**	**H7-H10**
	7.1-7.2	8.1-8.6	7.0-7.1	7.6-7.9
	H11	**H12**	**H13-H14**	**H15**
	4.1	4.6	7.6-7.9	2.4-2.5
	**H1**	**H2-H5**	**H6**	**H7-H10**
	7.1-7.2	8.2-8.6	7.0-7.1	7.6-8.0
	H11	**H12**	**H13-H14**	
	4.1	4.63	7.6-8.0	
	**H1**	**H2-H5**	**H6**	**H7-H10**
	7.5	8.2 – 8.4	7.2	7.8 – 8.0
	H11	**H12**		
	4.1	4.6		

^{1}H NMR spectra of the polymers in DMSO show a signal broadening resulting from polymerization, but the chemical shifts are consistent with the proposed polymer structures. The signals of the methylene group linked with ester bond and of another methylene linked with a tertiary amine in all polymers are in the same range. In the case of polyimide **P1** the peaks in the range 2.40-2.50 are assigned to methyl group.

The obtained results from FTIR and NMR spectroscopy for PEIs are in accordance with the proposed structures.

The solubility of synthesized polyesterimides has been determined for the powdery samples in excess of solvents at room temperature. The polymers are soluble not only in amide polar solvents (NMP, DMA) but also in DMSO and less polar *m*-cresol and even in conventional solvents such as pyridine, partially in THF, 1,1,2-trichloroethane and in acetone (**P1, P2**). The enhanced solubility of the polyimides may result from the presence of the flexible ester linkages and aliphatic groups in the polymer chain.

Thermal properties of polyesterimides have been studied using differential scanning calorimetry (DSC) and thermogravimetrical analysis (TGA). Thermal properties of polymers are listed in Tab. 4.

Tab. 4. Thermal properties of polyesterimides

Polymer	**T_g[a] [^{0}C]**	**Decomposition temp.[b] [^{0}C]**	
		T_5 (T_{10})	**RW [%]**
P1	179	270 (280)	41
P2	183	280 (290)	45
P3	210	280 (330)	52

[a] determined on the second heating scan. Scanning rate 20^0C min^{-1},

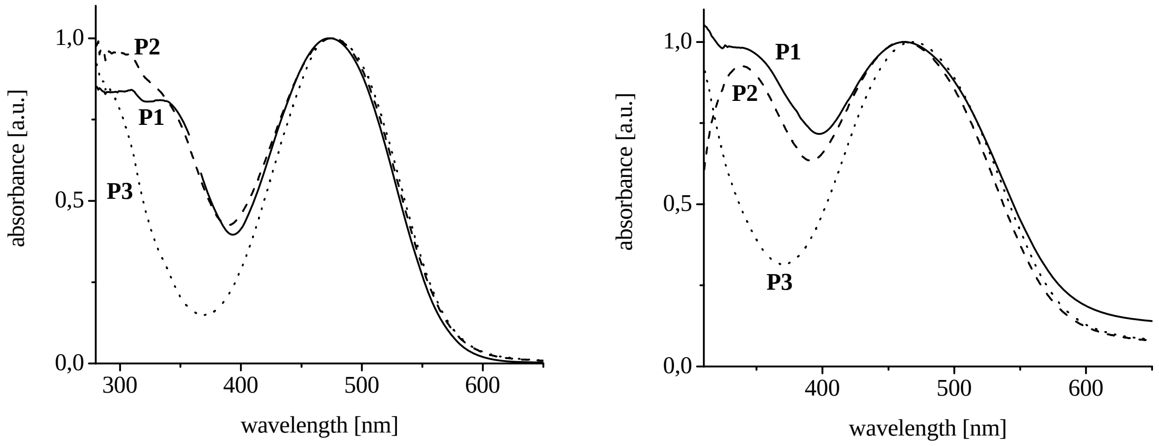
[b] temperature of 5% and 10% weight loss (T_5 and T_{10}) and residual weight percentage (RW%) at 800^0C were determined by TGA under N_2 atmosphere.

The glass transition temperatures of the polyesterimides have been determined by differential scanning calorimetry (DSC). The glass transition is a physical property resulting from thermal motion (rotation or translation) of mobile groups and associated with flexibility of substituted group and spatial vacancies within polymers [43]. Despite the presence of the flexible ester bond and the aliphatic groups in the backbone that may cause a relatively easy motion among the polymeric main chain, T_g values are high. The high values of T_g are attributed to the imide groups. The DSC thermograms of the polyesterimides obtained from the second heating trace show T_g values between 179-210°C. The highest value of T_g among studied polymers is shown by the polymer **P3** i.e. polyesterimide with one azobenzene group in polymer unit. No considerable change in T_g is observed when substituents on second azobenzene group $-CH_3$ and $-OCF_3$ are changed (the case of polymers **P1** and **P2)**. The thermal stability of the polyesterimides has been evaluated by thermogravimetrical analysis (TGA) under nitrogen (Tab. 4). The 5% and 10% weight loss has been recorded within temperature ranges of 270–280°C and 280-330°C, respectively. The residue at 800°C of investigated polyimides is between 41 and 52%. Polyesterimides obtained from the diamine-chromophores (**P1, P2**) exhibited lower temperature of 10% weight loss and smaller residue at 800°C when compared to polyimide **P3**.

