

Post and Prepolymerization Strategies to Develop Novel Photochromic Poly(esterimide)s

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ABSTRACT: This paper reports novel photoresponsive, processable poly(esterimide)s functionalized with the azobenzene and tricyanovinylene groups. Post and prepolymerization strategies were utilized for preparation of the new photochromic polymers with imide rings. The postpolymerization method of azopolymer synthesis included a functionalization of precursor poly(esterimide) containing dialkylaminophenyl groups with diazonium salt of aniline. The precursor poly(esterimide) was obtained from synthesized 2,2' [N-phenylethyl-aniline-di(4-estiro-1,2-dicarboxylic)]anhydride and 4,4'-methylene bis(2,6-dimethylaniline). The prepolymerization strategy based on polycondensation of 2,4-diaminoazobenzene with two dianhydrides, that is, with or without the azobenzene group. The new dianhydride with azobenzene unit was obtained. The reaction of post-tricyanovinylolation was carried out for substitution of prepared

polymers with tricyanovinylene groups. The synthesized polymers were characterized and evaluated by FTIR, ¹H NMR, X-ray, UV-Vis spectroscopies, and DSC. The polymers exhibited glass transition temperatures in the range of 119–208°C and good solubilities in common organic solvents, providing optical-quality films. Thermal stability of the polymers films was investigated by UV-Vis spectroscopy. Preliminary investigations of the optical anisotropy in chosen poly(esterimide)s were carried out by photoinduced birefringence measurements. Relatively high photoinduced birefringence ($\Delta n = 0.01$) was measured for polyimide with covalently bonded azobenzene substituted with strong acceptor group. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 631–643, 2011

Key words: polyimides; photochromic polymers; azobenzene chromophores; photoinduced anisotropy

INTRODUCTION

Polymers are promising materials for applications in the fields of photonics and optoelectronics due to the advantage over inorganic crystals, such as good processability to form optical devices, high mechanical and dimensional stability, chemical resistance, low dielectric constants, and potentially large electrooptic coefficients.^{1–3} Moreover, polymers have great flexibility in the range of polymer-chromophore combinations that can be selected to particular applications. To develop practical devices, the nonlinear optical (NLO) polymer materials must fulfill many requirements including thermal, chemical and photochemical stability, low optical propagation losses, and mechanical properties for multilayer films processing.^{4,5} One of the major challenges is to achieve the reasonable tradeoff among all these properties in a one sample.⁶ For practical applica-

tions, long-term chemical and orientational stabilities of polymeric NLO materials are required at the operating temperatures, which may vary between 80 and 125°C in dependence on the application. When polymeric materials are fabricated as electrooptic devices, they may also be exposed to temperatures of ~ 200–250°C for a short period of time.⁷ Several strategies have been suggested to achieve this goal. One approach is the utilization of high glass transition temperature (T_g) polymers, such as polyimides, which have played a key role in the materials for the microelectronics, optics and aerospace industries due to their superior thermal stability, chemical resistance, and mechanical durability.⁸ Moreover, polyimides are found to be promising candidates also because of their low dielectric constants, optical transparency, and compatibility with semiconductor device technology.^{9–11} Polyimide derivatives have been attracting attention in the design of photochromic and second-order nonlinear optical polymers for improving the temporal stability of poled polymer films.^{12–14}

The chromophores can be introduced into polymers in two main ways: by dissolution in a polymer host (a guest-host system) and by covalent bonding of the chromophore to the macromolecular chain. It

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is generally believed that covalently bonded polymers will ultimately be necessary for use in practical devices.¹⁵ Such polymers may be realized by a variety of configurations by a number of different synthetic approaches.¹⁶ One of them is a direct polycondensation of the chromophore containing monomers. Another one involves the postpolymerization strategy, which allows chromophores to be introduced into reactive precursor polymers without the exposure of the chromophores to aggressive polymerization conditions.¹⁷ In this method, because of mild conditions, there are no restrictions for the kind of chromophore which may be incorporated into the polymer structure. The another advantage of postpolymerization strategy is the possibility of tuning the chromophore loading level. The various postpolymerization reactions were developed. Two of them are the most utilized, that is, Mitsunobu condensation between hydroxy groups in polymers and alkyl hydroxyl groups of the chromophores^{6,18,19} and post-azocoupling reaction between polymer and diazonium salts.^{20,21}

One of the basic requirements for materials are proper chromophores. It was found that azobenzene compounds are preferred as photosensitive structures because photochemical side reaction, leading to irreversible destruction of the compounds, can be avoided for the majority of them.²² Azobenzene groups are known to exist in two isomeric states, a thermodynamically stable *trans* and a *meta*-stable *cis* form. When irradiated with light of an appropriate wavelength they undergo a multiple reversible *trans*↔*cis* photoisomerization processes.²³ For random distribution of the azobenzene groups in a viscous polymeric matrix a linearly polarized laser light causes the orientation of the azobenzene moieties perpendicular to the electric field vector of the incident light, which results in the induction of the optical anisotropy. The phenomenon of photoinduced optical anisotropy is a key for photonic processes.²⁴ In this article, azobenzene units were selected as chromophores. To obtain the polymer with required properties the understanding of the relationship between polymer structure and the relevant macroscopic properties including photoinduced ones is necessary. Extensive studies carried out in our laboratory involve the investigations of influence of polymer structure on its properties induced by polarized light.^{25–30} The polyimides designed and synthesized for this work contain in the main chain ester linkages and aliphatic groups and pendant azobenzene units. Additionally, azobenzene units were substituted with tricyanovinylene groups⁶ known to be very strong electron acceptors.⁹ Such tricyanovinylene functionalized polymers in which chromophores form push-pull type of molecule may exhibit good electrooptic properties when a polar order in

chromophore alignment is created. Usually the poling process is carried out near the glass transition temperature, which is high in the case of polyimides. However, due to the presence of the azobenzene derivatives in polymers described in this article, the required order could be achieved far below the T_g by a photoassisted poling.³¹ Thus, the presence of the azobenzene units and tricyanovinylene moieties makes the polymers attractive multiproperty materials that combine the photochromic and electrooptic activity.³² As a part of our continuing effort in developing new azopolymers, this work deals with the synthesis and characterization of novel poly(esterimide)s and preliminary investigation of the photoinduced optical anisotropy in chosen polymers, which was studied by measurements of the photoinduced birefringence.

EXPERIMENTAL

Materials

N-Methyl-2-pyrrolidone (NMP), 4,4'-methylenebis(2,6-dimethylaniline), tetracyanoethylene (TCNE), chloro(trimethyl)silane (CTMS), trimellitic anhydride acid chloride, *N*-phenyldiethanolamine were purchased from Aldrich Chemical Co. and were used without purification. Aniline was purchased from Aldrich Chemical Co. and was purified by distillation before use. 2,4-Diaminoazobenzene and 2,2'[*N*-phenylethyl]aniline-di(4-*est*-1,2-dicarboxylic)anhydride were synthesized according to the published procedure³³ and,³⁴ respectively.

Measurements

FTIR spectra were recorded on a BIO-RAD FTS 40 A Spectrometer using KBr pellets. ¹H NMR spectroscopy was carried out on a Varian 300 Spectrometer using DMSO-*d*₆ as a solvent. UV-vis spectra were recorded in NMP solution of polymers and as films casted on glass using a Jasco V570 UV-V-NIR Spectrometer. The X-ray diffraction patterns on solid samples were recorded using CuK α radiation on a wide-angle HZG-4 diffractometer working in the typical Bragg geometry. Differential scanning calorimetry (DSC) measurements were done using a Du Pont 1090B apparatus with a heating rate of 20°C/min under nitrogen. Weight-averaged molecular weight and molecular weight distribution (M_w/M_n) values of polymers were determined by SEC measurements conducted in THF at 35°C with flow rate of 1 mL/min, using a set of two PLgel 5 μ m MIXED-C ultrahigh efficiency columns. Isocratic pump Spectra Physics 8800 as a solvent delivery system, differential refractive index detector (VE3580, Viscotek), viscometer detector (270 Dual Detector

Array, viscometer, Viscotek) were applied. A volume of 100 μL of sample solution in THF (concentration of 2% w/v) was injected. Polystyrene standards with narrow molecular weight distributions were used to generate a calibration curve. The light-induced birefringence was measured using excitation light at 450 nm (5.2 mW) delivered by an optical parametric amplifier (OPA 800C, Spectra Physics). The laser diode operating at 690 nm was used as the probing light. The transmission of polymer film by means of the probe beam passing through crossed polarizers setup was detected by a lock-in amplifier using a mechanical chopper for modulation of the reading beam.

