СИНТЕЗ ПОЛІМЕРІВ

POLYMER SYNTHESIS

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AROMATIC POLYMER HAVING BOTH AZOBENZENE AND AZOMETHINE UNITS IN THE MAIN CHAIN AS AN EFFICIENT PHOTO-RESPONSIVE MATERIAL

Azobenzene and aromatic azomethine groups acting as versatile photoreversible optically switchable scaffolds attract much interest as efficient building blocks for the construction of light-responsive materials. The pronounced interest in light-sensitive polymers originates from their unique ability to become anisotropic after irradiation by polarized light. Despite the significant progress that has been made on the synthesis of either polyazobenzenes or polyazomethines, numerous challenges remain, and they have become the catalyst for the ongoing research. The polymer having both azobenzene and azomethine groups are fundamentally less developed. In this work, a strategy to the synthesis of the light-responsive polymer with azobenzene and azomethine units in the backbone is proposed. The polymer is prepared by condensation polymerization of octafluorobiphenylene-based bis-hydroxybenzaldehyde with aromatic meta-linked octafluorobiphenylene-based diamine. The structure of the polymer is characterized by Fourier transform infrared spectroscopy. The synthesized polymer can be solution-cast into flexible solid films with a tensile strength of 25 MPa. Furthermore, the polymer displays elevated glass transition temperatures (T_g), reaching 235 °C, and demonstrates an admirable thermal stability, retaining resilience at

temperatures up to 390 °C. The polymer film underwent photoisomerization and exhibited changes in light-induced birefringence when exposed to 365 nm UV light and both polarized and unpolarized blue (405 nm) and green (532 nm) light. The ability to record optical information using polymer films in the form of diffraction gratings is demonstrated.

Keywords: azobenzene, polyazomethine, photoisomerization, light-responsive material, photoinduced birefringence.

Introduction

The introduction of photoswitchable units, including azobenzene and azomethine groups, is a widely adopted strategy to create the light-sensitive polymer systems with a broad spectrum of applications [1–4]. Azobenzene-based photochromic molecules undergo significant geometrical changes through photoisomerization, inducing optical anisotropy under polarized light irradiation [5–8]. This property has made them a focus in the development of various materials, including both low molecular weight switchers and emerging polymer materials [9–12]. Aromatic azomethine-based fragments, similar to azobenzene, display photoinduced molecular reorientation perpendicular to incident light polarization. Upon UV exposure, they undergo *trans-cis* photoisomerization. However, the *cis* form generated by azomethine is less stable than that of azobenzene, swiftly reverting to its original form [13–15]. This characteristic is beneficial for rapid-state reversion in applications like pump devices or Braille display systems [16]. Hence, significant attention is being directed towards advancing polymer systems that concurrently contain azobenzene and azomethine groups [2]. Challenges such as insufficient solubility, low molecular weight, and the complexities involved in achieving mechanically stable free-standing films from polymers having chromophores throughout the backbone hinder the practical application of these polymers. As a result, endeavors in creating new azo-azomethine polymers primarily focus on enhancing solubility and mechanical attributes while preserving their beneficial characteristics [2].

Previously, we synthesized polymers with azobenzene and azomethine fragments in the main chain using fluorinated *bis*-hydroxybenzaldehydes and hexamethylenediamine [17, 18]. These polymers showed promising potential as light-sensitive polymers for creation of polarization holograms and various liquid crystal device fabrications. However, an increased presence of aliphatic units in the obtained polymers led to a natural deterioration of their thermal stability and shortening of the π-conjugation chain length. In this study, an approach is employed to enhance the solubility and mechanical characteristics of fully aromatic polymers containing both azobenzene and azomethine fragments by controlling their configuration and conformation. Specifically, we increased the content of both fluorinated electron-withdrawing non-coplanar biphenylene and *meta*-oxyphenylene fragments in the polymer structure. Our prior research demonstrated that these fragments enhance solubility and thermal stability, increase molecular weight, and facilitate film-forming characteristics [17, 19]. Notably, the introduction of a hydroxyl group at the *ortho* position to the azomethine unit results in the formation of N-salicylideneaniline scaffold, capable of self-isomerization through excited state intramolecular proton transfer (ESIPT) [20, 21].