The crystallinity of the new polyesterimides has been evaluated by wide-angle X-ray diffraction experiments. According to the wide-angle x-ray spectroscopy, in the region of $2\theta=5\text{-}80^0$ at room temperature, polyesterimides are amorphous. Amorphous structure is evidenced by the absence of a melting endotherm in the DSC thermograms as well.

Optical properties

The optical properties of polyesterimides have been investigated by UV-Vis absorption spectroscopy. The UV-Vis spectra of the polymers synthesized in this study have been acquired both in solutions and in films. The UV-Vis spectra of polyesterimides in NMP solution are compared in Fig. 3a.

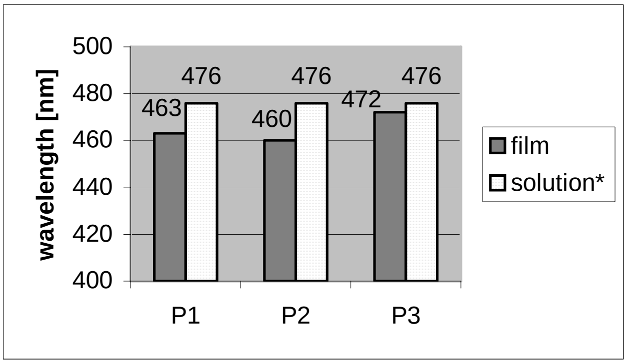


(a) (b)

Fig. 3. UV-Vis absorption spectra of the studied polyesterimides (a) in NMP solution (conc. 1x10^{-5} mol/l) and (b) as films.

In UV-Vis spectra the strong absorption band with maximum at 476 nm is observed for all polyesterimides. All polyimides contain the azobenzene chromophore which consists of nitro group acting as electron acceptor and amino group acting as electron donor. This amino-4'-nitroazobenzene moiety is a typical push-pull substituted azobenzene group characterized by a long wavelength absorbance and very short lifetime of its Z isomer. So this absorption maximum peak at 476 nm mainly results from $\pi\pi^*$ electronic transition of the chromophore i.e. amino-4'-nitroazobenzene [44]. Independent of the presence one or two azobenzene group in polymer constitutional unit, only one absorption band in UV-Vis spectra of polyesterimides is observed. The absorption band of the azobenzene group being a part of diamine fragment present in the case of polyesterimides **P1** and **P2** is probably overlapping with the absorption ascribed to the amino-4'-nitroazobenzene. The second azobenzene group (i.e. which is a fragment of diamine) is a part of the backbone connected in the 2 and 4 position with imide groups (Fig.1). Taking into account our previous result for polymers with the same type of chromophore [38] such azobenzene group absorbs at above 440 nm ($\pi\pi^*$ transition of E azobenzene isomer). This second azobenzene group is substituted in the 4´ position with methyl (**P1**) or trifluorometoxy (**P2**) group but no difference in the position of the absorption maximum of the band characteristic for azobenzene units is detected.

Investigated polyestreimides show good film forming properties. Films have been obtained by casting polymer solutions in NMP on glass substrates. Films have been examined by UV-Vis spectroscopy. The electronic spectra of the polymer films are showed in Fig.3b. The absorptions can be attributed directly to the spectra of the chromophore. The wavelength of the maximum absorption band position in polymer films is showed in Fig. 4.



**conc. $1x10^{-5}$ mol/l in NMP*

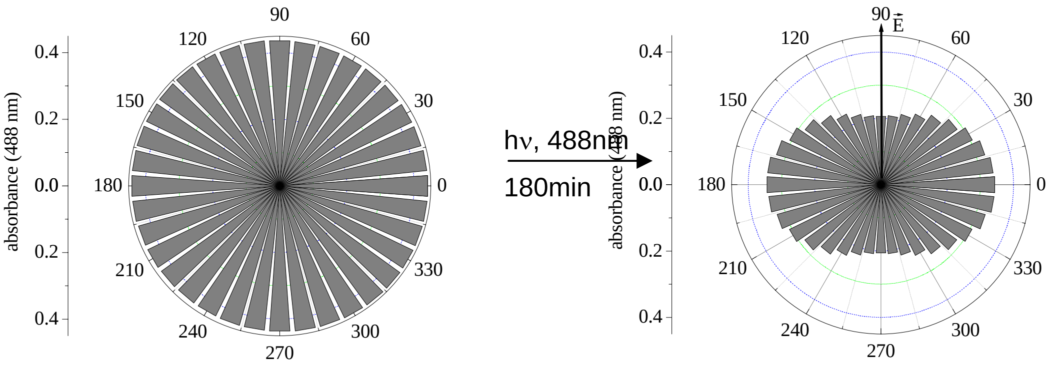
Fig 4. Comparison of absorption maximum peak positions in polyesterimides in solution and film.

The film from polyesterimide **P3** (λ_{max} = 472 nm) shows a shift of the absorbance maximum to longer wavelength in comparison with **P1** (λ_{max} = 463 nm) and **P2** (λ_{max} = 460 nm) (Fig.4). This is in agreement with the behavior of azobenzene side chain polymers, where an increase of the concentration of azobenzene groups usually induces a blue shift for the absorption maxima [45]. In our case polymers **P1** and **P2** exhibit higher concentration of chromophore than **P3** and due to these polymers (**P1** and **P2**) show blue shift of the absorption maxima compared to **P3**.

