

Investigations of Polymers with Chromophore Units I. Synthesis and Properties of New Poly(ester-imide)s from 2,4-dihydroxy-4'-nitroazobenzene

Danuta SĘK,[†] Eugenia GRABIEC, and Andrzej MINIEWICZ*

Centre of Polymer Chemistry, Polish Academy of Sciences, 34 M. Curie-Skłodowska St. 41–800 Zabrze, Poland

*Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, 50–370 Wrocław, Poland

(Received February 21, 2003; Accepted August 5, 2003)

ABSTRACT: A series of poly(ester-imide)s based on new azobenzene derivative 2,4-dihydroxy-4'-nitroazobenzene has been synthesized and characterised. An influence of macromolecules structures on the physical and chemical properties was investigated. The preliminary results of holographic recording in poly(ester-imide) foils are presented.

KEY WORDS Poly(ester-imide)s / 2,4-Dihydroxy-4'-nitroazobenzene / Thermal Stability / Optical Properties /

In the last decade polymers containing chromophore units for example azo benzene groups have attracted attention because of a variety of potential applications in the field of optical data storage, nonlinear optics and holographic applications.^{1–8} The reversible photoisomerisation process of azo-groups is particularly interesting. The involved molecular reorientation can initiate photo-induced birefringence, dichroism and even mass transport.^{9–12} Photoresponsive polymers could be prepared as Langmuir–Blodgett,^{13, 14} spin-coated or casted films differing in thickness. Chromophore can be introduced into polymer's main chain or be bonded as a side group and eventually dispersed in a polymer matrix. Despite the fact that the last way is the easiest one the former ones offer much better stability of Non-linear optical (NLO) properties. When a chromophore is attached to polymer as a side chain the optical properties of the polymer are mainly influenced by the structure of polymer backbone, the structure of the azo chromophore and the type of bonding of the chromophore to the main chain. High concentration of azo-groups in the polymer plays also a significant role.

In this work we have synthesized a series of poly(ester-imide)s from diesterdianhydride with azo groups in side chain and various diamines. The prepared materials will be tested for their use in dynamic holographic recording.

EXPERIMENTAL

Materials Used in Synthesis

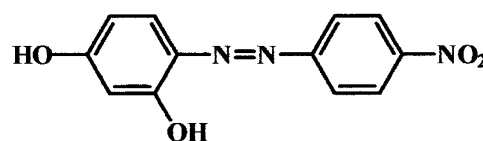
4,4'-Diaminediphenylether (Merck) was crystallised from methanol, 1,2-phenylenediamine and 1,4-phenylenediamine were crystallised from

methanol/water mixture in the presence of charcoal. 4,4'-Methylenedi-*o*-toluidine (Fluka) and 1,3-phenylenediamine (Aldrich), 2,3,5,6-tetramethyl-1,4-phenylenediamine (Aldrich), 4,4'-methylenedianiline (Aldrich), 3,3',5,5'-tetramethylbenzidine (Aldrich), 3,3'-dimethoxybenzidine (Aldrich), *o*-toluidine (Aldrich), 4,4'-diaminebiphenyl (Aldrich), 4,4'-methylene bis(2,6-dimethylaniline) (Aldrich), 4,4'-methylene bis(2,6-diethylaniline) (Aldrich), and 4,4'-(1,3-phenylenedioxy)dianiline (Aldrich) were used without purification. Dimethylacetamide (DMA) (Aldrich) and dimethylformamide (DMF) (Aldrich) were distilled in the usual manner, 1-methyl-2-pyrrolidinone (NMP) (Aldrich) was dried with 4 Å molecular sieves overnight.

Synthesis of Monomers

Synthesis of the Chromophore 2,4-Dihydroxy-4'-nitroazobenzene (Azo-Diol) having the structure (Scheme 1) was synthesized according to the following procedure:

Flask with the mixture of 10 mmol (1.44 g) of *p*-nitroaniline in 2.7 mL of concentrated hydrochloric acid and 10 mL of water, was placed in an ice bath. To the cooled mixture a solution of 10 mmol (0.7 g) of sodium nitrite in 1.5 mL of water was added dropwise and the mixture was stirred at a temperature between



Scheme 1.

[†]To whom correspondence should be addressed (Tel: +48-032-2716077, 2732214, Fax: +48-032-2712969, E-mail: danuta.sek@cchp-pan.zabrze.pl).