Here, we report on the synthesis of novel aromatic polymer with azobenzene and OH-functionalized aromatic azomethine-based units as well as with perfluorinated biphenylene and *meta*-oxyphenylene moieties in the backbone. The polymer's thermal, physical, and mechanical properties, along with its peculiarities in photooptical behavior and photoinduced birefringence, are demonstrated.

Experimental section

Materials. Fluorinated monomeric aldehyde **1** and diamine **2** were prepared according to the earlier described procedure [22]. The other reagents and solvents were purified routinely.

Synthesis of azo-azomethine polymer (AA-polymer). Monomer **1** (0.300 g, 0.385 mmol), diamine **2** (0.193 g, 0.376 mmol), and 2.3 ml of dimethylacetamide (DMAc) were added into a three-necked flask. The monomer ratio was 0.977, with a concentration of 20 wt. %. The mixture, in the presence of a catalytic amount of trifluoroacetic acid (TFA), was heated to 120 °C and stirred at this temperature for 24 hours. Subsequently, the reaction mixture was quenched with methanol,
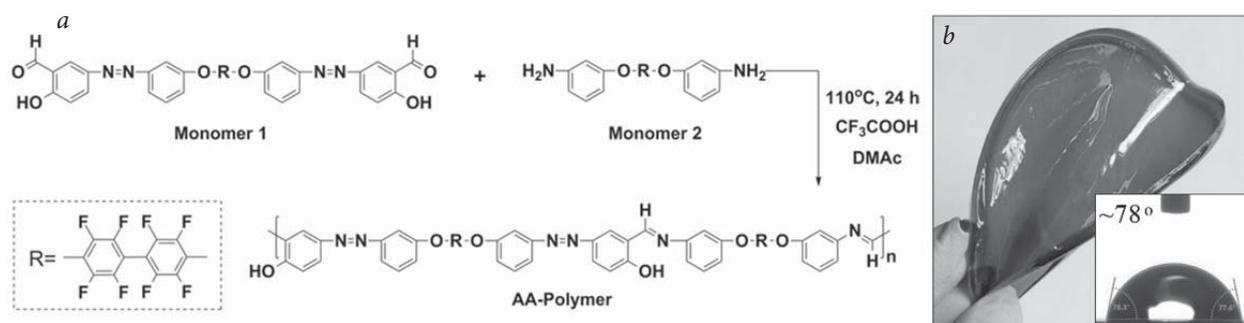
Figure 1. Scheme of AA-Polymer synthesis (*a*). Optical image of a self-supporting AA-Polymer film (*b*); the inset is the contact angle of a water droplet on the surface of the prepared film

and the resulting solid was collected by filtration. The polymer was purified by reprecipitation from a DMAc solution into methanol and then subjected to drying in a vacuum oven at 60 °C overnight. Yield: 95 %. FTIR: 3600–3250 cm^{-1} (OH), 3100–2850 cm^{-1} (C-H), 1660 cm^{-1} (CHO, end-group stretching), 1624 cm^{-1} (CH=N), 1599 cm^{-1}, 1487 cm^{-1} (C=C, arom.), 1223 cm^{-1} (C–O–C), 1001 cm^{-1}, 980 cm^{-1} (C–F). UV-vis spectrum (DMAc): λ_{max1} = 350 nm, λ_{max2} = 460 nm.

Characterization. Polymer films for analysis were prepared by casting from a DMAc solution (0.25 mg/mL) onto Teflon or glass substrates. Fourier transform infrared (FTIR) spectra (4000–400 cm^{-1}) of the synthesized compounds were recorded on a TENSOR 37 spectrometer in KBr pellets. The UV-vis spectra were recorded on a Shimadzu UV-2450 spectrophotometer. For solid-state photoisomerization, the resulting polymer film underwent UV irradiation at a distance of 4 cm. Back-isomerization under visible light occurred at a distance of 2.5 cm, utilizing a compact deuterium lamp with an intensity ranging from 30 to 52 mW. Tensile strengths were measured using a 2166 P-5 tensile-testing machine with a stretching speed of 50 mm/min. DSC analyses were conducted on a TA Q200 instrument, covering the temperature range of 0 to 250 °C with a heating rate of 20 °C/min under an air atmosphere. Thermo-oxidative destruction of the polymer was investigated through thermal gravimetric analysis (TGA) using a TA Instruments Q-50 apparatus (USA) in air, applying a heating rate of 20 °C/min from 20 to 700 °C.