The spectra of polyesterimide films are compared with spectra obtained in solution and are quite similar. However, the maximum of the absorption band in the film is hypsochromically shifted (4-16 nm) with respect to the solution (Fig.4) it could be explained as the consequence of partial H-aggregation of azobenzene units [46].

Photoinduced properties

To induce optical anisotropy, polymer films have been irradiated at room temperature with the linearly polarized light of an Ar^+ laser (λ = 488 nm, P = 100 mW/cm^2). The photoorientation process takes place via the E/Z photoisomerization of azobenzene groups (Scheme 1) establishing a wavelength dependent steady state between both isomers.

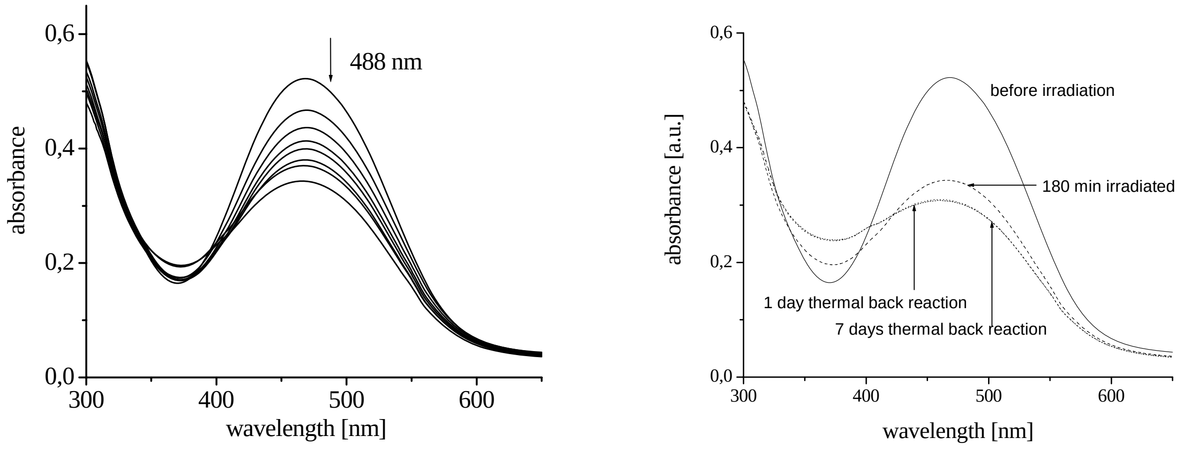


(a) (b)

Fig. 5. Angular dependence of the absorbance in polyimide **P3** in the initial state (a) and after polarized irradiation (b); E is the direction of the electric vector of actinic light.

Films have been irradiated up to 3 hours so that a large number of this photoisomerization cycles took place. The cast polymer films are optically isotropic before the irradiation as illustrated in Fig. 5a for polymer **P3** as an example. As can be seen from this Fig. 5b the irradiation with laser light induced anisotropy in polymer film.

After the irradiation UV-Vis spectra of all polyesterimides exhibited the gradual decrease of absorbance with the exposure time due to induction of anisotropy. As an example the changes in the UV-Vis absorption spectra of polymer **P3** after exposure are shown in Fig. 6a.



(a)

(b)

Fig. 6. Change of absorbance of polyesterimide **P3** film (a) during irradiation with linearly polarized light at 488 nm and (b) during thermal back reaction.

The observed decrease of absorbance could be caused by the establishing of both steady states of the photoisomerization reactions and by the photoorientation populating preferably all directions perpendicular to the electric field vector of incoming light. In this way dichroism is induced and an increase of the out-of plane component of absorption is observed. The irradiated films have been examined by UV-Vis spectroscopy after 1 and 7 days of relaxation. The spectra after 1 and 7 days show a slight increase of absorbance indicating a week molecular and matrix relaxation (Fig. 6b). But the initial value of absorbance is not rebuilt even after 7 days at room temperature. Similarly, the changes can be explained as due to the large alignment stability these polymers possess.

The in-plane orientational distribution of the azobenzene moieties has been monitored after 20 sec, 1 min, 5 min, 30 min, 60 min, 120 min and 180 min by polarized UV-Vis spectroscopy. From the absorbance change, the value of dichroism has been estimated using following calculation:

$$D = (abs_{max} - abs_{min})/(abs_{max} + abs_{min}) \qquad (1)$$

where the absorption has been measured at 488 nm.

The polarized exposure induces a dichroism with a preferred orientation of the azobenzene groups towards a direction perpendicular to the electric field vector of the actinic light. Fig. 7 shows the kinetics of the process for all polyesterimides under investigation.

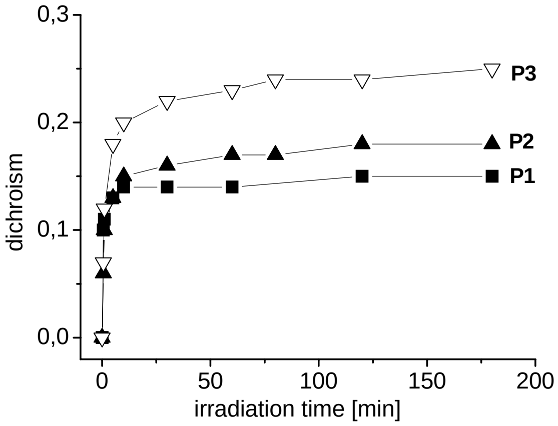


Fig. 7. Dichroism induced with linearly polarized light at 488 nm as a function of irradiation time.