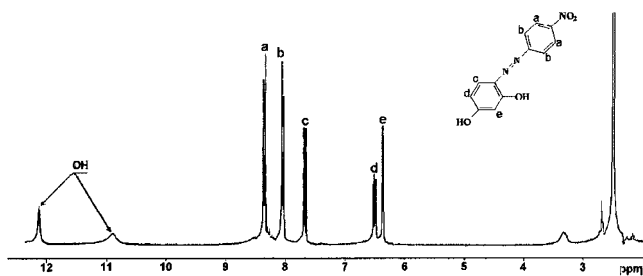
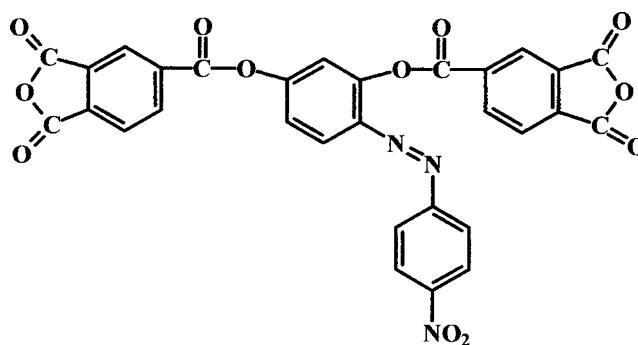


Figure 1. ^1H NMR (in $\text{DMSO-}d_6$) spectrum of the 2,4 dihydroxy-4'-azobenzene.



Scheme 2.

0 and 5°C during 15 min. Then it was poured slowly into a solution containing 10 mmol (1.1 g) of resorcinol in 8 mL of methanol. The mixture was stirred at a temperature between 0 and 5°C for 30 min and then was neutralised with sodium acetate to pH 5–6. After that temperature was raised to 20°C and the mixture was stirred for 1 h. The product was filtered, washed with water and dried in vacuum at 70°C . Yield: 85.1%.

Elemental analysis: found (calc.); C 55.72 (55.60)%, H 3.52 (3.50)%, N 16.12 (16.21)%; MS $m/e = 259$; Mp: $209\text{--}211^\circ\text{C}$ (dec) (differential scanning calorimetry, DSC). Proton nuclear magnetic resonance (^1H NMR) spectrum of Azo-Diol detected in $\text{DMSO-}d_6$ is shown in Figure 1.

In the ^1H NMR spectrum the following peaks (ppm) are observed: 10.8 (s, $-\text{OH}$), 12.2 (s, $-\text{OH}$), (a) 8.36–8.33 (d, ArH, 2 H), (b) 8.06–8.03 (d, ArH, 2 H), (c) 7.69–7.66 (d, ArH, 1 H), (d) 6.52–6.49 (m, ArH, 1 H), (e) 6.36–6.35 (d, ArH, 1 H).

The peaks at 10.8 and 12.2 ppm are characteristic for hydrogen in phenol group. The phenomenon that protons of the two hydroxylic groups bonded with phenyl ring at different positions gives two peaks at ^1H NMR spectrum can be explained by possibility of creation of chelate bonds. Such chelate ring can be formed between nitrogen of azo group and hydrogen of $-\text{OH}$ group placed in *o*-position. In this way two different signals of protons can be observed in the moiety of Azo-Diol.

In FT-IR (KBr) spectrum the following absorption bands were found and assigned as: 3280 cm^{-1} (O–H stretching vibration in phenolic group), 1634, 1605 , 1594 cm^{-1} ($-\text{phenyl}$ ring stretching), 1511 and 1340 cm^{-1} (NO_2 group stretching), 1261, 1224 cm^{-1} (C–O stretching vibrations), 1161, 1188 cm^{-1} (1,4 subst. phenyl ring C–H deformation), 995, 964 cm^{-1} (1,2,4 subst. phenyl ring C–H deformation), 845, 853 cm^{-1} (C–H aromatic out of plane deformation).

In UV-vis spectrum of the Azo-Diol in DMA solution the absorption peaks at about 551 nm and at about 455 nm are observed.

Synthesis of the Diesterdianhydride. The new diesterdianhydride with the structure (Scheme 2) was prepared as follows: in a flask equipped with a condenser, stirrer and dropping funnel, 2.2 mmol of trimellitic anhydride acid chloride and 3 mL of dry acetone were placed under an argon atmosphere. The solution was heated under reflux and 1 mmol of Azo-Diol in 3 mL of acetone with 2.8 mmol of dry pyridine were added slowly over a 15 min. The mixture was stirred and heated under reflux during 1.5 h. After cooling to room temperature the product was filtered and dried in a vacuum oven at 50°C for 24 h.

The crude product was crystallized from a mixture of acetic anhydride and acetic acid (3:1 v/v).

Elemental analysis: found (calc.) C%: 59.62 (59.32), H%: 2.61 (2.15), N%: 6.33 (6.92). Melting point: 207°C (DSC)

The structure of the dianhydride was confirmed by FT-IR (KBr): 1860 , 1782 cm^{-1} (C=O anhydride vibration), 1743 cm^{-1} (C=O ester group vibration), 1605, 1487, 1426 cm^{-1} ($-\text{phenyl}$ ring stretching), 1523 and 1345 cm^{-1} (NO_2 group stretching), 1264, 1223 cm^{-1} (C–O stretching vibrations), 1165, 1143 cm^{-1} (1,4 subst. phenyl ring C–H deformation), 1006, 958 cm^{-1} (1,2,4 subst. phenyl ring C–H deformation).

In UV-vis spectrum of diesterdianhydride dissolved in DMA two absorption bands were observed at about 350 nm and at 590 nm.

Synthesis of the Polymers

Poly(ester-imide)s were synthesized using two-step method.