Photoinduced birefringence measurements (film thickness ~80 μm) were conducted using an optical setup detailed in [17, 23]. The polymer film, irradiated with polarized light from an Ar laser (λ = 532 nm, 50 mW), was placed between crossed polarizers for a He-Ne laser (λ=628 nm, 5 mW) as a probe beam. Changes in birefringence during irradiation were monitored over time. Additionally, to investigate the wavelength dependency of birefringence change in the AA-Polymer film, the polymer was exposed to both polarized and non-polarized light from λ=532 nm (green) and λ=405 nm (blue) lasers, along with a neutral
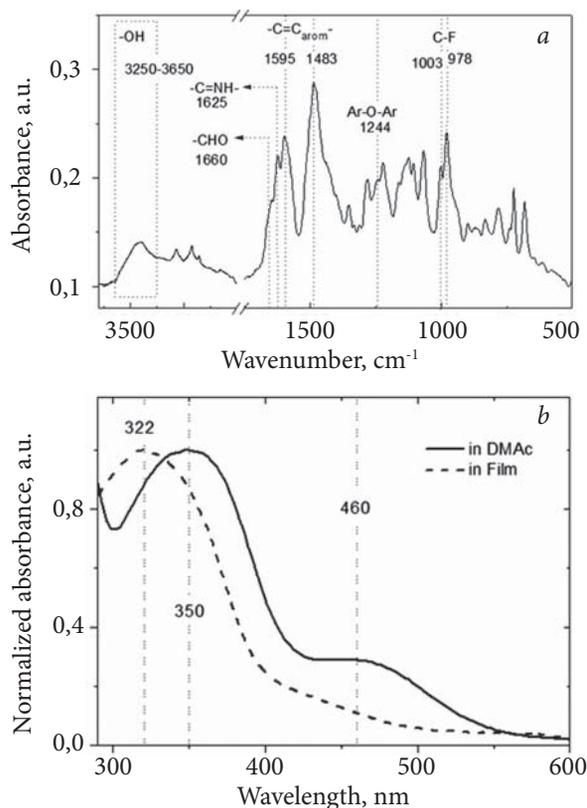

Figure 2. FTIR spectrum of AA-Polymer (*a*). UV-vis absorbance spectra of AA-Polymer in DMAc (about 0.006 mg/mL) and solid film (*b*)

red (test) beam from a Ne-Ne laser. The diffraction gratings were formed by two spatially modulated Ar laser with P ≤ 10 mW at 532 nm with two linear p-polarizations. The recording of the polarized gratings was performed using experimental scheme represented in [17].

Results and discussion

The desired new aromatic azo-azomethine polymer (AA-polymer) was synthesized by polycondensation reaction from azo-containing octafluorobiphenylene-based dialdehyde (**1**) and *meta*-linked diamine (**2**) in DMAc using a catalytic amount of TFA (Figure 1*a*). The resulting polymer should be classified as polyazomethine, as the polymer chain extends through the formation of an azomethine linkage.

Figure 3. UV-vis spectra of AA-Polymer at various concentrations (from 0.0150 to 0.003 mg/mL) in DMAc (*a*). Trans-cis photoisomerization of AA-Polymer in thin film (λ=370 nm, LED with 3.4 mW power) (*b*)

The polymer is insoluble in dimethyl sulfoxide, tetrahydrofuran, chloroform and the most of other organic solvents. The AA-Polymer polymer exhibits complete solubility in DMAc and N-methylpyrrolidone, and was successfully cast into a flexible solid film (stress at break: 25 MPa; elongation at break: 5%; Young modulus: 0.58 GPa) using solution-casting technique (Fig. 1*b*). The water contact angle (WCA) value for the AA-Polymer film was ca. 78°. The good film-forming ability of AA-Polymer indicates that its molecular weight is reasonably high.