The behavior of all studied polyesterimides is similar. A high value of dichroism is reached after 10 min of irradiation. Then slow increase of dichroizm along with extension of illumination time is observed and after 120 min the saturation value of dichroizm is achieved. The maximum values of the photoinduced dichroism for all investigated polyimides under identical experimental conditions are summarized in Fig 8.

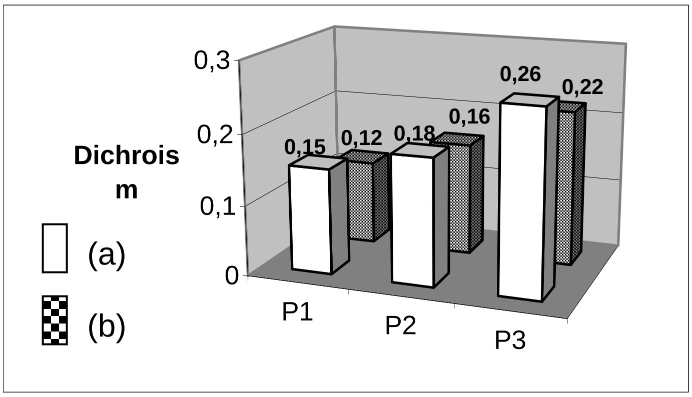


Fig. 8. The values of the photoinduced dichroism (λ=488 nm) for the polyesterimides under identical experimental conditions: (a) calculated just after irradiation and (b) after 7 days of thermal back reaction.

The highest value of dichroism of about 0.26 is found for polyesterimide **P3** without the second azobenzene group (i.e. being a part of diamine fragment). It seems that under irradiation with laser wavelength at 488 nm (100 mW/cm^2) mainly the amino-4'-nitroazobenzene photoisomerizes. Under the applied irradiation conditions the second azobenzene group does not participate actively in the photoorientation process. However, it is not expected that the value of induced dichroism is smaller in polyimides with two azobenzene units (**P1** and **P2**) in comparison with **P3**. In the case of **P1** and **P2** two azobenzene groups have to undergo photoisomerization and possibly in order to achieve the same level of photoinduced anisotropy they need others wavelengths of irradiation. The explanation of this phenomenon needs more experiments.

The relaxation behavior in these polyimides has been examined after 1 and 7 days at room temperature by calculation of the dichroism value. Due to the thermal Z/E isomerization and structural relaxation the value of dichroism slightly decreases (Fig. 8). The polyesterimides exhibit similar relaxation behavior. The remnant dichroism is stable at about 85% for **P3**, 89% for **P2** and 80% for **P1**.

Optical grating recording experiments

Kinetics of holographic grating recording in the polyesterimides films has been studied using a standard degenerate two-wave mixing technique (DTWM) [47] with 514.5 nm line of Ar^+ laser (I_1=I_2=560 mW/cm^2). The experimental DTWM set-up is shown in Fig. 9.

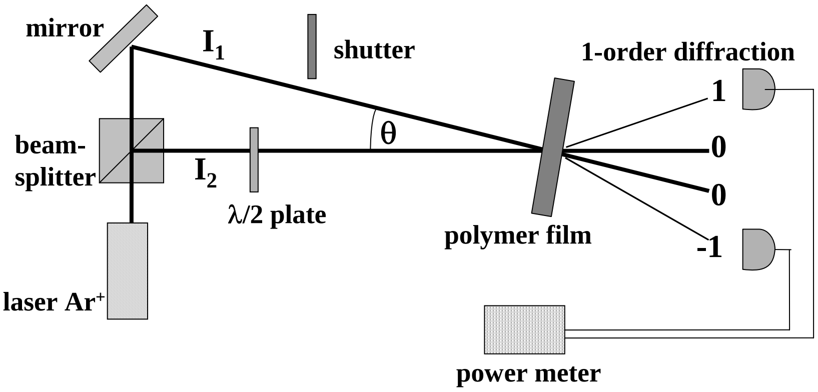


Fig. 9. Two-wave mixing experimental set-up with possibility of *s-s* and *s-p* polarization grating recording using Ar^+ (514.5 nm) laser as an excitation source. The beam intersection angle was θ=2.6^0, giving spatial period of the grating Λ=5.5 μm.

Diffraction gratings have been recorded for two different polarization geometries (i) *s-s* polarization when two incoming beams I_1 and I_2 are linearly polarized with electric field vectors perpendicular to the incidence plane and (ii) *s-p* polarization when one of the incoming beam polarizations is rotated by 90^0.