Synthesis of dianhydride with azobenzene group (DA-Az)

The synthesis of **DA-Az** consisted of two parts: in the first one aniline was converted to the diazonium salt, which was subjected to a coupling reaction with *N,N*-di(2-hydroxyethyl)aniline to give (*N,N*-di-2-hydroxyethyl)aminoazobenzene (**D-Az**).³³ In the second one **D-Az** was subjected to the condensation reaction with trimellitic anhydride acid chloride to obtain **DA-Az**.³⁴

D-Az. ¹H NMR (DMSO- d_6 , δ , ppm): 3.56 (t, CH₂, 4H), 3.59 (t, CH₂, 4H), 4.86 (t, OH, 2H), 6.84 (d, 2H), 7.41 (t, 1H), 7.51 (t, 2H), 7.76 (d, 4H). FTIR (KBr, cm⁻¹): 3456 (OH), 2939, 2871 (CH₂). UV-Vis (NMP): $\lambda_{\text{max}} = 384, 432 \text{ nm}$, m.p. = 139°C.

DA-Az. ¹H NMR (DMSO- d_6 , δ , ppm): 3.98 (t, CH₂, 4H), 4.54 (t, CH₂, 4H), 7.09 (d, 2H), 7.43 (t, 1H), 7.52 (t, 2H), 7.77 (d, 4H), 8.08 (d, 2H), 8.11 (d, 2H), 8.24 (d, 2H). FTIR (KBr, cm⁻¹): 1859, 1781, (O=C in anhydride), 1724 (-O-CO- ester), 2973, 2925 (CH₂), 1600 (Ar). UV-Vis (NMP): $\lambda_{\text{max}} = 376, 420 \text{ nm}$, m.p. 175°C.

Polymer synthesis

Synthesis of poly(esterimide)s PEI-I and PEI-II

The polymers were obtained from 2,2'[*N*-phenylethyl]aniline-di(4-estero-1,2-dicarboxylic)anhydride and 4,4'-methylenebis(2,6-dimethylaniline) (polymer **PEI-I**), and 2,4-diaminoazobenzene (polymer **PEI-II**). The details of synthesis and characterization of these poly(esterimide) **PEI-I** were reported in our previous work.³⁴

PEI-I. ¹H NMR (DMSO- d_6 , δ , ppm): 2.01 (s, CH₃, 12H), 3.87 (m, CH₂, 6H), 4.51 (t, CH₂, 4H), 6.59 (t, 1H), 6.91 (d, 2H), 7.12 (t, 2H), 8.01 (s, 4H), 8.26-8.32 (m, 6H). FTIR (KBr, cm⁻¹): 1782, 1723 (C=O in imide), 1372, 732 (C-N), 2957, 2923 (CH₂).

Polymer **PEI-II** was obtained according to the published procedure.³⁵

2,4-diaminoazobenzene (0.424 g, 2 mmol) in 1.4 mL NMP was stirred at room temperature under argon atmosphere until all solid was dissolved. Then the

required amounts of CTMS (0.51 mL, 4 mmol) and pyridine (0.32 mL, 4 mmol) were slowly added and the solution was stirred for 15 min to ensure the formation of the silylated diamine. After this time, the solution was cooled to 0°C and dianhydride **DA** (1.06 g, 2 mmol) was rapidly added followed by pouring of 2 mL of NMP. The reaction mixture was stirred for 15 min at 0°C and then the temperature was raised up to room temperature and left overnight. Acetic anhydride (1.13 mL, 12 mmol) and pyridine (0.64 mL, 8 mmol) were then added to promote imidization and the reaction mixture was stirred at room temperature for 6 h followed by heating for a further hour at 60°C. The resultant polymer was precipitated with water, washed several times with water, and purified by extraction with methanol in Soxhlet apparatus for 72 h and then dried at 100°C in vacuum.

PEI-II. ¹H NMR (DMSO- d_6 , δ , ppm): 3.87(t, CH₂, 4H), 4.51 (t, CH₂, 4H), 6.57 (t, 1H), 6.93 (d, 2H), 7.15 (t, 2H), 7.43 (t, 2H), 7.55 (s, 1H), 7.63 (s, 1H), 7.80 (t, 2H), 7.89 (t, 2H), 8.07 (s, 1H), 8.32 (d, 2H). FTIR (KBr, cm⁻¹): 1785, 1726 (C=O in imide), 1363, 726 (C-N), 2953 (CH₂).

Synthesis of poly(esterimide) PEI-III

The polymer was obtained from dianhydride **DA-Az** and 2,4-diaminoazobenzene in the same method as polymer **PEI-II**.

PEI-III. ¹H NMR (DMSO- d_6 , δ , ppm): 3.94 (t, CH₂, 4H), 4.52 (t, CH₂, 4H), 7.09 (d, 2H), 7.44 (t, H), 7.52 (t, 2H), 7.77 (d, 4H), 7.95 (s, 1H), 7.98 (d, 2H), 8.08 (t, H), 8.11 (t, 2H), 8.26 (d, 2H), 8.29 (d, 2H), 8.48 (d, 2H), 8.60 (d, 2H). FTIR (KBr, cm⁻¹): 1782, 1725 (C=O in imide), 1368, 721 (C-N), 2925 (CH₂).

Synthesis of azobenzene functionalized poly(esterimide) PEI-Ib

Polymer **PEI-Ib** was obtained according to the published procedure²⁹ using aniline instead of *p*-nitroaniline.

A solution of hydrochloric acid (36%, 0.47 mL) was added slowly to aniline (0.14 g, 1.55 mmol) in water (0.47 mL) and stirred at room temperature. Then the solution was cooled down to 0–5°C and sodium nitrite (0.12 g, 1.70 mmol) in 0.44 mL of water was added dropwise and the mixture was stirred for 60 min. **PEI-I** (1.12 g, 1.5 mmol) dissolved in NMP (6.25 mL) and was added dropwise into the prepared diazonium salt solution. The mixture was stirred for 5 h at 0–5°C and then precipitated into the mixture of methanol (30 mL) and water (30 mL). The polyimide was purified by extraction with methanol in Soxhlet apparatus for 72 h and then dried at 100°C in vacuum.

PEI-Ib. ¹H NMR (DMSO- d_6 , δ , ppm): 2.01 (s, CH₃, 24H), 3.8-4.03 (m, CH₂, 12H), 4.53 (t, CH₂, 8H), 6.6 (t, 1H), 6.95 (d, 4H), 7.07 (d, 4H), 7.14 (s, 8H), 7.45 (s,

1H), 7.50 (t, 2H), 7.75 (d, 2H), 8.04 (s, 2H), 8.3 (d, 4H). FTIR (KBr, cm^{-1}): 1781, 1722 (C=O in imide), 1372, 732 (C—N), 2955, 2922 (CH_2).

Synthesis of tricyanovinylene functionalized poly(esterimide)s (PEI-Ia, PEI-Ic, PEI-IIa, PEI-IIIa)

Polymers were synthesized according to the modified procedure.^{6,9} An exemplary synthesis of **PEI-Ia** is given below.