According to the FTIR spectrum of AA-polymer in Fig. 2*a*, the appearance of the absorption band at 1625 cm^{-1} indicates formation of –CH=N– linkages in polymer.

The Ar–OH bands are located in the range 3200–3600 cm^{-1} while the peak at 1244 cm^{-1} is due to the vibrations of the aromatic ether linkage. Additionally, the FTIR spectrum shows peaks which correspond to C–F, C=C$_{arom}$, and CH groups (Fig. 2*a* and see Experimental part).

An absorption band (in DMAc solution) related to the $\pi{\rightarrow}\pi^*$ transitions of the azo-azomethine chromophore system appears at λ_{max1}=350 in the UV-vis spectrum of AA-Polymer (Fig. 2*b*). A very broad band observed in the visible region at 440–530 nm (λ_{max2} at about 460 nm) can be assigned to the $n{\rightarrow}\pi^*$ transitions, intramolecular charge transfer interaction involving the conjugated azo-azomethine blocks and hydrogen-bonded complexes of the obtained polymers with the highly polar aprotic solvent such as DMAc [17, 24]. At the same time, the strong π-π^* transition band for AA-Polymer in solid state is slightly broadened and is about 25 nm blue-shifted compared to solution spectra. Note, that AA-Polymer in solid state possesses overlapped π-π^* and n-π^* transitions resulting in a single absorbance peak at around 322 nm (Fig. 2*b*). This behavior is typical due to the aggregation of chromophore molecules (namely H-aggregates) [25].

The UV absorption maximum slightly shifted bathochromically when reducing the concentration of AA-Polymer in a solution due to the stronger interaction of the solvent with polymers and, therefore, the equilibrium shift towards hydrogen-bonded complex (Fig. 3*a*).