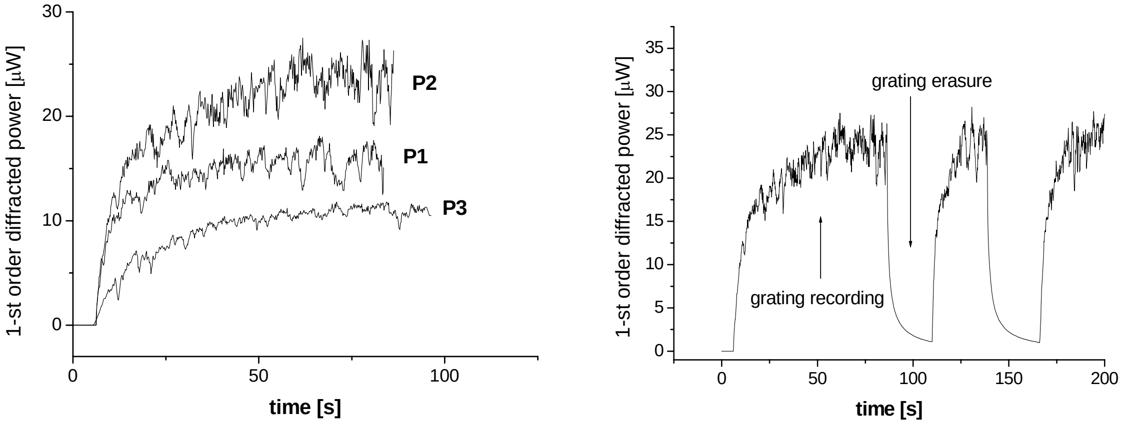


Fig. 10. (a) Kinetics of holographic grating recording in polyesterimides films for *s-p* polarization, (b) Repetitive recording – erasing cycles in **P2** films for *s-p* polarization geometry.

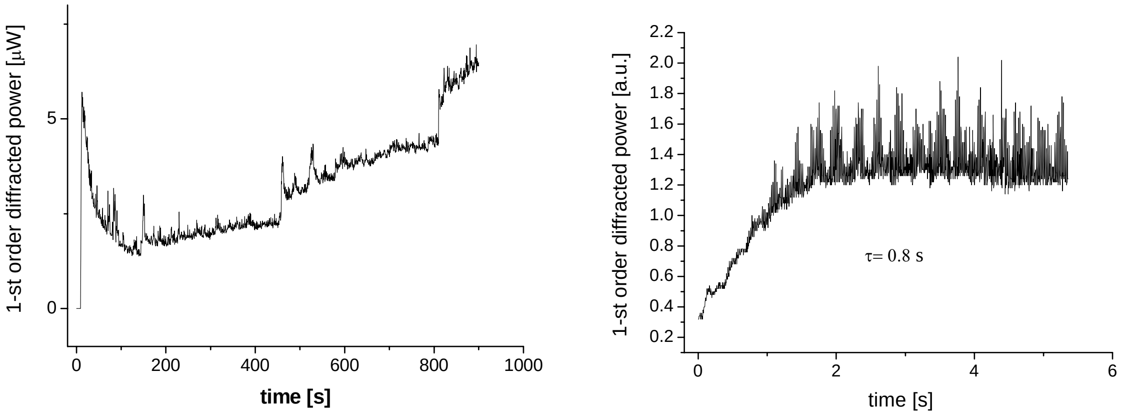
Diffraction grating build-up process has been evidenced by an appearance of a light self-diffraction. By monitoring the first order diffracted beam's power as a function of time, the kinetics of grating formation has been studied. Fig. 10a shows the obtained results – temporal evolution of the first-order diffraction power for polyesterimides in the case of *s-p* polarization geometry. Taking into account first-order diffraction efficiency η defined as the ratio between the first-order diffracted beam intensity I_{1diff} and the input beam intensity I_1:

$$\eta = (I_{1diff}/I_1)\mathrm{x}100, \qquad (2)$$

it is observed that the smallest value of η occurs for polymer with one azobenzene unit – **P3** ($\eta_{s\text{-}p}$~ 0.11%). For other polymers diffraction efficiencies are $\eta_{s\text{-}p}$~ 0.16% and $\eta_{s\text{-}p}$~ 0.24% for **P1** and **P2,** respectively.

The exemplary curves of the optical grating recording (*s-p*) and erasure are shown in Fig. 10b for polymer **P2.** After blocking one of the writing beams the light induced grating erasure is observed. The diffraction signal drops almost to zero within several seconds. After opening the blocked writing beam the diffraction signal returns to its previous value, and the process of erasure can be applied again. Such grating inscription and erasure is qualitatively similar for all investigated polyesterimides during *s-p* recording.

In the case of qualitatively different polarization conditions *s-s,* where the light interference pattern shows intensity fringes, the temporal evaluation of diffraction signal is significantly different in form as compared to *s-p* configuration. An example of the kinetics of grating recording for *s-s* polarization in polyesterimides **P2** is presented in Fig. 11a



(a) (b)

Fig. 11. (a) An example of kinetics of grating recording in polyesterimide **P2** for *s-s* polarization, (b) oscilloscope trace of first-order diffraction signal of fast grating build-up process for *s-s* configuration.

It can be noticed that the shape of obtained grating build-up curve, for *s-s* configuration (Fig. 11a), is different from typical ones observed previously for polyimides [22, 23]. In the latter case signal shapes were described by exponential growth functions. In the present case of *s-s* polarization two stages are observed. Initially the first-order diffraction power reaches a maximum value in a short period of time after beam opening and then it decreases rapidly and starts growing slowly again. Such "untypical" behavior is characteristic for grating inscription under *s-s* polarization geometry for all investigated polyesterimides. Our preliminary hypothesis tempting to explain such a behavior of these PEIs assumes that the first stage of grating formation is due to chromophore reorientation. This is followed by a slower process, which we link with the reorientation of polymer main chain [48]. These two subsystems may be described by two refractive index ellipsoids rotating as function of exposure. Similar curves were also observed by Chen et al. [49] and Hvilsted et al. [50] for other polymers.