One mmol of a proper diamine was dissolved in dry DMF (10 mL) and 1 mmol of a dianhydride contained azo-chromophore was added slowly during 30 min.

The reaction was carried out at room temperature for 6 h under a nitrogen atmosphere. Then the mixture of pyridine and acetic anhydride (1:2 v/v) was added into reaction solution for chemical imidization. The mixture was stirred at room temperature during 16 h and then was heated at 80°C for 1 h. After cooling down to

room temperature the reaction mixture was poured into vigorously stirred methanol. The precipitated polymer was filtered, washed with boiling methanol in Soxhlet apparatus and dried in a vacuum at 70 °C overnight.

Measurements of Some Physical Properties

The glass transition temperatures and the melting points of the obtained polymers were determined with DSC 2010 TA Instrument at a heating rate of 20 °C min⁻¹ using sealed aluminium pan (sample weight about 20 mg) at nitrogen atmosphere (flow rate was about 30 mL min⁻¹).

For elemental analysis CHNS PerkinElmer 2400 was used.

Infrared spectra were recorded with a BIO-RAD FTS 40 A spectrometer in KBr pellets.

The reduced viscosity was measured in NMP at 25 °C using an Ubbelohde viscometer. Molecular masses were determined on Finnigan MAT 95S doubly focusing instrument. Spectra were acquired in a positive-ion mode (magnetic scan).

¹H NMR spectra were recorded with a Varian Inova 300 Spectrometer using dimethylsulfoxide (DMSO-*d*₆) as a solvent and tetramethylsilane (TMS) as an internal reference.

Derivatograph Q-1500D MOM was used for thermogravimetric (TG) analysis (in nitrogen).

The optical transmission spectra were performed at room temperature in DMA solution with BECKMAN Acta M-IV spectrophotometer within the 200–600 nm range.

A deuterium lamp was a source of ultraviolet light, while tungsten lamps were used for visible and near infrared regions in this spectrophotometer.

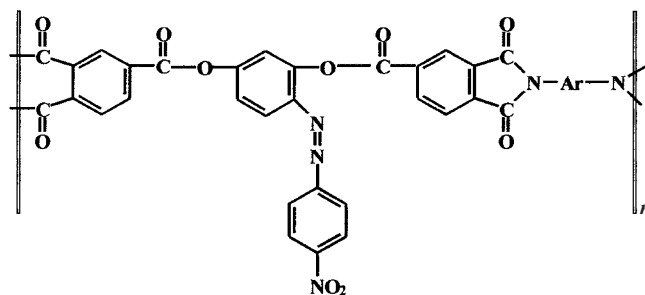
X-Ray diffraction measurements were performed on TUR-M62 apparatus at room temperature in the reflection mode, using Ni-filtered Cu-K α radiation. The scanning rate was over a range of $2\theta = 10^\circ - 80^\circ$.

RESULTS AND DISCUSSION

New chromophore 2,4-dihydroxy-4'-nitroazobenzene was used for synthesis of functionalised polymers. The Azo-Diol was condensed with trimellitic anhydride acid chloride to give the proper dianhydride being used for condensation with various aromatic diamines. The poly(ester-imide)s have the structure shown below (Scheme 3).

The properties of the poly(ester-imide)s synthesized along with the groups -Ar- are listed in Table I.

All polymers exhibited good solubility in common organic solvents and formed bright and transparent films even though the reduced viscosities of the poly-



Scheme 3.

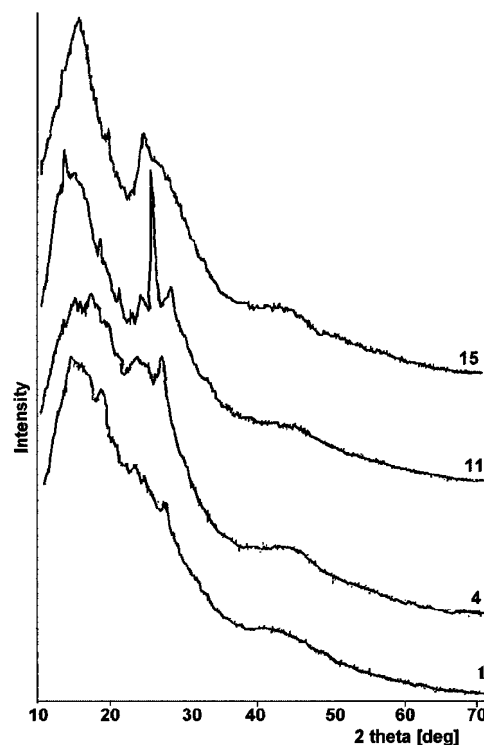


Figure 2. X-Ray diffractograms of some polymers.

mers connected with their molecular weights were low.

