



# Poly(amic acid)s and their poly(amide imide) counterparts containing azobenzene moieties: Characterization, imidization kinetics and photochromic properties



Jolanta Konieczkowska<sup>a, b</sup>, Henryk Janeczek<sup>a</sup>, Anna Kozanecka-Szmigiel<sup>c, \*</sup>,  
Ewa Schab-Balcerzak<sup>a, \*\*</sup>

<sup>a</sup> Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M. Curie-Skłodowska Str., 41-819 Zabrze, Poland

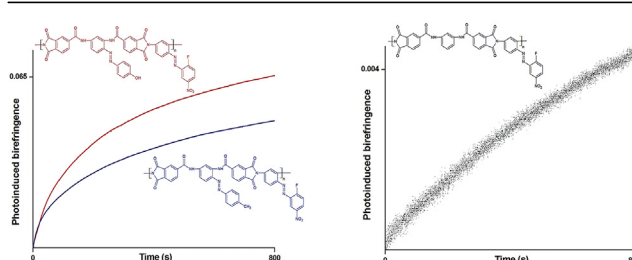
<sup>b</sup> Institute of Chemistry, University of Silesia, 9 Szkolna Str., 40-006 Katowice, Poland

<sup>c</sup> Faculty of Physics, Warsaw University of Technology, 75 Koszykowa Str., 00-662 Warszawa, Poland

## HIGHLIGHTS

- Three azopoly(amide imide)s were obtained from azopoly(amic acid)s.
- Chosen physicochemical properties and photochromic responses were measured.
- Desired optical response was found for polymers with two azo-dyes in repeating unit.
- Structure-property relations were shown.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 10 February 2016

Received in revised form

24 May 2016

Accepted 30 May 2016

Available online 8 June 2016

### Keywords:

Polymers

Optical materials

Chemical synthesis

Differential scanning calorimetry

Optical properties

Thermal properties

## ABSTRACT

We report on a series of novel photochromic poly(amide imide)s and their poly(amic acid) precursors bearing azobenzene chromophores as the side groups. The chemical structures of the polymers were designed so that they exhibited an enhanced thermal stability combined with a large and stable birefringence photogenerated by light of the wavelengths belonging to a wide spectral range. The polymers possessed rigidly attached azochromophores in the content of either one or two per a repeating unit, which in the latter case differed in their structures. The imidization kinetics of the poly(amic acid)s was investigated by differential scanning calorimetry and the kinetic parameters were estimated using Ozawa and Kissinger methods. Measurements of the selected physical properties of the polymers, such as solubility, supramolecular structure, linear absorption, thermal stability, glass transition and photochromic response were performed and used for determination of the structure-property relations. The measurements of photochromic properties showed a very efficient generation of optical anisotropy upon blue and violet irradiation, for both the poly(amide imide)s containing two different chromophores in the repeating unit and for their precursors. For these poly(amide imide)s and for their precursors an exceptionally slow decrease in the photoinduced optical anisotropy in the dark was also observed.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Photochromic azobenzene polymers are scientifically important materials and attractive candidates for various applications in

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [annak@if.pw.edu.pl](mailto:annak@if.pw.edu.pl) (A. Kozanecka-Szmigiel), [eschab-balcerzak@cmpw-pan.edu.pl](mailto:eschab-balcerzak@cmpw-pan.edu.pl) (E. Schab-Balcerzak).

photonics, e.g. as materials for high-density optical data storage and switching, optical waveguides, diffractive elements or liquid crystal alignment layers [1–4]. Large applicational potential of azopolymers arises from their unique photoinduced properties appearing as a result of a reversible *trans-cis-trans* isomerization and subsequent reorientation of the azobenzene moieties induced by the polarized light of a proper wavelength. The linearly polarized light may generate the alignment of azochromophores in the plane perpendicular to the polarization direction of the optical beam. This leads to the local changes of the absorption coefficient ( $\Delta\alpha$ ) and the refractive index ( $\Delta n$ ), the effect known as photoinduced optical anisotropy (POA) or photoinduced dichroism and birefringence [5]. Moreover, *trans-cis-trans* isomerization is responsible for a large-scale mass transport of the polymer chains observed as a sinusoidal modulation of the polymer film illuminated with two interfering laser beams [6,7]. The efficiency and dynamics of the photoinduced phenomena are strongly dependent on the details in the structure of polymer backbone and azochromophore, the type of its linkage to the macromolecules, as well as on the experimental conditions. For that reason, finding the chemical and physical factors influencing the POA is necessary from the viewpoint of designing and developing new materials desired for specific applications.

Polyimides (PI) are a group of polymers exhibiting excellent thermal stability, good mechanical properties and high chemical resistance [8,9]. They are suitable materials for a wide range of applications in electronics, aerospace and automotive industries, medical technologies and optics [8,9]. Azobenzene polyimides comprise important materials for certain applications in photonics due to their high glass transition temperature ( $T_g$ ), which is one of the factors ensuring an enhanced stability of the POA in the dark.