Investigations of the short time diffraction signals evolution (*s-s* polarization) for all polyesterimides have been made using oscilloscope and a faster responding photodiode. The exemplary result is presented in Fig. 11b for polyesterimide **P2**.

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

$$\sqrt{P_1(t)} = A_1\left[1-\exp\left(-\frac{t}{\tau_1}\right)\right] + A_2\left[1-\exp\left(-\frac{t}{\tau_2}\right)\right] \qquad (3)$$

This fitting allows us to estimate the changes of refractive index and absorption coefficient amplitudes, as the diffraction efficiency is proportional to $(\Delta n)^2$ and $(\Delta\alpha)^2$. Here τ_1 and τ_2 describe time constants of two different grating build-up processes fast and slow, respectively [51]. The fast process is connected with the *trans-cis-trans* isomerization rates and the local mobility of azobenzene groups, which are determined by the size of azobenzene groups, the free volume around it, 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. Fitting has been performed for both polarization geometries *s-p* and *s-s* (only for first stage), according to eq.3, and the results are collected in Tab.5.

Tab. 5. Time constants of the diffraction grating build-up process estimated for *s-p* and *s-s* polarization configurations

Polymer code	**Polarization *s-p***		**Polarization *s-s***
	τ_1 [s]	τ_2 [s]	τ [s]
P1	0.4	9.2	0.3
P2	1.2	19.8	0.8
P3	1.7	17.1	1.2

Considering the time constants of grating formation in *s-p* configuration one can conclude that there is no significant difference between studied polyesterimides. As can be seen from Tab. 5; for the case of *s-s* polarization the polymers show substantial diffraction in less than a single second after opening of the shutter. The fastest grating inscription, for both *s-s* and *s-p* configurations, is observed for polyesterimide **P1** with the second azobenzene unit substituted with methyl group. The relatively fast grating inscription at low light intensities in these polymers is promising for dynamic holography purposes. Materials in which recording, reading out, and erasure of the optical information can be performed at real time are interesting for many applications and therefore intensively studied.

Conclusions

The synthesized new soluble photochromic polyesterimides exhibit high glass transition temperatures and high thermal stability. Optical anisotropy is induced in polyesterimides films upon irradiation with linearly polarized light causing such orientation of the azobenzene groups which is perpendicular to the electric field vector of the incident polarized light. The increase of chromophore concentration in polymer unit does not improve the photoinduced anisotropy under utilized irradiation conditions. Polyesterimide with one azobenzene unit exhibits the highest value of the photoinduced dichroism (D=2.6). The photoorientation process is only slightly influenced by the 4'-substitution of the second azobenzene group, which is a part of diamine fragment. The polymers show pronounced long-term stability of the induced optical anisotropy (the remnant dichroism is stable at about 85%). In our experimental conditions the influence of the second azobenzene group in polymer unit on holographic grating formation is negligible. However, the investigated polyesterimides exhibit fast grating inscription. Polyesterimides thus form a class of materials with a potential for dynamic holography purposes.

Experimental part

Materials

1,3-Phenylenediamine and trimellitic anhydride chloride (Aldrich) are reagent grade from Aldrich and have been used as supplied. N,N-Methyl-2-pirrolidone (NMP) (Aldrich), 1,2-dichlorobenzene (Aldrich) and other reagents have been applied as received without further purification. Acetone and pyridine have been dried and distilled. 4'-Nitrophenylazo-[N,N-bis(2-hydroxyethyl)] aniline (DR-19) has been synthesized according to the literature [52].

Synthesis of 2,2'-{4-[(4-nitrophenyl)-azo}phenyl]iminobis(ethyl benzene-1,2-dicarboxylic acid anhydride-4-carboxylate)

Dianhydride was synthesized by the esterification of trimellitic anhydride chloride and DR-19 [40, 53, 54]. DR-19 (10 mmol) and pyridine (1.2 mmol) in 25 ml of acetone was added dropwise to the solution of trimellitic anhydride chloride (15 mmol) in 25 ml of acetone. The mixture was stirred for 1 h at 70°C under nitrogen. After cooling the mixture, the resulting precipitate was filtered off and dried at 100°C in vacuum. A dark, violet-red solid was obtained.

^{1}H NMR (DMSO-d$_6$, δ, ppm): 4.06 (s, CH$_2$, 4H), 4.60 (s, CH$_2$, 4H), 7.14-7.17(d, ArH, 2H), 7.80-7.83 (d, ArH, 2H), 7.90-7.94 (d, ArH, 2H), 8.13-8.42 (m, ArH, 6H).

FTIR (KBr, cm^{-1}): 1854, 1782 (C=O, acid anhydride), 1728 (C=O, ester), 2967 (CH$_2$), 1515, 1334 (N=O), 1234 (C-O).

UV-vis: (10^{-5} mol/l, NMP): λ_{max}= 483 nm.