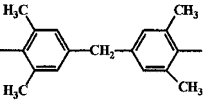
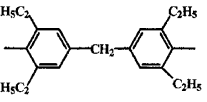
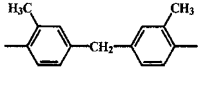
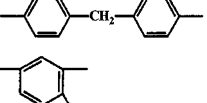
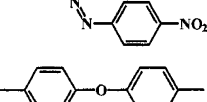
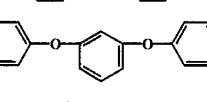
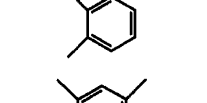
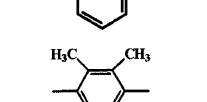
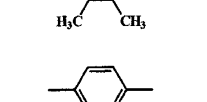
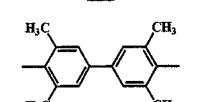
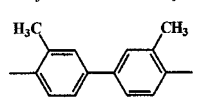
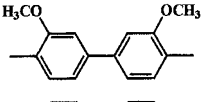
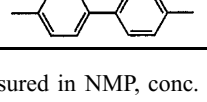
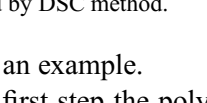
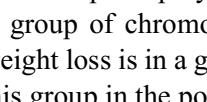
The X-ray diffractograms (Figure 2) confirm some ordering in the poly(ester-imide)s, being little higher in the case of the polymers synthesized from unsubstituted stiff diamines, *i.e.*, 1,4 phenylenediamine **11** and benzidine **15**. The higher crystallinity of polymers **11** and **15** was in agreement with their weaker solubility.

These polymers show good thermal resistance.

The thermal behaviour of the polymers was investigated by means of thermogravimetric analysis (TG) and differential scanning calorimetry (DSC). The thermogravimetric curves show that poly(ester-imide)s decompose under a nitrogen atmosphere in two steps. The first step is relatively fast and takes place in the range of about 250–320 °C, while the polymers loss about 5% of their weight. Then the decomposition is slow and the second step starts at about 500 °C. At 1000 °C residue of a char is about 50%.

Figure 3 shows the TG-curve obtained for the poly-

Table I. Structures and some properties of poly(ester-imide)s

No	Ar (in Scheme 3)	Yield [%]	η_{red}^a [dL g ⁻¹]	UV-vis λ_{max}^b [nm]	TG			DSC [°C]		
					Temp. of beginning weight loss [°C]	Temp. of 5% weight loss [°C]	Residual weight at 1000 °C [%]	T_g	T_m	Temp. start of exotherm. process [°C]
1		74	0.19	350 590	~270	310	54	185	242	~260
2		86	0.18	350 590	~270	320	62	158	—	~265
3		80	0.15	351 590	~250	320	54	156	234	~250
4		85	0.18	351 590	~255	320	57	147	231	~245
5		34	0.14	—	~230	270	55	138	211	~230
6		81	0.23	—	~260	325	53	138	232	~270
7		89	0.11	—	~220	310	49	117	206	~280
8		87	0.17	350 590	~260	310	50	165	256	~280
9		88	0.98	351 590	~280	330	51	165	243	~280
10		85	0.10	—	~260	320	50	136	270	~280
11		86	0.25	350 591	~220	300	48	136	236	~280
12		78	0.31	—	~270	320	50	177	—	~270
13		81	0.12	—	~250	310	55	138	—	~275
14		90	0.12	—	~280	310	55	157	238	~280
15		89	0.28	—	~230	305	52	ND	257	~280

^aMeasured in NMP, conc. = 0.2 g/100 mL at 25 °C. ^bMeasured in DMA (anhydrous) solution ($c = 1 \times 10^{-5}$ mol L⁻¹), ND – not detected by DSC method.

mer 4 as an example.

In the first step the poly(ester-imide)s loss probably the nitro group of chromophore unit^{15,16} and the observed weight loss is in a good agreement with the content of this group in the polymer.

The temperature of the beginning of decomposition process was confirmed also by DSC measurements. On DSC-grams for all the poly(ester-imide)s investigated an exothermic process starting within the range of 240–280 °C was detected being probably responsible for the

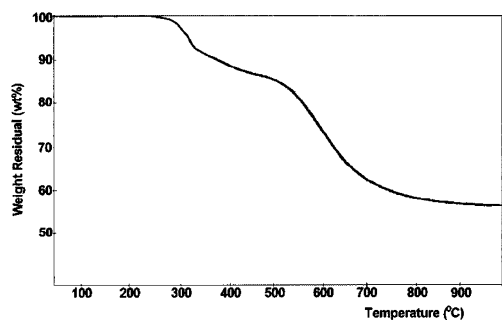


Figure 3. TG-curve of the polymer 4.

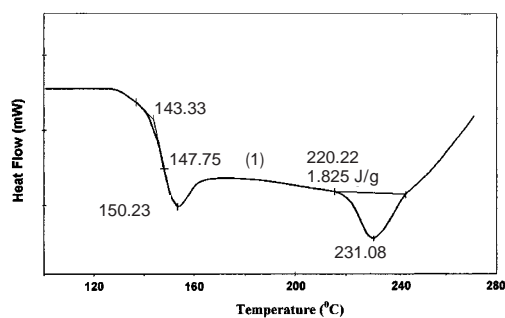


Figure 4. DSC-gram of the polymer 4.

beginning of the decomposition.