Polymer **PEI-I** (0.42 g, 0.56 mmol) in 12.5 mL DMF was stirred at room temperature under argon atmosphere until all solid had dissolved. Then, the small portions of TCNE (0.3 g, 2.26 mmol) were slowly added to this solution at room temperature. After the addition of TCNE, the reaction temperature was raised to 60°C and the solution was maintained at this temperature for 24 h with stirring. After being cooled to room temperature the solution was added into the mixture of methanol (30 mL) and water (30 mL) to precipitate the polymer. The precipitate was collected by filtration and washed with water repeatedly till the filtrate was almost colorless, followed by washing with ethanol for three times. The resulting polymer was dried at 40°C in vacuum for 24 h.

PEI-Ia. ¹H NMR (DMSO- d_6 , δ , ppm): 2.02 (s, CH_3 , 12H), 3.9 (s, CH_2 , 2H), 4.15 (t, CH_2 , 4H), 4.64 (t, CH_2 , 8H), 6.94 (t, 2H), 7.13 (s, 4H), 7.32 (d, 2H), 8.03 (d, 1H), 8.19 (s, 1H), 8.3 (d, 1H). FTIR (KBr, cm^{-1}): 1781, 1723 (C=O in imide), 1372, 731 (C—N), 2923 (CH_2), 2218 (CN), 1602 (Ar).

Polymers **PEI-Ic**, **PEI-IIa**, and **PEI-IIIa** were obtained according to the synthesis procedure of the polymer **PEI-Ia** using polymer **PEI-Ib**, **PEI-II**, and **PEI-III**, respectively, instead of polymer **PEI-I**.

PEI-Ic. ¹H NMR (DMSO- d_6 , δ , ppm): 2.02 (s, CH_3 , 12H), 3.81 (s, CH_2 , 2H), 4.15 (t, CH_2 , 4H), 4.64 (t, CH_2 , 4H), 6.94 (d, 2H), 7.07 (d, 2H), 7.14 (s, 4H), 7.32 (t, 2H), 7.87 (t, 2H), 8.04 (s, 1H), 8.3 (d, 2H). FTIR (KBr, cm^{-1}): 1781, 1723 (C=O in imide), 1372, 731 (C—N), 2956, 2921 (CH_2).

PEI-IIa. ¹H NMR (DMSO- d_6 , δ , ppm): 4.14 (t, CH_2 , 4H), 4.61 (t, CH_2 , 4H), 7.32 (t, 2H), 7.46 (t, 2H), 7.5–7.7 (m, 3H), 7.81 (d, 2H), 7.87 (d, 2H), 8.05 (s, 1H), 8.29 (t, 2H). FTIR (KBr, cm^{-1}): 1785, 1727 (C=O in imide), 1362, 726 (C—N), 2956 (CH_2), 2217 (CN).

PEI-IIIa. ¹H NMR (DMSO- d_6 , δ , ppm): 3.97 (t, CH_2 , 4H), 4.55 (t, CH_2 , 4H), 7.07 (d, 2H), 7.51 (t, 2H), 7.7 (d, 4H), 7.94 (s, H), 7.97 (d, 2H), 8.10 (t, 2H), 8.23 (d, 2H), 8.29 (d, CH, 2H), 8.48 (d, 2H), 8.58 (d, 2H). FTIR (KBr, cm^{-1}): 1782, 1723 (C=O in imide), 1380, 727 (C—N), 2927 (CH_2), 2199 ($\text{C}\equiv\text{N}$).

Polymer film preparation

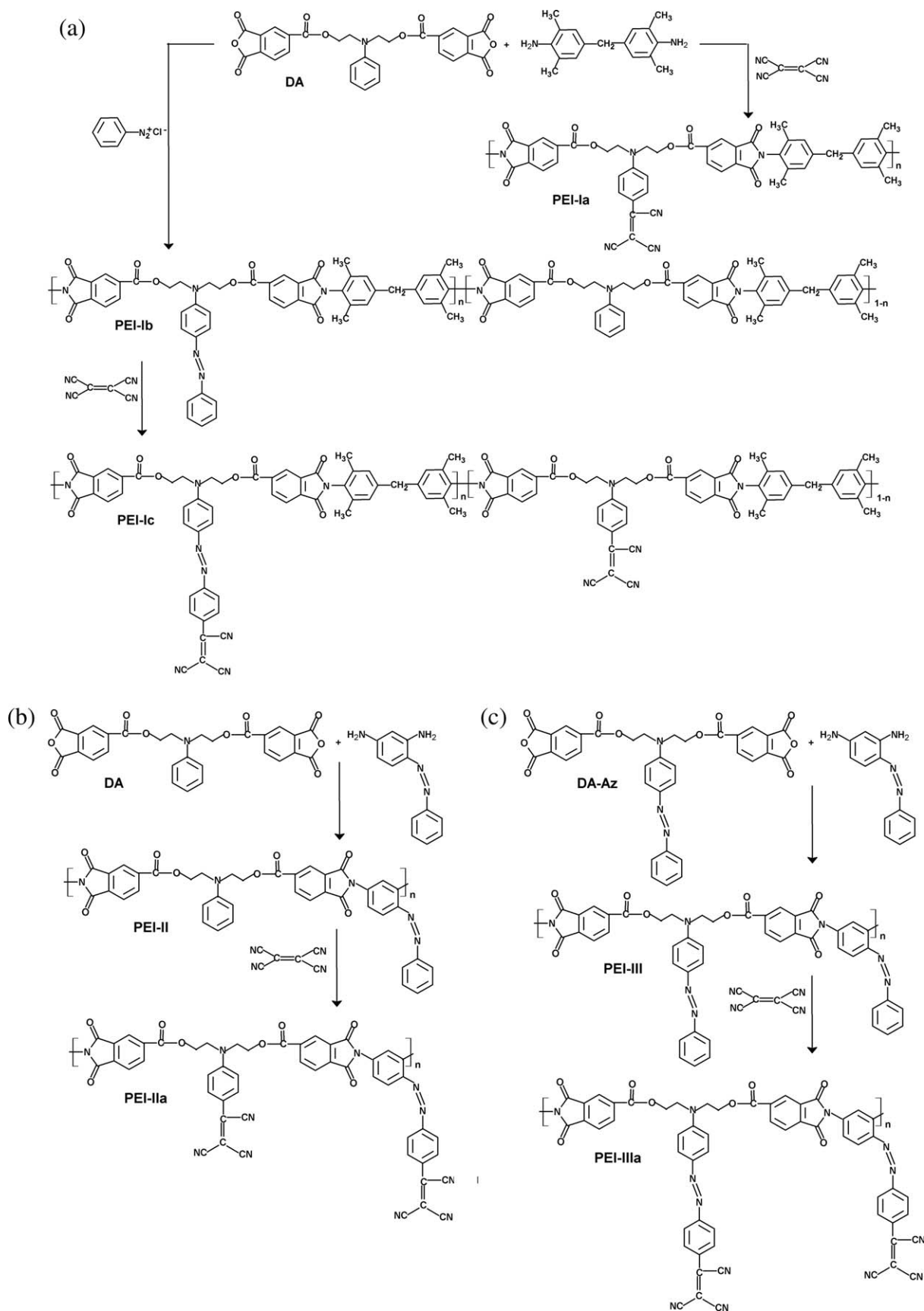
The homogeneous solutions of the azopolymers in NMP were filtered through 0.2 μm membranes and

casted onto glass substrates. Residual solvent was removed from the films by heating for 2 h at 110–200°C near the polymer T_g ; a temperature at which polymer segmental motion is large enough to free possibly trapped solvent molecules.

RESULTS AND DISCUSSION

The post and prepolymerization strategies were utilized for preparation of the new chromophore functionalized poly(esterimide)s. Figure 1 shows the synthetic route and the chemical structure of obtained poly(esterimide)s.