($C_{34}H_{22}N_4O_{12}$) (678.6):

Calcd. C 60.18 H 3.27 N 8.26; Found C 59.97 H 3.60 N 8.82

M.p. 264°C

Synthesis of diamines

Diamines were synthesized according to the procedure described in our previous papers [38, 55].

Synthesis of polymers

The method of high-temperature polycondensation was utilized for the preparation of the polyesterimides. A solution of equimolar amounts of diesterdianhydride (1 mmol) and diamine (1 mmol) in NMP and 1,2-dichlorobenzene (80/20 (v/v), 20% total monomer concentration) was stirred at 175°C for 3.5 h under nitrogen atmosphere. The polymers was precipitated by methanol and further purified by Soxhlet extraction with methanol.

Measurements

IR spectra were recorded on a BIO-RAD FTS 40 A Spectrometer using KBr pellets. ^{1}H NMR spectra was carried out on a Varian 300 Spectrometer using DMSO-d_6 as solvent and TMS as the internal standard. Differential scanning calorimetry (DSC) measurements were done using a TA DSC 2010 apparatus with a heating rate of 20°C/min under nitrogen. Thermogravimetric analyses (TGA) were performed on a Paulik-Erdey apparatus at a heating rate of 10°C min^{-1} under nitrogen. Carbon, hydrogen, and nitrogen elemental analyses were performed using Elementar vario EL III. The reduced viscosity was measured in NMP at 25°C using an Ubbelohde viscometer. The X-rays diffraction pattern on powder samples was recorded using CuKα radiation on a wide-angle HZG-4 diffractometer working in the typical Bragg geometry. UV-Vis spectra have been recorded in NMP solution of polymers and as films casted on glass using a Perkin-Elmer spectrometer Lambda 2S. The dichroism has been induced in the films by irradiating them with Ar^{+} laser (Coherent Innova 90-4, 488 nm, 100 mW/cm^{2}, linearly polarized). The photochemical conversion and photoinduced dichroism was measured using a Perkin-Elmer Lambda 19 spectrometer equipped with a Glan-Thomson prism polarizer measuring at each 10°. The holographic gratings were recorded in standard degenerate two-wave mixing set-up using 514.5 nm Ar^{+} laser light. The grating formation rate in the polymer film was evaluated by real-time monitoring of intensity changes of a first-order diffraction beam. 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 $\theta=2.6^{0}$, giving spatial period of the grating $\Lambda=5.5$ μm.

References

[1] Yang Ch.P.; Yang H.W. ; *J. Appl. Polym. Sci*. **2000**, *75*, 87.

[2] Feger C.; Khojasteh M. M.; McGrath J. E.; Polyimides: Materials, Chemistry, and Characterization Elsevier:Amsterdam, **1994**.

[3] Ghosh M. K.; Mittal K. L.; Polyimides: Fundamentals and Applications New York: Dekker **1996**.

[4] Sazanov Y. N.; Russian *J. Appl. Chem.* **2001**, *74*, 1253.

[5] Walsh Ch. J.; Mandal B. K.; *Chem. Mater*. **2001**, *13*, 2472.

[6] Dorr M.; Zentel R.; Sprave M.; Vydra J.; Eich M.; *Adv. Mater*. **1997**, *9*, 225.

[7] Meng X.; Natansohn A.; Rochon P.; *J. Polym. Sci. Part B* **1996**, *34*, 1461.

[8] Gubbelmans E.; Verbiest T.; Beylen M.; Persoons A.; Samyn C.; *Polymer* **2003**, *43*, 1581.

[9] Hasegawa M.; Horie K.; *Prog. Polym. Sci.* **2001**, *26*, 259.
[10] Chen T. A.; Jen A. K. Y.; Cai Y.; *J. Am. Chem. Soc*. **1995**, *117*, 7295.
[11] Verbiest T.; Burland D. M.; Jurich M. C.; Lee V. Y.; Miller R. D.; Volksen W.; *Science* **1995**, *268*, 1604.
[12] Leng W. ; Zhou Y. ; Xu Q. ; Liu J. ; *Macromolecules* **2001**, *34*, 4774.