The glass transition temperatures of the poly(ester-imide)s were observed in the range of 117–185°C and are related to the diamine structure.

The polymer **1** being a product of condensation of tetramethyl substituted diaminediphenylmethane and the diesterdianhydride exhibited higher T_g (185°C) in comparison to the polymer **3** with two methyl groups ($T_g = 156^\circ\text{C}$) and to the polymer **4** without methyl substituents ($T_g = 147^\circ\text{C}$).

In the series of the poly(ester-imide)s obtained from derivatives of benzidin (4,4'-diaminebiphenyl), T_g values differed in the same way as it was detected for the polymers **1**, **3**, and **4**. The polymer **12** containing tetramethyl substituted biphenyl exhibited higher T_g (177°C) than dimethyl substituted one **13** (138°C). Presence of two methoxy substituents in polymer **14** caused an increase of T_g value to 157°C.

Similar influence of the methyl substituents at ortho position to amine group on glass transition temperature of polymers was reported in ref 17, 18.

Unexpectedly, polymer **10** from tetramethyl-1,4-phenylenediamine and from 1,4-phenylenediamine **11** had the same values of T_g (136°C).

The presence of two ether linkages in the diamine in the polymer **7** causes lowering of the T_g in comparison to the polymer **6** bearing one ether group.

The poly(ester-imide)s have similar degree of crystallinity as it was confirmed by X-ray diffractograms.

On DSC-grams an endothermic process due to melting of the crystalline phase was observed in the range of 206–270°C. But this melting process was followed by exothermic destruction reaction. Figure 4 shows DSC-gram for the polymer **4** as an example.

The UV-vis spectra of poly(ester-imide)s in DMA solution (conc. 1×10^{-5} mol L⁻¹) exhibited two absorption bands.

The shapes of the spectra were very similar for all the polymers presented in Table I.

The main absorption peak was observed at 350 nm and the second at about 590 nm (very low intensity) and the λ_{max} wavelengths were almost independent of the

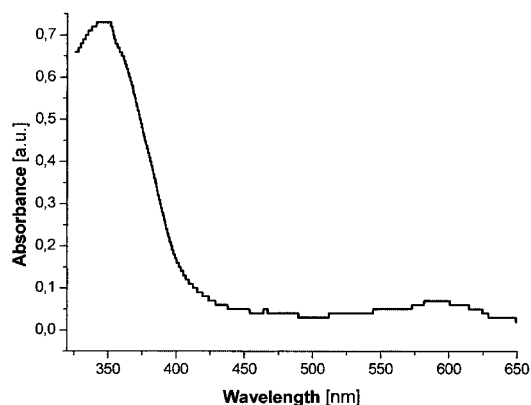


Figure 5. UV-Vis spectrum of polymer **1** as an example of absorption in DMA solution.

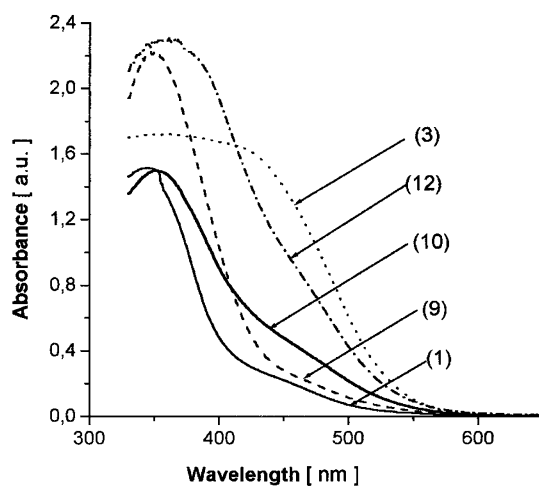


Figure 6. UV-Vis spectra of poly(esterimide) films.

polymer structures. Figure 5 shows UV-vis spectrum of the polymer **1** as example of spectra in DMA solution.

When UV-vis spectra were recorded in solid state (thin film) absorption at about 590 nm was not detected (Figure 6). Probably the presence of solvent enhances of $n-\pi^*$ transition in azo group.

The presence of the azo-groups in the synthesized polymers enables reversible photoisomerisation. Such polymeric systems form interesting class of NLO optical and photochromic materials.

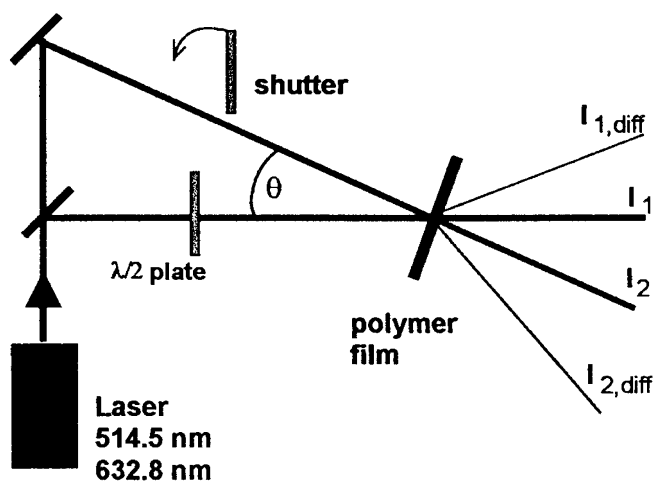


Figure 7. Experimental set-up of degenerate two-wave mixing (DTWM) using either He–Ne ($\lambda = 632.8$ nm) or Ar⁺ (514.5 nm) lasers as excitation sources. Half-wave retardation plate was used in order to perform polarisation (sp) grating recording experiments.