The most common method of polyimide synthesis includes a two-step procedure. In a first step, a poly(amic acid) (PAA) precursor is obtained by a low temperature polycondensation reaction. Subsequently, the imide ring closure (imidization) is performed by chemical or thermal dehydration. In practice, as PAAs exhibit better solubility than PIs, the PAAs are dissolved in solvent, casted onto the base and then thermally converted (250–400 °C) to the PIs in the solid state [10]. The imidization kinetics can be monitored by several techniques such as FTIR spectroscopy, fluorescence, thermogravimetric analysis, UV spectroscopy or differential scanning calorimetry (DSC) [11–15]. The DSC method may be considered as the most powerful one because the thermal conversion of PAA to PI is a highly endothermic process. Knowledge of thermal imidization kinetics of the azopoly(amic acid)s permits controlling the degree of the PAA conversion and avoiding a destruction of some chromophores in this process [16].

This work is a continuation of our effort in the preparation of new photoactive azopolymers and in the systematic studies on complex relationships between the chemical structure and relevant physicochemical properties of azopolyimides including photoinduced optical anisotropy. Such studies are necessary for determination of the polymer application ability, but also they are valuable from a fundamental point of view. The aim of this work was to develop processable azopolymers showing firstly, a high thermal stability and secondly, a large and stable optical anisotropy generated by light of the wavelengths spanning a wide spectral range. Thus, we report on a preparation and characterization of novel azobenzene poly(amide imide)s and their poly(amic acid)s precursors, which differ in a number of the azobenzene derivatives in the polymer repeating units, and in the absorption ability of the chromophores. Our motivation for incorporation of two different azochromophores in the repeating unit was both to extend the absorption band of the prepared azopolymers and to achieve large values of photoinduced birefringence. This approach appears to be

an alternative way for generating the photoinduced anisotropy by the laser beams of various wavelengths than using an azo-dye of specially designed structure [17]. All the investigated polymers possess the 2,4-diamino-2'-fluoro-5'-nitroazobenzene chromophore in their structures, which exhibit a complex absorption spectrum ranging from 320 up to 550 nm [18]. Apart from the physicochemical properties of the polymers we also study the kinetics of imidization of PAAs using the DSC measurements and Ozawa as well as Kissinger methods for analyzing the data [19]. The polymer photochromic properties are determined by photoinduced birefringence measurements and investigated from a point of view of (i) a structure of the polymer main chain, that is either poly(amic acid) or poly(amide imide), (ii) a chromophore number in the repeating unit, (iii) a chromophore structure in the case of the polymers possessing two azo-dyes in the repeating unit.

## 2. Experimental section

### 2.1. Materials

4-aminophenol, *m*-phenylenediamine, *p*-tolidyne, trimellitic anhydride chloride, 4-nitro-fluorobenzene, methanol, *N*-methyl-2-pyrrolidone (NMP) were purchased from Sigma-Aldrich Chemical Co. Chloric acid, sodium nitrate and sodium hydroxide were purchased from POCH.

### 2.2. Measurements

$^1\text{H}$  NMR spectra were carried out on an Avance II 600 MHz Ultra Shield Plus (Bruker) Spectrometer in DMSO- $d_6$  as solvents and TMS as the internal standard. The infrared (IR) spectra of the polymer films were recorded with a Nicolet 6700 FTIR apparatus (Thermo Scientific) using KBr pallets. Elemental analyses were performed using Perkin Elmer Analyzer 2400. The reduced viscosity has been measured in NMP at 25 °C with an Ubbelohde viscometer. UV–Vis absorption spectra in NMP (solution  $10^{-5}$  mol l $^{-1}$ ) and polymer film were recorded in solution using a PerkinElmer Lambda Bio 40 UV–Vis. The X-ray diffraction pattern of solid samples were recorded using CuK $\alpha$  radiation on a wide-angle HZG-4 diffractometer (Carl Zeiss Jena) working in the typical Bragg geometry. Differential scanning calorimetry was performed with a TA-DSC 2010 apparatus (TA Instruments, Newcastle, DE, USA). For DSC analysis, small amounts (~5 mg) of poly(amic acid) were loaded into aluminum sample pans. The DSC scans were taken in a temperature range from 90 °C to 300 °C at the heating rates of 2.5, 5, 10, 20, and 30 °C min $^{-1}$  under nitrogen flow of 50 ml min $^{-1}$ . An empty cell was used as the reference. The instrument was calibrated with high purity indium. The glass transition temperature was determined as the midpoint of the increase of the specific heat associated with the transition. The DSC measurements for the obtained amorphous polyimides were taken at a heating rate of 20 °C min $^{-1}$ . Thermogravimetric analysis (TGA) was performed using pre-calibrated TA Instruments SDT Q600 analyzer operating under high-purity argon purge-flow of 100 ml/min. Samples were placed inside open alumina pans and the measurements were carried out in 10° min $^{-1}$  constant heating rate conditions. Prior to the TGA measurements the poly(amide imide)s have been dried at 120 °C for 20 min in argon to remove water. The birefringence in the polymer films was induced using the excitation beams at 405 and 445 nm from diode lasers. The generated birefringence was probed by a second weaker and smaller in diameter 690-nm beam. The transmission of the probing beam through the sample placed between two crossed polarizers was detected by a silicon photodetector and measured using a lock-in amplifier [20]. For a maximum resulting change in the transmission signal the polarization of the

Download English Version:

<https://daneshyari.com/en/article/1520528>

Download Persian Version:

<https://daneshyari.com/article/1520528>

[Daneshyari.com](https://daneshyari.com)