A postpolymerization method of azopolymer synthesis included a functionalization of precursor poly(esterimide)s (**PEI-I**) which was obtained from 2,2' [*N*-phenylethyloaniline-di(4-*est*-1,2-dicarboxylic)]anhydride and 4,4'-methylene bis(2,6-dimethylaniline). The polymer **PEI-I** due to the presence of *N,N*-diethylamino-benzene groups is able for functionalization by connecting various chromophores to main polymer chain through an azocoupling reaction. The azocoupling reaction, a common method used to synthesize the azo dyes, was found to be applicable to the functionalized polymers. The diazonium salt and tetracyanoethylene attack the benzene rings pendant from the backbone at the position with higher electron density. The bulkiness of the attacking group and the resulting steric hindrance limit the electrophilic substitution exclusively at the *para* position.³⁶ Polymer **PEI-I** was functionalized with the azobenzene chromophore by an azocoupling reaction using aniline as coupling component, which resulted in polymer denoted as **PEI-Ib** [cf. Fig. 1(a)]. The prepolymerization strategy for preparation of azopolymers based on polycondensation of 2,4-diaminoazobenzene with 2,2' [*N*-phenylethyloaniline-di(4-*est*-1,2-dicarboxylic)]anhydride giving the polymer **PEI-II** [cf. Fig. 1(b)] and with newly synthesized dianhydride **DA-Az** giving the polymer **PEI-III** [cf. Fig. 1(c)]. A polycondensation under the *in situ* silylated diamines in the presence of chloro(trimethyl)silane and pyridine as catalyst was carried out.³⁵ Polymers **PEI-I**, **PEI-Ib**, **PEI-II**, and **PEI-III** were subjected to post-tricyanovinylolation leading to polymers denoted as **PEI-Ia**, **PEI-Ic**, **PEI-IIa**, and **PEI-IIIa**, respectively, (cf. Fig. 1). The obtained polymers differ in the kind of azobenzene group and its content in their repeating units. The poly(esterimide)s **PEI-Ib**, **PEI-Ic**, **PEI-II**, and **PEI-IIa** contain one azobenzene moiety, while **PEI-III** and **PEI-IIIa** possess two chromophoric groups in the polymer repeating units. Two kinds of chromophores were introduced into the polymer backbone, that is, the azobenzene group tethered by tertiary amine units with the polymer chain (**PEI-Ib**, **PEI-Ic**) and the azobenzene group with one of the aromatic cores being a part of



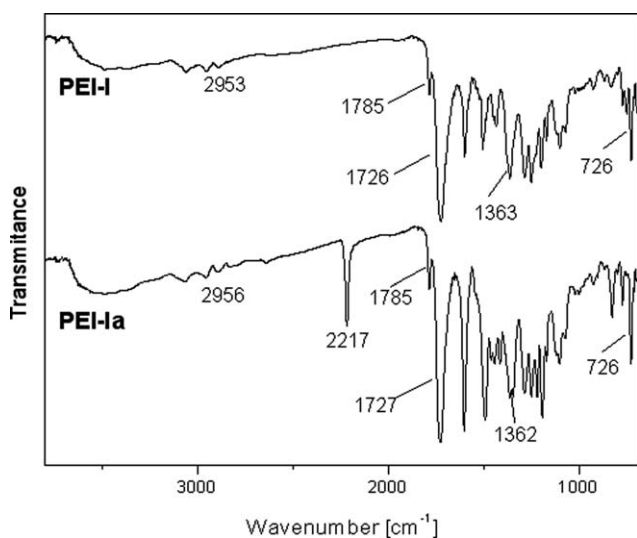


Figure 2 FTIR spectra of the polymers **PEI-I** and **PEI-Ia**.

the polymer backbone (**PEI-II**, **PEI-IIa**). The polymers **PEI-III** and **PEI-IIIa** contain both types of chromophores.

Polymer characterization

Instrumental techniques including FTIR and ^1H NMR spectroscopies were performed for characterization of the polymer molecular structure. The FTIR spectra of the poly(esterimide)s clearly showed characteristic imide absorption bands at around 1785 and 1726 cm^{-1} attributed to the asymmetric and symmetric stretching vibration of the carbonyl group in the five-membered imide ring. The absorption band at 1363 cm^{-1} corresponds to the C–N stretching and that at 726 cm^{-1} to the imide ring deformation vibration. Figure 2 shows exemplary FTIR spectra of the poly(etherimide) before functionalization, that is **PEI-I** and after functionalization with tricyanovinylene **PEI-Ia**.

As the post-tricyanovinylation reaction proceeded a new band appeared in the FTIR spectra at 2226 cm^{-1} due to the cyano group (**PEI-Ia**, **PEI-Ic**, **PEI-IIa**, and **PEI-III**).

The ^1H NMR spectrum of poly(esterimide) **PEI-I** showed a signal at 6.60 ppm ascribed to the proton in benzene ring in *para* position to amine group which was selected for observation of the functionalization reaction. As the post-tricyanovinylation reaction proceeded in the polymers (**PEI-I**, **PEI-II**, and **PEI-III**) this proton peak completely disappeared (see Experimental) indicating that tricyanovinylene units were attached at *para* position of the benzene ring (**PEI-Ia**, **PEI-Ic**, **PEI-IIa**, and **PEI-IIIa**). Nevertheless, full substitution of the azobenzene group onto polymer **PEI-I** was not achieved as shown by the presence of 6.60 ppm peak in the spectrum of **PEI-Ib**. In this study, the level of functionalization of

PEI-I was determined by UV-Vis spectroscopy.³⁰ The degree of chromophore substitution in **PEI-Ib** was calculated from the calibration curves obtained from UV-Vis spectra of the chromophore solution with various concentration of chromophore **DA-Az**. From the comparison of the peak absorbance of the polymer **PEI-Ib** in solution with known concentration and the calibration curve, the degree of functionalization was estimated. The calculated experimental percentage content of the chromophore in **PEI-Ib** was about 59% it means that 59% of the *N,N*-diethylamino-benzene groups reacted with diazonium salt of aniline and other 41% remained intact.

The ideal material for many end-use applications should be highly amorphous as the crystallites introduce unwanted light scattering. Thus, the crystallinity of the poly(esterimide)s films was evaluated by wide-angle X-ray diffraction experiments. X-ray patterns obtained from these measurements are shown in Figure 3 for exemplary polymers.

One broad diffraction peak of diffusion type centered at about 23 deg (2θ) was observed for all studied samples (cf. Fig. 3). All the polymers showed the same diffraction patterns typical for perfectly amorphous materials.

It is well known that typical polyimides are generally poor soluble in organic solvents. However, the introduction of aliphatic and ester groups to the polyimide structure enhanced their solubility and processability. The solubility properties of all poly(esterimide)s were determined qualitatively by the dissolution of 2.5 mg of the solid polymer in 1 mL of organic solvent and the results are reported in Table I.

All the prepared polymers dissolved easily not only in strong polar organic solvents such as NMP, DMA, and DMSO but also in low-boiling-point solvent such as ether-type—tetrahydrofuran (THF). Moreover,

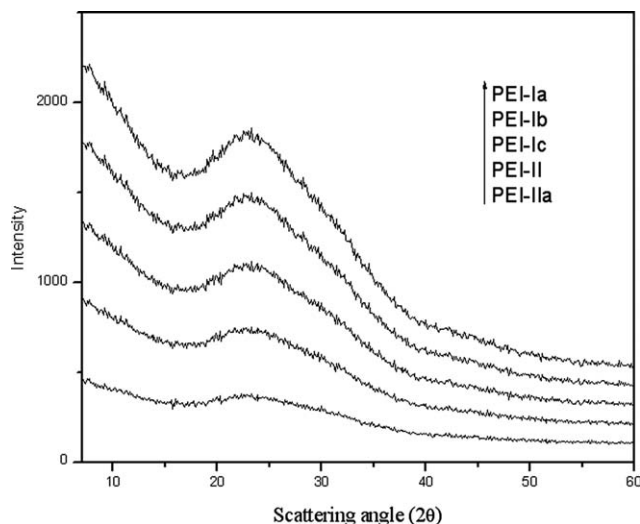


Figure 3 X-ray diffraction patterns of exemplary poly(esterimide)s.