Optical Grating Recording Experiments

Materials containing photoresponsive chromophores are attractive in the field of optical communication and high-density optical data storage because of the reversible photoisomerisation process of azo-groups leading to photoinduced birefringence, dichroism and even mass transport.^{1, 19–21} The basic mechanism responsible for the storage effect in these materials is the reorientation of azobenzene chromophores induced by light. The material ability for these purposes can be easily checked in simple experiment of degenerate two-wave mixing and observation of self-diffraction process (Figure 7). When two coherent laser beams of arbitrary polarisation cross each other within optically isotropic and slightly absorbing medium, the state of polarisation of the total field changes spatially in its magnitude and orientation.

In the simplest case of the so called *s-s* polarisation (*i.e.*, when two incoming beams I_1 and I_2 are linearly polarised with electric field vectors perpendicular to the incidence plane, VV means vertical-vertical polarisation) the phase variation between the beams produces an intensity fringe pattern of the form:

$$I(x) = I_0[(1 + m \cos(Kx))] \quad (1)$$

where, $I_0 = I_1 + I_2$, m is the modulation factor $m = 2\sqrt{I_1 I_2}/(I_1 + I_2)$ and $K = 2\pi/\Lambda$ is the grating wave-vector. Grating spacing $\Lambda = \lambda/2 \sin(\theta/2)$ depends on the light wavelength λ , and an angle θ between the two incident beams. Alternatively various polarisation grating recording geometries can be used when incident beams are orthogonally polarised (*s-p* or VH vertical-horizontal polarisation) or having opposite circular polarisations.^{22–26} The rigorous Jones matrix formalism used in the papers quoted above allows predicting of

polarisations of all orders of diffraction for arbitrary polarised laser beam diffracted on such gratings. Depending on the value of Klein's parameter $Q = \frac{2\pi\lambda d}{n\Lambda^2}$ gratings can be classified as thin ($Q < 1$) or thick ($Q > 10$). For the studied polymer foils of thickness $d = 1.5$ μm , $n \approx 1.6$, $\Lambda = 3.4$ μm and $\lambda = 0.5145$ μm one gets $Q = 0.26$. This value suggests the Raman-Nath scattering regime, which is additionally supported by the observation of multiple diffraction orders.

In the photochromic material one expects respective "local" modulation of the complex refractive index $\Delta\hat{n}$:

$$\Delta\hat{n}(x) = \Delta n'(x) + i\Delta n''(x) \propto \cos(Kx) \quad (2)$$

causing photoinduced anisotropy. The refractive index modulation $\Delta n'$ and absorption modulation $\Delta n''$ occurring during the grating recording process are simultaneously intensity and time dependent. There is no simple theory describing the grating formation in a photochromic material upon a cw laser illumination due to the coexistence of phase ($\Delta\bar{n}$), amplitude ($\Delta\bar{a}$) and surface relief ($\Delta\bar{d}$) gratings.¹ A full theory describing light diffraction in a material with a photo-induced dichroism and birefringence including complex spatial and intensity variation of $\Delta\bar{n}$ and $\Delta\bar{a}$ parameters is given in the Reference.²³ In most cases (weak gratings) the diffraction efficiency defined as the ratio of the diffracted to incident beam intensity $\eta = I_{\text{diff}}/I_{\text{inc}}$ is roughly proportional to the photoinduced birefringence (and/or absorption) according to relation:

$$\eta \propto \left(\frac{\pi\Delta n d}{\lambda}\right)^2 \quad (3)$$

The preliminary results of kinetics of holographic grating recording using 514.5 nm Ar⁺ laser light with ss-polarisation for the chosen polymers functionalised with azo-groups are presented in Figure 8 and 9. Plots of self-diffraction efficiency measured at first order diffraction versus time are given. For the comparative purposes all the experimental conditions, *i.e.*, incident light power ($P_{\text{inc}} = 12.5$ mW corresponding to $I_1 = I_2 \cong 700$ mW cm⁻²), intersection angle ($\theta = 8.6^\circ$) and recording time were kept unchanged. It seems that slightly faster recording can be obtained in polymers with lower T_g temperature. However, the differences in recording speed are not pronounced. Diffraction efficiencies are in the range 0.01–0.8% and gratings have mixed amplitude-phase character. However, we cannot rule out the possibility of surface relief grating formation and its contribution to the overall diffraction efficiency. Lacking the AFM study we can only comment that the used *s-s* polarisation usually does not induce large surface deformations.¹