The capacity of azobenzene-based compounds to undergo photoisomerization serves as an effective tool for controlling their properties. The
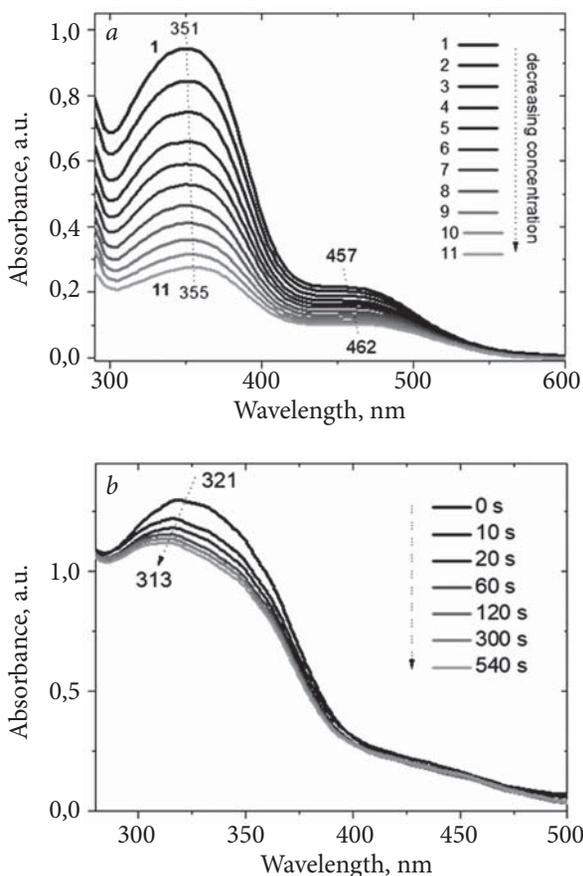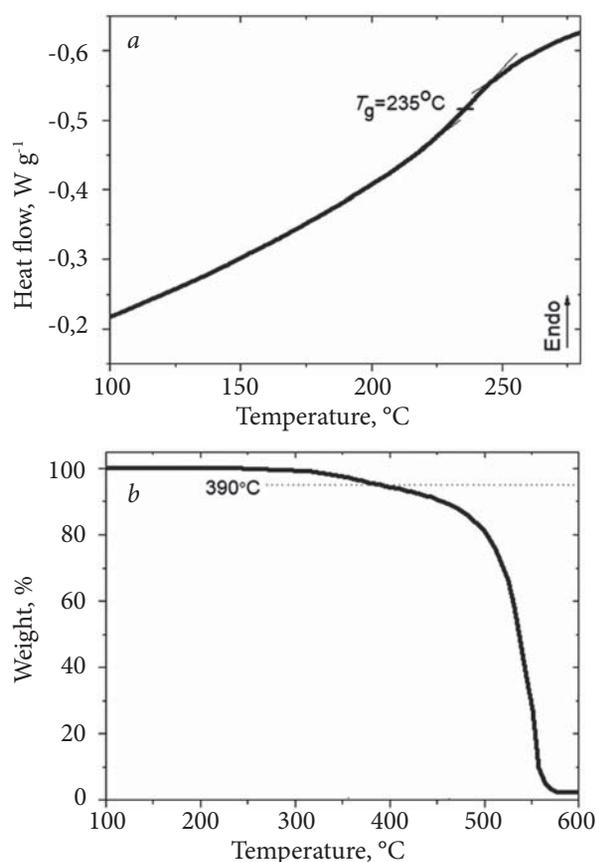
Figure 4. DSC second heating cycle of AA-Polymer sample (20 °C/min; air atmosphere) (*a*). TGA trace of AA-Polymer sample in an air atmosphere (heating rate 20 °C/min with a temperature from 0 to 700 °C) (*b*)
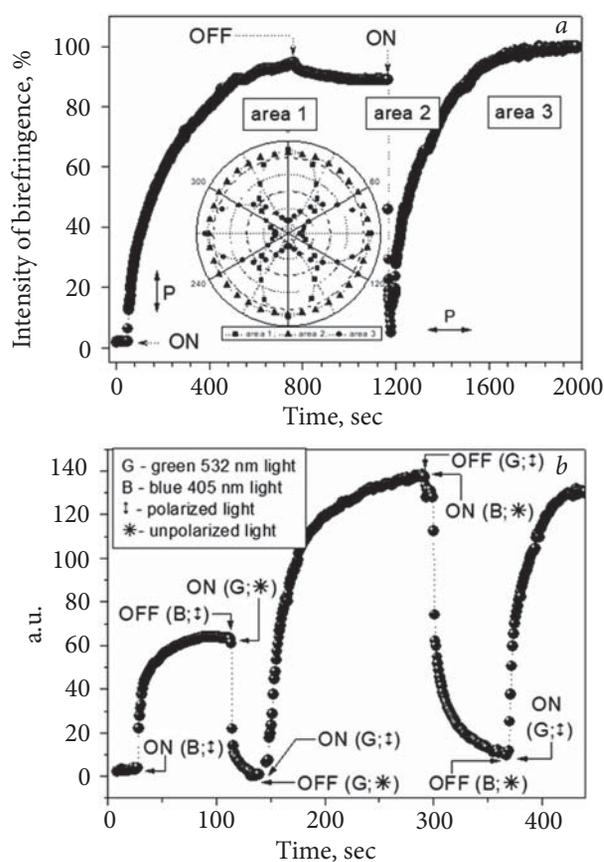

Figure 5. Changes in the birefringence within the AA-Polymer film sample over time under Ar laser irradiation (λ=532 nm, P = 50 mW). Linearly polarized light was activated (ON,↕*P* – vertical polarization), then deactivated (OFF); subsequently, irradiation was initiated while rotating the light polarization by 90 degrees (ON, ↔*P* – horizontal polarization). The directions of the irradiating polarization P and the alteration in absorption dichroism (in polar coordinates) are depicted schematically in the inset (*a*). Photoinduced refractive index changes of AA-Polymer film (at the same point) when irradiated with polarized/non-polarized blue (λ=405 nm, P = 5 mW) and polarized/ non-polarized green light (λ=532 nm, P = 10 mW) lasers in varying sequences of exposure (*b*)

trans-cis transition of AA-Polymer in the DMAc solution was not detected. However, *trans-cis* photoisomerization in the AA-Polymer film occurred upon exposure to UV light (Fig. 3*b*). A photostationary state for the AA-Polymer film was reached after approximately 540 s of UV irradiation. Importantly, cis-trans back-isomerization could be achieved within several minutes by exposing the samples to white light.