TABLE I
Solubility of the Poly(esterimide)s

Polymer code	Solubility ^a					
	NMP	DMF	DMSO	THF	CHCl ₃	CH ₃ CN
PEI-I	+	+	+	+	+	-
PEI-Ia	+	+	+	+	±	±
PEI-Ib	+	+	+	+	+	±
PEI-Ic	+	+	+	+	+	±
PEI-II	+	+	+	+	+	±
PEI-IIa	+	+	+	+	±	±
PEI-III	+	+	+	+	±	±
PEI-IIIa	+	+	+	+	±	±

+, soluble at room temperature; ±, partial soluble on heating; -, insoluble on heating. Solvents: DMF, *N,N*-dimethylformamide; DMSO, dimethylsulfoxide; THF, tetrahydrofuran.

^a The qualitative solubility was tested with 2.5 mg samples in 1 ml of solvent.

some of the polymers were soluble in chlorinated solvent–chloroform. From a comparison of the solubility of the polymers after functionalization with tricyanovinylene (**PEI-Ia** and **PEI-IIa**) with respect to corresponding precursor polymers (**PEI-I** and **PEI-II**) in chloroform, it was observed that the polymers **PEI-I** and **PEI-II** were better soluble than poly(esterimide)s with tricyanovinylene units. On the other hand introduction of tricyanovinylene units into polymer **PEI-I** improved their solubility in acetonitrile. Azobenzene functionalized polymer **PEI-Ib** showed better solubility in acetonitrile than the corresponding polymer without chromophore, that is, **PEI-I**. The increased solubility of chromophore functionalized polymer may be caused by the existence of pendant azobenzene groups that leads to loose chain packing and to the decrease of the intermolecular interactions.

The molecular weight of chosen polymers was determined using SEC in THF. To improve the conventional calibration, SEC results were recalculated according to universal calibration with use of an additional detector, that is, a viscometer and the results are collected in Table II.

SEC analysis revealed a moderate molecular weight of polymers and unimodal weight distribution. In any case the obtained values should be treated indicatively only, since the calibration with

polystyrene standards may lead to questionable results when the polymers differ strongly from solvodynamic volumes of polystyrene.³⁷

Thermal properties

Thermal properties of the prepared poly(esterimide)s were examined by differential scanning calorimetry (DSC). The glass transition temperatures (T_g), defined by the midpoint of the base line shift of the polymers, were observed between 119 and 208°C. T_g is an essential parameter when material applications are considered because it is closely associated with a processing condition and stability of the devices.¹¹ All polymers gave similar DSC profiles with no melting endotherms and a clear T_g . These findings also clearly indicated their amorphous nature. The glass transition temperature of the poly(esterimide)s are summarized in Figure 4.

Glass transition temperature is a physical property originating from thermal motion (rotation or translation) of mobile groups and associated with flexibility of substituted group and spatial vacancy within polymers.¹¹ It is obvious that thermal properties depend on the structure of polymers. Considering the polymer backbone microstructure it was found that the polymer without azobenzene units (**PEI-I**) possessed higher T_g than polymer functionalized

TABLE II
SEC Characterization of the Studied Azopolymers

Polymer code	SEC (THF, PS)					
	Conventional calibration detector: differential refractive index			Universal calibration detector: differential refractive index with viscometer		
	$M_w (\times 10^{-3})$	$M_n (\times 10^{-3})$	PD	$M_w (\times 10^{-3})$	$M_n (\times 10^{-3})$	PD
PEI-I	16.2	3.9	4.1	13.2	3.4	3.9
PEI-Ia	26.7	6.9	3.9	26.0	5.6	4.6
PEI-Ic	28.1	5.3	5.3	23.1	4.4	5.2

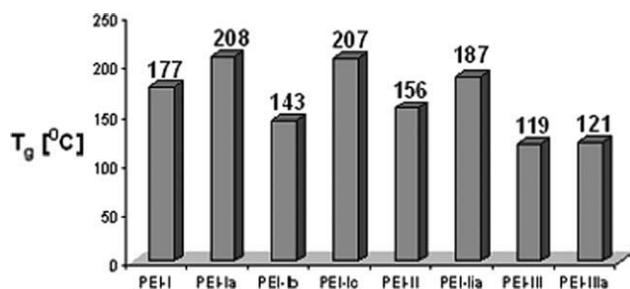


Figure 4 The glass transition temperatures of the investigated poly(esterimide)s.

with azobenzene unit (**PEI-Ib**) because pendant azobenzene groups tend to large vacancy between polymer chains. Therefore, the number of azobenzene moieties in polymer repeating unit also affects the T_g values. The lowest T_g exhibited polymer with two chromophores in repeating unit, that is, **PEI-III**. On the other hand the incorporation of electron acceptor i.e., tricyanovinyl moieties into polymer resulted in an increase of T_g value (cf. Fig. 4).

Thermal properties of the obtained poly(esterimide) films were indicated with the help of UV-Vis spectroscopy.³⁸ After deposition each thin polymer film was heated to below and above its T_g , that is, 90, 110, 130, 150, 170, 200°C (**PEI-III** and **PEI-IIIa**) and 120, 130, 170, 190, 200, 220, 240°C (the others) and kept at that temperature for 20 min under vacuum. After thermal treatment the absorption spectra were recorded for all the polymer films except for **PEI-I**, that is, parent polymer without both azobenzene and tricyanovinylene units, because of the presence of the absorption band below 300 nm (i.e., below the glass transparency range). The changes in absorbance, that is, position and level of absorption band characteristic for the azobenzene group transition are shown in Figure 5.

Taking into consideration the obtained results, it was found that the best thermal stability, also above their T_g , exhibited film prepared from polymer **PEI-II** which contains the azobenzene moieties a part of the backbone connected in the 2 and 4 position with imide rings [cf. Fig. 5(d)]. Both the absorption band maximum (λ_{max}) position and its level in **PEI-II** changed very slightly after annealing of this polymer film at temperature range from 25 to 240°C. In the case of polymer films, except for **PEI-III** with two azobenzene groups in repeating units [cf. Fig. 5(f)] and the short-wavelength band of **PEI-IIa**, in which also one of the aromatic cores of the azobenzene group is a part of the polymer backbone [cf. Fig. 5(e)], the hypsochromic effect i.e., decrease in absorption band intensity with an increase of annealing temperature was detected. The largest changes of the level of absorption bands exhibited **PEI-Ia**, and **PEI-IIa** polymer films [cf. Fig. 5(a,e)]. These poly-

mers (**PEI-Ia** and **PEI-IIa**) contain substituted with tricyanovinylene group the benzene ring tethered with the polymer backbone by tertiary amine units. For these polymer films the changes up to 22% of the original absorbance at temperature slightly below their T_g were found. In films of **PEI-Ib** and **PEI-Ic** [cf. Fig. 5(b,c)] which contain azobenzene moieties connected by tertiary amine with polymer chain, the relative absorbance decreased of about 16–17%, while in the other polymers **PEI-III** and **PEI-IIIa** with additional azobenzene moiety in polymer repeating unit [cf. Fig. 5(f,g)], the absorbance changed slightly of 0–4%. Furthermore, the position of the absorption bands changed after heat treatment of the films. Mentioned changes are showed as the function of temperature (the inserts to all figures in Fig. 5). For all investigated polymer films, except for **PEI-II**, the position of λ_{max} was shifted hypsochromically (to a higher energy region) during heating up to 200 or 240°C. That indicates the influence of temperature on the conformation of polymer chains, and the blue shift of the short-wavelength absorption band was observed. However, up to T_g the shift of λ_{max} seems to be insignificant (0–2 nm) for the polymer films: **PEI-Ib**, **PEI-Ic**, **PEI-III**, and **PEI-IIIa** [Fig. 5(b,c,f,g)], while for polymers **PEI-Ia** and **PEI-IIa** [Fig. 5(a,e)] this changes are also slight but only to the temperatures 170°C and 150°C, respectively, that is, much below their T_g values.