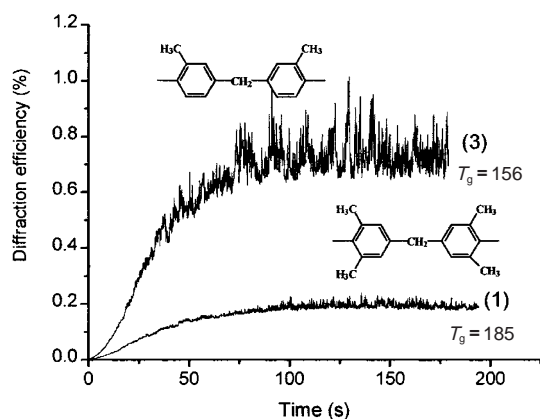


Figure 8. Plots of diffraction efficiency measured during DTWM experiment in polymers **3** and **1**. The illumination power $I_1 = 12.5$ mW, $I_2 = 16.5$ mW, wavelength 514.5 nm, grating period $\Lambda = 3.4$ μm .

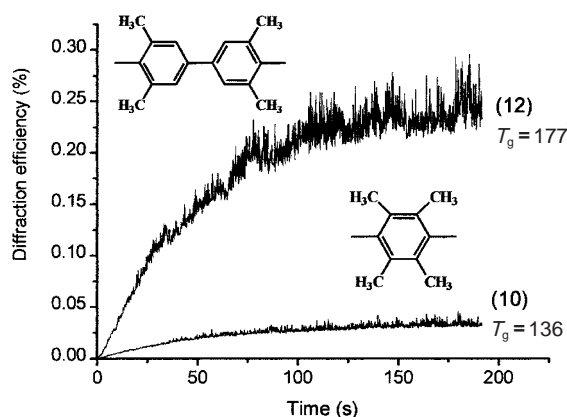


Figure 9. Plots of diffraction efficiency measured during DTWM experiment in polymers **10** and **12**. The illumination power $I_1 = 12.5$ mW, $I_2 = 16.5$ mW, wavelength 514.5 nm, grating period $\Lambda = 3.4$ μm .

In one of the polymers **3** we checked the intriguing property of polarisation grating recording, *i.e.*, when two beams were orthogonally polarised with respect to each other, one *s*- (V) and one *p*-polarised (H-horizontal). In such a case there is no associated intensity modulation at the overlapping area. Instead one observes a pure polarisation interference pattern which has the same periodicity as for *s-s* polarisation case.²² Grating in this case will arise as a result of angular absorption selectivity by different polarisation states of the light along the grating period (linear, circular-left, linear, circular-right^{24,25}) and subsequent molecular reorientations. In Figure 10 we present polarisation grating recording kinetics for polymer **3** but this time performed with weakly absorbed He-Ne laser light of wavelength $\lambda = 632.8$ nm and the power 10 mW. The speed of recording is much slower than for strongly absorbed 514.5 nm light. The plot shown in Figure 10 is a combination of VH recording registered by laser power meter during 63 min, next we observed

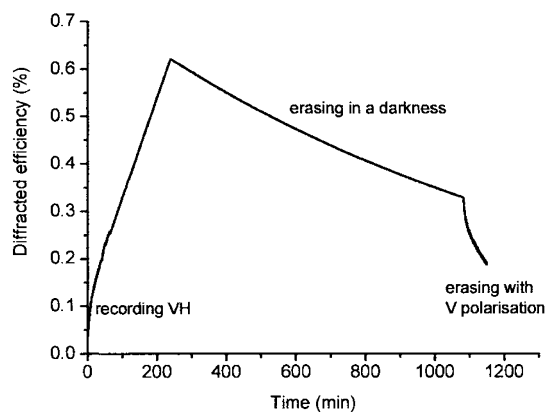


Figure 10. Polarisation grating recording experiment performed with (sp) VH orthogonal light polarisations in polymer **3**. The erasing process in darkness was monitored during the night and the fast erasing with V polarised single beam are shown as well. The illumination powers $I_1 = 9.5$ mW, $I_2 = 10$ mW, beam diameters 1.5 mm, wavelength 632.8 nm, grating period $\Lambda = 15.4$ μm .

diffracted power at 240 min and switched off the laser. After 14 h of relaxation of the grating in the darkness we measured the kinetics of grating erasure by illuminating it with a single *s*-polarised beam. The diffraction efficiency η_{sp} for the polarisation grating in polymer **3** is higher than the diffraction efficiency η_{ss} for the intensity grating in this polymer under the same experimental conditions.

Two main mechanisms are responsible for hologram formation in polymers containing azo-groups: molecular reorientation and presence of both *trans* and *cis* isomer populations. Molecular reorientation can be regarded as arising from the combination of three consecutive processes: the angular selective *trans* to *cis* photoisomerisation, the angular diffusion and the *cis* to *trans* relaxation. Depending on the structure and viscosity of the polymer matrix (mobility of polymer chains), the relaxation times of *cis* molecules and orientational relaxation times, different characteristics of recording kinetics and gratings strengths in different polymers were observed.^{22,24} The detailed analysis of the origin of the gratings in the investigated polymers will be our future task.