The thermal properties of the AA-Polymer were studied through DSC and TGA analyses. The polymer exhibited a glass transition (T_g) at 235 °C and it had a glass transition region value (ΔT_g) of approximately 20 °C (Fig. 4*a*). The TGA experiment demonstrated excellent thermal stability of the polymer, as shown in Fig. 4*b*. The synthesized AA-Polymer displayed a two-step decomposition process, with minimal weight loss up to around 350 °C. The first decomposition step, occurring between 350 and 400 °C, is attributed to the thermal breakdown of azo bonds. The second degradation

stage (from 400 to 560 °C) is likely associated with the decomposition of other structural units of polymer chains, such as azomethine and ether bonds, aromatic fragments, and so on. The temperature at which the studied polymer experienced a 5 % weight loss ($T_{5\%}$) was determined to be 390 °C.

The TGA results of the AA-Polymer revealed a significantly higher $T_{5\%}$ value compared to the azo-containing polyazomethine derived from monomer **1** and aliphatic 1,6-hexamethylenediamine ($T_{5\%}$ approximately 300 °C) [18].
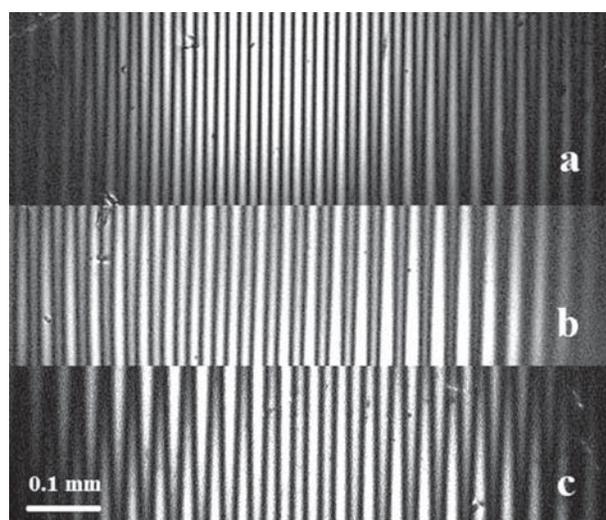
Figure 6. Photo of diffraction gratings in a polarizing microscope: grating period 30 μm (*a*); 40 μm (*b*) and 50 μm (*c*)

Light-Induced Birefringence and Diffraction Gratings. Optically induced birefringence was investigated by irradiation of the polymer film to a linearly polarized laser beam at 532 nm (50 mW). The typical behavior of the photoinduced birefringence in AA-Polymer is represented in Fig. 5a. The polymer sample was initially optically isotropic and no transmission of the probe beam through the crossed polarizers was observed. When the polarized light (532 nm) was turned on, birefringence (Δn) was induced and the transmission increased with time until a maximum level was reached. The direction of the birefringence follows the polarization of the irradiated light. The process can be repeated a number of times with the same almost 100 % effectiveness. At room temperature and in the absence of illumination, the photoinduced birefringence diminished rapidly. However, its absolute relaxed value remains above 90 % of the saturated value. The significant residual anisotropy in the acquired polymer is attributed to strong intermolecular interactions among macromolecules [26], which contribute to the stabilization of the alignment states of azobenzene and azomethine fragments similar to findings in our previous studies [17, 18]. Importantly, the induced anisotropy has been observed to be stable for several months.

Photoinduced birefringence in amorphous polymers can be erased using techniques such as applying circularly polarized light or changing

the polarization direction of the radiation by 90° [27]. We observed a phenomenon where shifting the polarization direction of the radiation caused changes in birefringence, called rewriting, confirming anisotropy changes in the film. The direction of photoinduced anisotropy in the AA-Polymer film is perpendicular to the direction of irradiation polarization, which is confirmed by the angular dependence of the absorption of polarized light (Fig. 5*a*, inset). Moreover, it was demonstrated that the birefringence signal could be reversibly modulated by irradiating the polymer at a specific point with a linearly polarized laser beam at both 405 nm and 532 nm wavelengths (Fig. 5*b*). The polymer is more responsive to the latter light source, although non-polarized light at a 405 nm wavelength can also eliminate birefringence as effectively as a change in the polarization direction.