Summing up, the UV-Vis study indicates the good thermal stability of **PEI-II** polymer in a whole investigated temperature range (up to 240°C) and for polymers **PEI-Ib**, **PEI-Ic**, **PEI-III**, and **PEI-IIIa** to their T_g temperatures. On the other hand, the polymers **PEI-Ia** and **PEI-IIa** turned out to be stable to the temperatures below their T_g values. Taking into consideration of the structure–properties relationship it was found that the presence in poly(esterimide)s the azobenzene groups which one of the aromatic cores is a part of the polymer backbone prevents the thermals stability of the polymer films. On the other hand, the presence substituted with tricyanovinylene group the benzene ring tethered with the polymer backbone by tertiary amine units, slightly decrease their thermals stability. It should be pointed out that all obtained NLO polymers satisfy the demand of the high thermal stability required for the optical device fabrication.

Optical properties

The optical properties of the poly(esterimide)s were examining by UV-Vis spectroscopy. UV-Vis spectra of polymers were acquiring both in solution and in polymer films on a glass. The range of UV-Vis measurements was limited by transparency of the used solvent or substrate. The representative absorption

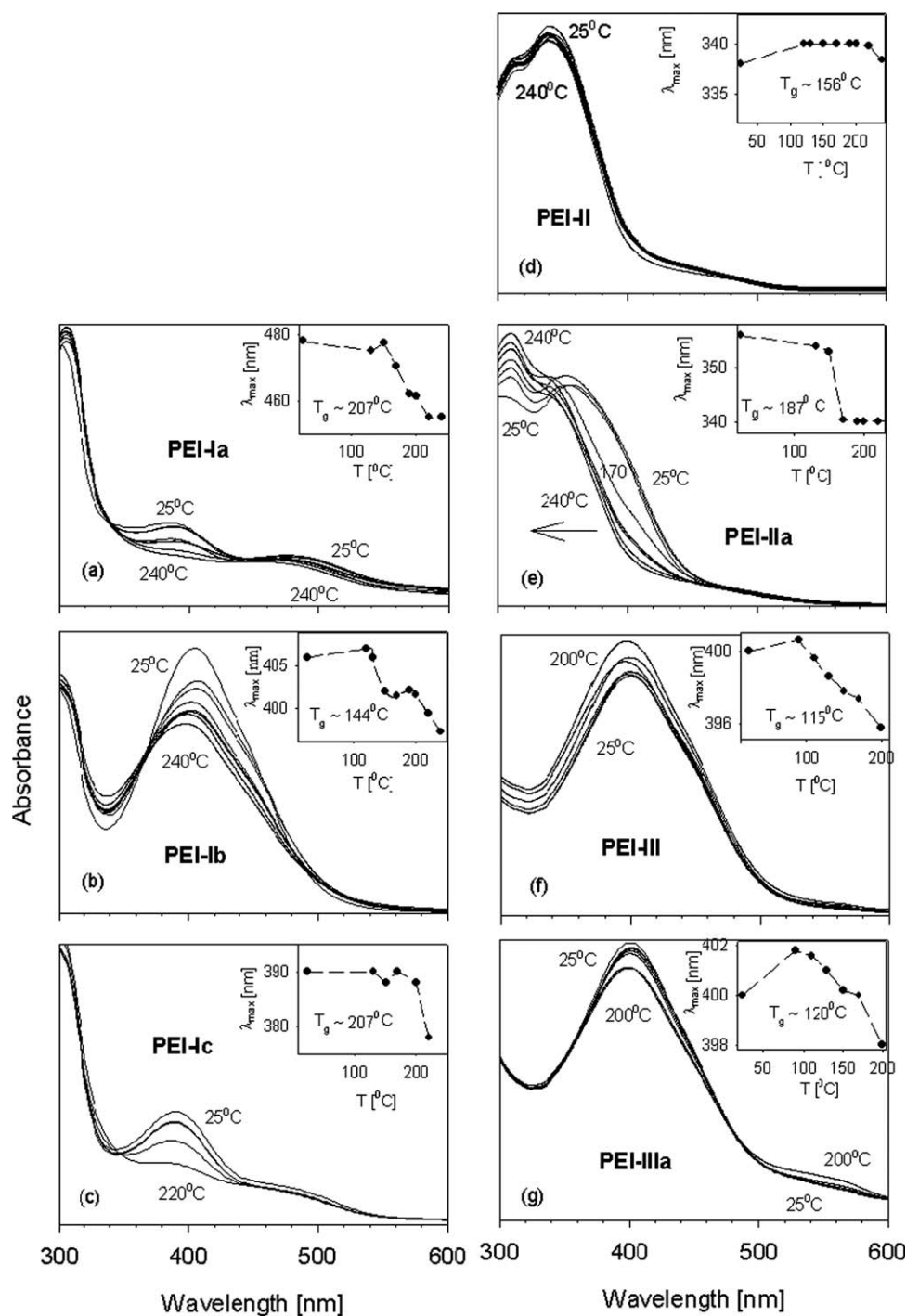


Figure 5 Absorption properties of the poly(esterimide) films after annealing at various temperatures.

spectra of chosen polymers in NMP solution are compared in Figure 6.

Absorption spectra of the studied azopolymers showed similar characteristics [cf. Fig. 6(a)], that is, the strong band with the maximum located in the range of 325–550 nm and attributed to the electronic transition moment of the *trans*-azo chromophore. This band is clearly separated from the absorption in the UV in the range of 263–320 nm characteristic for the transition within the polymer backbone. The

precursor, that is, poly(esterimide) PEI-I exhibited no light absorption above 350 nm [cf. Fig. 6(b)]. The presence of the tricyanovinylene units in the polymer chain (PEI-Ia) caused that such a polymer exhibited two absorption bands, the strong one with a maximum at 383 nm and another one with much lower intensity at 415 nm [cf. Fig. 6(b)]. The influence of chromophore type on absorption range of polymers was observed. The presence of chromophore with amine group (PEI-Ib) caused bathochromic shift of

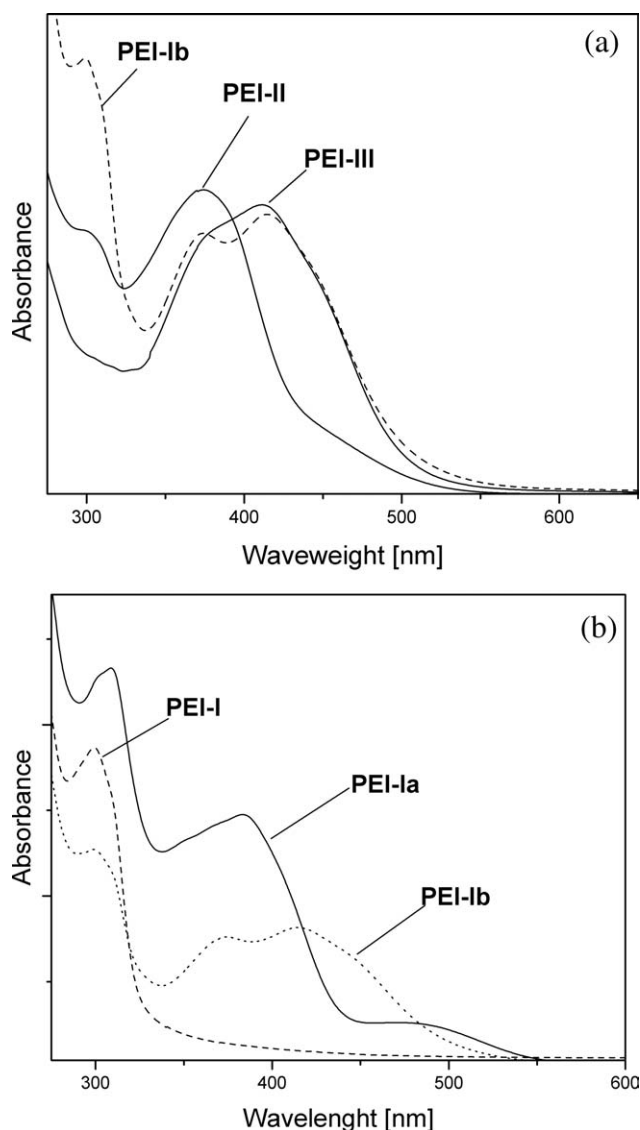


Figure 6 UV-Vis spectra of the polymers in NMP solution (a) PEI-Ib, PEI-II, and PEI-III, (b) PEI-I, PEI-Ia, and PEI-Ib.