[13] Iftime G. ; Labarthet F. L. ; Natansohn A. ; Rochon P. ; Murti K. ; *Chem. Mater*. **2002**, *14*, 168.
[14] Delaire J. A. ; Nakatani K. ; *Chem. Rev*. **2000**, *100*, 1817.
[15] Viswanathan N. K. ; Kim D. Y. ; Bian S. ; Williams J. ; Liu W. ; Li L. ; Samuelson L. ; Kumar J. ; Tripathy S. K. ; *J. Mater. Chem*. **1999**, *9* ,1941.
[16] Yager K. G.; Barrett Ch. J.; *Current Opinion in Solid State and Materials Science* **2001**, *5*, 487.
[17] Tripathy S. K.; Kim D. Y.; Li L.; Kumar J.; *Chem. Technol*. May **1998**:*34.*
[18] Yesodha S. K.; Pillai Ch. K. S.; Tsutsumi N.; *Prog. Polym. Sci*. **2004**, *29*, 45.
[19] Yaroshchuk O. V.; Dumont M.; Zakrevskyy Y. A.; Bidna T. V.; Lindau J.; *J. Phys. Chem. B* **2004**, *108*, 4647.
[20] Natansohn A.; Rochon P.; *Chem. Rev*. **2002**, *102*, 4139.
[21] Iftime G.; Natansohn A.; Rochon P.; *Macromolecules* **2002**, *35*, 365.
[22] Sek D.; Schab-Balcerzak E.; Solyga M.; Miniewicz A.; *Synthetic Metals* **2001**, *9123*, 1.
[23] Miniewicz A.; Komorowska K.; Sek D.; Schab-Balcerzak E.; Solyga M.; **Polish J Chem.** *2000*, *76*, 395.
[24] Kamanina N. V.; Kaporskii L. N.; Sizov V. N.; Stasel’ko DI. *Optics Comm*. **2000**, *185*, 363.
[25] Kamanina N. V.; Putilin S.; Stasel’ko D.; *Synthetic Metals* **2002**, *127*, 129.
[26] Belfied K. D.; Najjar O.; Sriram S. R.; *Polymer* **2000**, *41*, 5011.
[27] Chen J. P.; Labarthet F. L.; Natansohn A.; Rochon P.; *Macromolecules* **1999**, *32*, 8572.
[28] Kim H. T.; Lee J. W.; Sung Sh. J.; Park J. K.; *Liq. Cryst*. **2000**, *27*, 1343.
[29] Shin D. M.; Song D. M.; Kim Y. B.; *Materials Sciences and Engineering* **2004**, *C24*, 127.
[30] Lee S. W.; Kim S. I.; Lee B.; Choi W.; Chae B.; Kim S. B.; Ree M.; *Macromolecules* **2003**, *36*, 6527.
[31] Song D. M.; Shion D. M.; Choi K. Y.; Yi M. H.; *Colloids and Surface A: Physicochemical and Engineering Aspects* **2002**, *198-200*, 875.
[32] Sakamoto K.; Usami K.; Kikegawa M.; Ushioda S.; *J. Appl. Phys*. **2003**, *93*, 1039.
[33] Song D. M.; Jung K. H.; Moon J. H.; Shin D. M.; *Optical Materials* **2002**, *21*, 667.
[34] Kim G. H.; Keum Ch. D.; Kim S. J.; Park L. S.; *J. Polym. Sci. Part A* **1999**, *37*, 3715.
[35] Wang C.; Zhang C.; Wang P.; Zhu P.; Wu W.; Ye C.; Dalton L. R.; *Polymer* **2000**, *41*, 2583.
[36] Lee Ch.; Seo J.; Shul Y.; Han H.*; Polym. J*. **2003**, *35*, 578.
[37] Helgert M.; Wenke L.; Hvilsted S.; Ramanujam P. S.; *Appl. Phys. B* **2001**, *72*, 429.
[38] Schab-Balcerzak E.; Sapich B.; Stumpe J.; *Polymer* **2005**, *46*, 49.
[39] Turky G.; Schonhlas A.; *Polymer* **2004**, *45*, 255.
[40] Schab-Balcerzak E.; Sapich B.; Hass R.; Stumpe J.; *Proceedings of SPIE* **2005**, *5724*, 301.

[41] Chen T. A.; Jen A. K. Y.; Cai Y.; *Macromolecules* **1996**, *29*, 535.
[42] Schab-Balcerzak E.; Sek D.; Jarzabek B.; Zakrevskyy Y.; Stumpe J.; *High Performance Polymers* **2004**, *16*, 585.
[43] Do J. Y.; Park S. K.; Ju J. J.; Park S.; Lee M. H.; *Optical Materials* **2004**, *26*, 223.
[44] Kim E. H.; Moon I. K.; Kim H. K.; Lee M. H.; Han S. G.; Yi M. H.; Choi K. Y.; *Polymer* **1999**, *40*, 6157.
[45] Iftime G.; Labarthet F. L.; Natansohn A.; Rochon P.; Murti K.; *Chem. Mater*. **2002**, *14*, 168.
[46] Date R. W.; Fawcett A. H.; Geue T.; Haferkorn J.; Malcolm R. K.; Stumpe J.; *Macromolecules* **1998**, *31*, 4935.
[47] Eichler H. J.; Gunter P.; Pohl D.; Laser-Induced Dynamic Gratings. Springer-Verlag, Berlin **1986**.
[48] Sobolewska A.; Miniewicz A.; Kusto J.; Moczko K.; Sek D.; Schab-Balcerzak E.; Grabiec E.; Kajzar F.; *Proceedings of SPIE* **2005**, *5724*, 21.
[49] Chen J. P.; Labarthet F. L.; Natansohn A.; Rochon P.; *Macromolecules* **1999**, *32*, 8572.
[50] Hvilsted S.; Ramanujam P. S.; *Monatshefe fur Chemie* **2001**, *132*, 34.
[51] Ho M. S.; Natansohn A.; Rochon P.; *Macromolecules* **1995**, *28*, 6124.
[52] Chen M.; Yu L.; Dalton L. R.; Shi Y.; Steier W. H.; *Macromolecules* **1991**, *24*, 542.
[53] Yokoyama S.; Kakimoto M.; Imai Y.; *Langmuir* **1993**, *9*, 1086.
[54] Lu J.; Yin J.; *J. Polym. Sci. Part A* **2003**, *41*, 303.
[55] Schab-Balcerzak E.; Janeczek H.; Kaczmarczyk B.; Bednarski H.; Sek D.; Miniewicz A.; *Polymer* **2004**, *45*, 2483.