The AA-Polymer sample was utilized in the recording of diffraction gratings [28] with periods of approximately 30, 40, and 50 μm. Photomicrographs of the resulting gratings, captured using a polarizing microscope, are illustrated in Fig. 6. These gratings were generated through the two-beam irradiation of the AA-Polymer film by a spatially modulated Ar laser ($\lambda = 532$ nm, $P \leq 10$ mW) employing two linear p-polarizations.

Upon considering the beam intensities associated with the zero I_0 and $I_{\pm 1}$ orders, the diffraction efficiency within the Raman-Nath approximation [29] for AA-Polymer is estimated to be around $\eta \sim 1.9\%$. These encouraging results in the context of diffraction gratings suggest promising prospects for subsequent applications [30, 31].

Conclusion

A synthetic route for new *meta*-linked aromatic polymer having both azobenzene and azomethine groups as well as mono- and biphenylene perfluorinated aromatic units via a simple acid-catalyzed polycondensation of fluorinated *bis*-hydroxybenzaldehydes with *meta*-linked OFB-based diamine was developed. The obtained azobenzene-based polyazomethine AA-Polymer exhibited good solubility in DMAc and ability to form mechanically stable free-standing films in which *trans-cis* photoisomerization of azo/azomethine groups occurs under UV irradiation. The DSC and TGA measurements indicated the amorphous nature of the polymers, high glass transition temperature value

(T_g =235 °C), and remarkable thermal stability in air (up to 350 °C). It was found that after the irradiation by the polarized light the resulting polymers acquired time stable anisotropic properties due to the alignment both azobenzene and azomethine structural units inserted within the polymer chains. Importantly, the reversible birefringence switch was achieved upon alternating photoirradiation at 405 nm and 532 nm (polarized and non-polarized). Additionally, effective diffraction gratings were successfully inscribed into the surface of AA-Polymer film. Optical control of anisotropy in materials is highly advantageous for many technological applications, including real-time modulation of light signals in photonic switches, imaging systems, and sensor

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АРОМАТИЧНИЙ ПОЛІМЕР З АЗОБЕНЗОЛЬНИМИ ТА АЗОМЕТИНОВИМИ ФРАГМЕНТАМИ В ОСНОВНОМУ ЛАНЦЮЗІ ЯК ЕФЕКТИВНИЙ СВІТЛОЧУТЛИВИЙ МАТЕРІАЛ

Азобензольні та ароматичні азометинові групи, що діють як універсальні оптично перемикальні структури, викликають великий інтерес як ефективні будівельні блоки для створення світлочутливих матеріалів. Це зумовлено їхньою унікальною здатністю ставати анізотропними після опромінення поляризованим світлом. Незважаючи на значний прогрес у синтезі поліазобензолів і поліазометинів, залишається багато проблем, вирішення яких і стало основним завданням поточних досліджень. Так, полімери, які одночасно поєднують азобензольні та азометинові групи у своїй структурі, майже не досліджені. Запропоновано стратегію синтезу світлочутливого полімеру з азобензольними та азометиновими фрагментами в основному полімерному ланцюзі. Полімер отримано поліконденсацією октафторбіфеніленвмісних біс-гідроксибензальдегіду з ароматичним мета-похідним діаміном. Структура полімеру охарактеризована методом ІЧ-спектроскопії. Синтезований полімер може бути відлитий з розчину у гнучкі тверді плівки з межею міцності на розрив близько 25 МПа. Крім того, полімер має високу температуру склування, яка досягає 235 °C, і демонструє чудову термічну стабільність (5 %-ова втрата ваги спостерігається за температури близько 390 °C). В отриманій полімерній плівці реалізуються зворотні *цис-транс-цис* ізомеризаційні переходи хромофорів і здатність до фотоіндукованого двопроменезаломлення під впливом ультрафіолетового світла за довжини хвилі 365 нм, а також поляризованого і неполяризованого синього (405 нм) і зеленого (532 нм) світла. Продемонстровано можливість запису оптичної інформації з використанням отриманих полімерних плівок у вигляді дифракційних ґраток.

Ключові слова: азобензол, поліазометини, фотоізомеризація, світлочутливий матеріал, фотоіндуковане двопроменезаломлення.