λ_{\max} in relation to chromophore in which a part of azobenzene constituted the polymer backbone (PEI-II) [cf. Fig. 6(a)]. Additionally, the solvatochromic behavior of the polymers in solvents with a different dielectric constant (ϵ) and consequently with a different polarity, that is, NMP ($\epsilon = 33.0$) and THF ($\epsilon = 7.58$), was studied and presented in Figure 7.

In all cases the positions of azobenzene absorption band of polymers recorded in NMP were changed as compared with that in THF [cf. Fig. 7(a)]. Red shift (about 11–54 nm) of the transition of the azobenzene between azopolymers in THF and in NMP was observed. Taking into consideration the absorption of the polymer with tricyanovinylene moieties and without azobenzene groups (PEI-Ia), the differences in spectra acquired in NMP and THF solutions were significant [cf. Fig. 7(b)]. Absorption

spectral data of studied polymers are summarized in Table III.

The observed solvatochromism, that is, a bathochromic shift of the absorption maximum along with the increase of solvent polarity confirms the charge-transfer character of azobenzene and tricyanovinylene absorption band.

Taking into account the absorption properties of polymers in solid state and in NMP solution, it was found that poly(esterimide) with tricyanovinylene units (PEI-Ia, PEI-Ic, PEI-IIa, and PEI-IIIa) exhibited the same shape of absorption band as in NMP, which was bathochromic shifted in comparison to that in the solution. In the case of polymer films containing only azobenzene groups (PEI-Ib, PEI-II, and PEI-III) one absorption band was observed, while in NMP solution a band with two maxima were

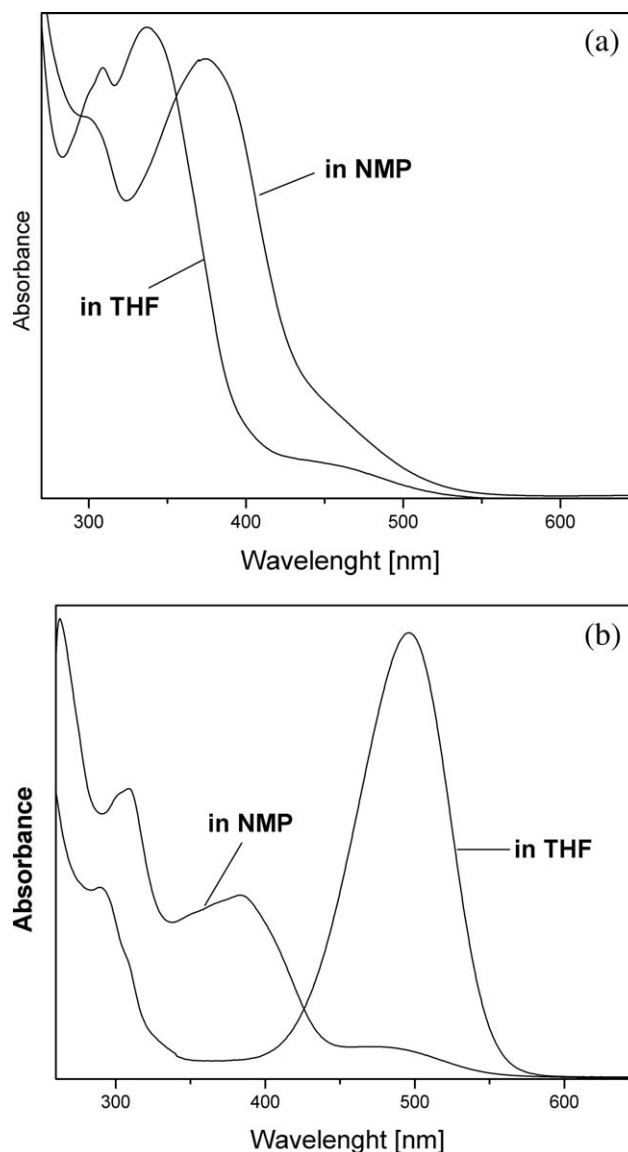


Figure 7 Solvatochromic behavior of chosen polymers in THF and NMP solutions (a) PEI-II (b) PEI-Ia.

TABLE III
Absorption Maxima (λ_{\max}) of the Poly(esterimide)s in Solutions and in Films Deposited onto Glass Slides and Their Refractive Index (n) Values

Polymer code	λ_{\max} [nm]			n
	in NMP	in THF	in film	
PEI-I	263, 307	–	–	–
PEI-Ia	263, 309, 383, 470	290, 497	384, 473	1.90
PEI-Ib	261, 299, 374, 415	249, 298, 361	406	1.87
PEI-Ic	269, 304, 352 ^a , 467	291, 497	390, 488 ^a	1.88
PEI-II	264, 306 ^a , 374, 473 ^a	309, 338	312 ^a , 338, 470 ^a	1.92
PEI-IIa	263, 312, 347, 474 ^a	294, 308, 336, 498	308, 356	1.92
PEI-III	373 ^a , 411	280 ^a , 401	400	1.82
PEI-IIIa	374, 421	250*, 280*, 405	400	1.87

^a The position of absorption band calculated using the second derivatives method (i.e. the minimum of the second derivative of absorption corresponds to the absorption maximum).

detected. Moreover, the absorption maximum in the these polymer films was shifted to higher energy region in comparison to that in the solution (up to 38 nm), indicating possible H-type aggregation of azobenzene chromophores in the film, similarly to what was observed for other azopolymers.^{39–41}

The refractive index (n) of the poly(esterimide)s was estimated (cf. Table III). Several different methods may be used to obtain the refractive index of the polymers. These include transmission and refractive spectroscopy, ellipsometry, grating coupling, and attenuated total reflection measurements.⁴² In this study reflection UV-Vis spectroscopy carried out in the wide wavelength interval in the range of 200–2500 nm was applied. The Kramers-Kronig analysis let to estimate the refractive index in the low-energy region of investigated polymers films.⁴³ Refractive index (n) and extinction coefficient (k) as a function of wavelength for exemplary PEI-III film is presented in Figure 8.

Photoinduced birefringence

The photoinduced birefringence (Δn) measurements were performed for two chosen polymers, that is, PEI-III and PEI-IIIa. The polymer films were placed between two crossed polarizers in the path of a probing laser beam of the wavelength outside the absorption band of the chromophores i.e., 690 nm. A pumping beam of the wavelength in the absorption band, i.e., 450 nm was incident on the sample and introduced the order in the chromophore alignment via the photoisomerization processes. For a maximum resulting change in the transmission signal the polarization of the pump beam was set at 45° with respect to the polarization direction of the probing beam. The probe beam transmission through crossed polarizers was monitored for 40 min from switching on the pumping beam and for 20 min after switching off the beam. The growth and decay of the trans-

mitted signal for the PEI-IIIa film is presented in Figure 9(a).