CONCLUSIONS

New photosensitive polymers – poly(ester-imide)s containing nitroazobenzene moieties as the side chain and various structures of the main chains have been synthesized.

The polymers possess good thermal stability, are soluble in aprotic solvents and exhibit film-forming properties. According to the preliminary study of optical grating recording these polymers seem to be interesting materials for optical applications. The preliminary

investigations of the polymer **3** confirmed the ability of polarisation holographic recording in the synthesised polymers. Systematic studies of these properties are in progress.

Acknowledgments. The authors thank Dr B. Jarząbek for UV-vis spectra measurements, Dr H. Janeczek for DSC measurements, Dr A. Burian for WAX diffractograms recording, Ms A. Sobolewska for diffraction measurements. One of the Authors (A. M.) acknowledges financial support of Polish Scientific Committee under grant no. 4T08A 03523.

REFERENCES

1. N. K. Viswanathan, D. Y. Kim, S. Bian, J. Williams, W. Liu, L. Li, L. Samuelson, J. Kumar, and S. K. Tripathy, *J. Mater. Chem.*, **9**, 1941 (1999).
2. X. Meng, A. Natansohn, and P. Rochon, *J. Polym. Sci., Part A: Polym. Chem.*, **34**, 1461 (1996).
3. T. Buffeteau, F. Lagunge Labarthe, M. Pezolet, and C. Sourisseau, *Macromolecules*, **31**, 7312 (1988)
4. K. Barrett, B. Choudhury, A. Natansohn, and P. Rochon, *Macromolecules*, **31**, 4845 (1998).
5. J. A. F. Boogers, P. Th. A. Klaase, J. J. de Vlieger, and A. H. A. Tinnemans, *Macromolecules*, **27**, 205 (1994).
6. D. H. Choi and J. H. Kim, *Polym. Bull.*, **46**, 395 (2001).
7. Z. Yuxi, L. Zhao, Q. Ling, Z. Jianfen, and Y. Peixin, *Eur. Polym. J.*, **37**, 445 (2001).
8. O. Varnavski, R. G. Ispasoiu, M. Narewal, J. Fugaro, Y. Jin, H. Pass, and T. Goodson III, *Macromolecules*, **33**, 4061 (2000).
9. D. Sęk, E. Schab-Balcerzak, M. Solyga, and A. Miniewicz, *Synth. Met.*, **127**, 89 (2002).
10. S. Yang, L. Li, A. L. Cholli, J. Kumar, and S. K. Tripathy, *J. Macromol. Sci., Pure Appl. Chem.*, **A38**, 1345 (2001).
11. Z.-S. Xu, A. Natansohn, and P. Rochon, *J. Macromol. Sci., Pure Appl. Chem.*, **A38**, 1305 (2001).
12. C. J. L. Constantino, R. F. Aroca, S. Yang, V. Zucolotto, L. Li, O. N. Oliveira, Jr., A. L. Cholli, J. Kumar, and S. K. Tripathy, *J. Macromol. Sci., Pure Appl. Chem.*, **A38**, 1549 (2001).
13. S. Yokoyama, M. A. Kakimoto, and Y. Imai, *Langmuir*, **9**, 1086 (1993).
14. S. Yokoyama, T. Yamada, K. Kajikawa, M. Kakimoto, Y. Imai, H. Takezoe, and A. Fukuda, *Langmuir*, **10**, 4599 (1994).
15. C. Jung, T. Aoyama, T. Wada, H. Sasabe, M. Jikei, and M. Kakimoto, *High Perform. Polym.*, **12**, 205 (2000).
16. M. Ahlheim and F. Lehr, *Macromol. Chem. Phys.*, **195**, 361 (1994).
17. G. C. Eastmond and J. Paprotny, *React. Funct. Polym.*, **30**, 27 (1996).
18. G. C. Eastmond, J. Paprotny, and I. Webster, *Polymer*, **13**, 2865 (1993).
19. T. Todorov, L. Nikolova, and N. Tomova, *Appl. Opt.*, **23**, 4309 (1984).
20. Z. Sekkat, D. Morichere, M. Dumont, R. Loucif-Saibi, and J. Delaire, *J. Appl. Phys.*, **71**, 1543 (1992).
21. P. Lefin, C. Fiorini, and J.-M. Nunzi, *Opt. Mater.*, **9**, 323 (1998).
22. J. Tervo and J. Turunen, *Opt. Commun.*, **190**, 51 (2001).
23. T. Huang and K. H. Wagner, *J. Opt. Soc. Am.*, **B13**, 282 (1996).
24. P.-A. Blanche, Ph.C. Lemaire, C. Maertens, P. Dubois, and R. Jerome, *Opt. Commun.*, **185**, 1 (2000).
25. G. Cipparrone and A. Mazzulla, *J. Opt. Soc. Am.*, **B19**, 1157 (2002).
26. I. Naydenova, L. Nikolova, T. Todorov, N. C. R. Holme, S. Hvilsted, and P. S. Ramanujam, *J. Opt. Soc. Am.*, **B15**, 1257 (1998).