At the beginning of the experiment the sample was isotropic and without the writing beam no transmission of the probe beam through the system was observed. Switching on the pump light [time A in Fig. 9(a)] induced the sample birefringence. That led to a monotonous increase in probe beam transmission signal, which did not saturate within the time period of the writing process. Switching off the pump beam [time B in Fig. 9(a)] led to a c.a. 20% drop in the detected signal after the 20 min-monitoring. To remove the remaining material anisotropy the sample was exposed again to the pumping light but of circular polarization [time C in Fig. 9(a)]. The conversion of the directionally aligned trans isomers to a state of their random orientations gave an initial zero transmission signal. Similar transmission curve was observed for the PEI-III polymer film. The measured transmittance was used for the determination of the optically induced birefringence knowing

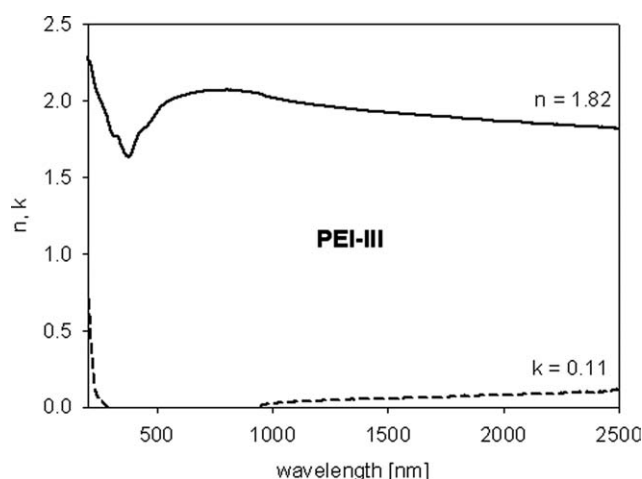


Figure 8 Refractive index (n) and extinction coefficient (k) spectral dependences for the PEI-III polymer film.

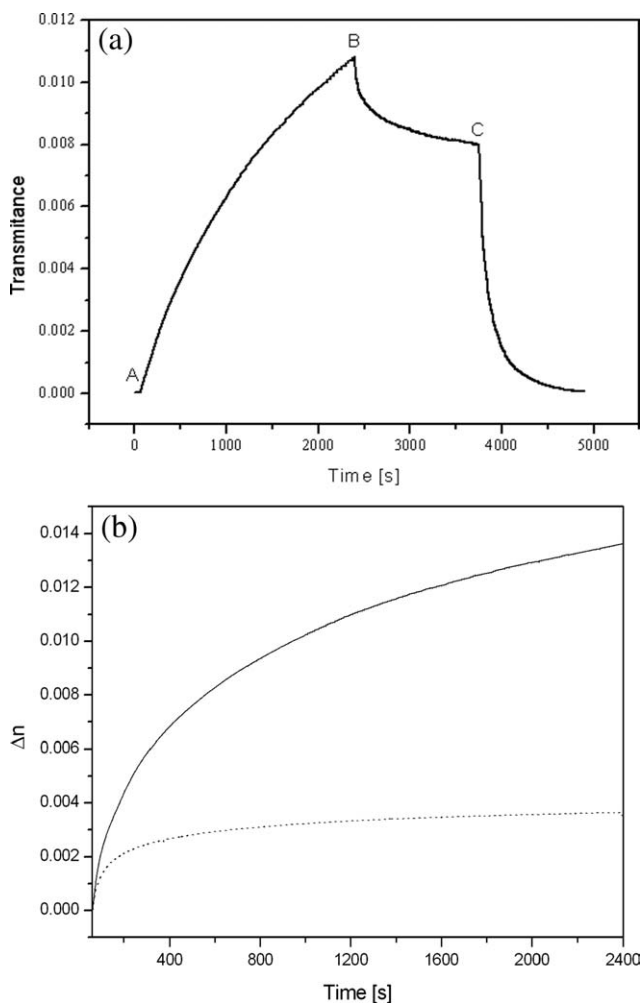


Figure 9 (a) Writing sequence for PEI-IIIa: A-switching on the writing beam, B-switching off the writing beam, C-switching on the circularly polarized writing beam. (b) Birefringence growth as a function of time for the PEI-III (dotted line) and PEI-IIIa (solid line) polymer films.

that $\Delta n = \frac{\lambda}{\pi d} \sin^{-1} \sqrt{T}$, where λ is the writing beam wavelength, d is the film thickness (measured with a stylus profiler), T is the transmittance of the two polarizers setup and Δn is the difference in refractive indices for polarizations parallel and perpendicular to the polarization direction of the pump beam. Figure 9(b) shows the generation of induced birefringence in the PEI-IIIa and the PEI-III films. The optically induced birefringence estimated after 40 min of the writing sequence was of the order of 0.01 and 0.001 for the PEI-IIIa and the PEI-III films, respectively. The influence of polymer chemical structure on optically induced birefringence was observed. The significantly higher value of photoinduced Δn was measured in the case of the poly(esterimide) in which azobenzene units were substituted with strong acceptor, that is, tricyanovinylene groups. It seem to be interesting to compare our results with published data for similar polymer systems. To the

best of our knowledge, only in two articles, apart from our work,³⁰ the light-induced orientation in polyimides with azochromophores has been reported by measurements of photoinduced birefringence.^{44,45} Zlatanova et al.⁴⁴ studied photoinduced birefringence in polyimide doped with azobenzene chromophore, that is, methyl orange. The photoinduced changes in the refractive index were investigated holographically during recording with two linear parallel polarizations (recording: argon (Ar) laser with $\lambda = 488$ nm, $I = 150$ mW/cm²; reading: He-Ne laser with $\lambda = 632.8$ nm). The Δn value about 0.00038 was determined using an analytical expression for the diffraction efficiency during and after turn-off the recording. Natansohn et al.⁴⁵ investigated the polyimide which contained azocarbazole chromophores. They carried out *in situ* birefringence measurements during writing cycles (linearly polarized pump on using an Ar laser with $\lambda = 488$ nm, $I = 100$ mW/cm²), relaxation cycles (pump off), and photoinduced erasing processes (circularly polarized pump on). The birefringence was detected using a weak diode laser beam at 674 nm as a probe. The azocarbazole functionalized polyimide showed high value of birefringence about 0.035. However, as can be notice, the polyimides described in mentioned articles significantly differ from presented in this work. Polymers with much similar chemical structure as studied in this article were subject of our investigations.³⁰ In the series of six polyesterimides with side-chain azobenzene units the obtained photoinduced birefringence was in the range of 0.00026–0.01.³⁰ The birefringence was induced by a doubled-in-frequently cw YAG laser operating at 523 nm and the probe beam with $\lambda = 632.8$ nm read the Δn . The highest vale of Δn exhibited polymer containing cyano-substituted chromophores tethered by alkoxy spacer (—O—(CH₂)₆—O—). The value of photoinduced birefringence obtained for the PEI-IIIa polymer film may be considered high especially for polyimides with covalently bonded azobenzene derivatives.³⁰

CONCLUSIONS

The novel polymers with imide rings and photoisomerizable azobenzene moieties were synthesized and characterized. Chromophore-functionalized polymers exhibited high T_g and a very good solubility. The presence of azobenzene units and an increase in their content in the polymer repeating unit decreased the T_g comparing to the parent polymer, while the introduction of tricyanovinylene groups increased T_g value. The best thermal stability detected by UV-Vis spectroscopy exhibited the polymer in which one of the aromatic cores of the azobenzene moiety was a part of the backbone connected in the 2 and 4 position with imide rings (PEI-II). In polymers with tricyanovinylene

substituents relatively the highest changes in absorption were observed during heating. Nevertheless, all poly(esterimide)s appear to satisfy the demand of high thermal stability required for optical device fabrication. Preliminary birefringence measurements showed the ability of the synthesized polymers to undergo the photoisomerization cycles when exposed to polarized light of a proper wavelength. The advantageous influence of tricyanovinylene moieties on photoinduced birefringence was observed for the polyimides containing two azobenzene chromophores in the polymer unit. A relatively high value, of the order of 0.01, of optically induced birefringence for this kind of polymer was measured. The obtained poly(esterimide)s with push-pull type of chromophores (**PEI-Ic**, **PEI-IIIa**) may constitute the attractive multiproperty materials that possess the photochromic and electrooptic activity.

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