

New copolyhydrazides with anthrazoline fragments in the main chain: synthesis and optical properties

Mikhail Ya. Goikhman¹, Irina A. Valieva^{*1}, Nairi L. Loretsyan¹, Irina V. Podeshvo¹, Iosif V. Gofman¹, Ruslan Yu. Smyslov^{1,2}, Larissa S. Litvinova¹, Natalia V. Tsvigun³, Alexander V. Yakimansky¹

¹ Institute of Macromolecular Compounds of the Russian Academy of Sciences, Saint-Peterburg, Russian Federation

² Petersburg Nuclear Physics Institute NRC KI, PNPI, 1, Gatchina, Leningrad Region, Russian Federation

³ FSRC "Crystallography and Photonics" RAS, Moscow, Russian Federation

* Corresponding author. E-mail: valieva@hq.macro.ru

Abstract

A number of new 2,8-diphenylpyrido[3,2-g]quinoline-4,6-dicarbohydrazides were synthesized and copolyhydrazides based on them were obtained. The molecular weight, thermal, stress-strain and optical properties were investigated. It was shown that all polymer films exhibit significant luminescence in the 450-650 nm region, the profile and intensity of which depend on the nature and position of substituents in the phenylene fragment.

KEYWORDS: anthrazoline, copolyhydrazides, polycondensation, luminescence, structureproperties relationships

1 | INTRODUCTION

A promising direction in the field of the synthesis of optically active polymers is the design of new organic materials that combine the technological advantages of polymers, namely, strength, heat resistance, the possibility of creating self-supporting films, with a number of valuable characteristics of optically active low-molecular compounds, such as luminescence, photoconductivity, and others. It should be taken into account that in order to successfully solve the problems posed, it is necessary, first of all, to develop a synthetic method that would make it possible to easily vary the structure of an optically active monomer and, as a consequence, a polymer repeat unit, allowing one to tune finely the polymer characteristics to desired properties.

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/bio.4131

This possibility is provided by monomers based on nitrogen-containing heterocyclic compounds, in particular 1,9-anthrazoline. It was previously shown that the luminescent properties of copolyamides with anthrazoline units in the main chain could be effectively controlled by changing the nature and position of substituents in the optically active anthrazoline fragment [1, 2]. As is known from the literature [3], the closer a substituent is to the nitrogen atom in the anthrazoline ring, the stronger the chemical structure of the latter affects the aromaticity of the system and, as a consequence, the optical properties. In this regard, it seemed interesting to study the luminescence characteristics of solutions and films of polymers in which substituents are located in phenylene groups located at positions 2 and 8 of the anthrazoline ring. Such an opportunity is provided by polyhydrazides, which, as is known [4-6], are widely used as basic materials for creating luminescent systems.

2 | EXPERIMENTAL

2.1 | Materials

Chloral hydrate, hydroxylamine hydrochloride, *m*-phenylenediamine hydrochloride, sodium sulfate, sulfuric acid, acetophenone, 1-(*p*-tolyl)ethanone, 1-(2,4-dimethylphenyl)ethanone, 1-(4-methoxyphenyl)ethanone, potassium hydroxide, ethanol, diethyl ether, hydrazine hydrate, *N*-methylpyrrolidone, propylene oxide, 4,4'-diaminodiphenyl ether, terephthaloyl chloride, thionyl chloride, vanillic acid were purchased from Sigma-Aldrich (St Louis, MO, USA) and used without additional purification.

2.2 | Physicochemical characterization

¹H NMR spectra of the synthesized compounds were registered on an «Avance-400» spectrometer («Bruker», Germany) with the working frequency 400 MHz, using Me_6Si_2 as the internal standard, in DMSO-d₆ solutions with the concentration of 1 %.

The elemental analysis was performed on a Hewlett Packard 185B Carbon Hydrogen Nitrogen Analyzer device.

The X-ray diffraction study of the polymers was carried out on a Rigaku SmartLab3 diffractometer equipped with an X-ray tube with a copper anode and a DteX/250(H) semiconducting 1D detector. All diffraction patterns were recorded upon the following conditions: the X-ray irradiation wavelength λ (Cuk_{α}) = 1,54056Å; accelerating voltage and current 40 kV and 30 mA, respectively; the diffraction angle range: $2\theta = 5-80^{\circ}$; scanning step: 0.01°; scanning rate: 2 °/мин. The phase analysis was performed by comparing the experimental diffraction patterns with etalon patterns of the substances from ICSD (2015-2), PDF-2 and AMCSD databases.

Molecular weights (MW) of copolymers were determined by HPLC on an Agilent Technologies 1260 Infinity chromatograph (The Agilent 1260 Infinity Multi-Detector GPC/SEC System) equipped with three detectors: refractometric detector (DRI, wavelength 660 nm, calibration by PMMA standards, viscosimetric detector (VS, universal calibration by PMMA standards), and light scattering detector (LS: Rayleigh scattering angles 15° and 90°; Laser wavelength/power 660 nm/50 mW). The temperature of all detectors was 40°C. A set of successively connected chromatographic columns was used: PLgel 5 μ m Guard 50×7.5 mm precolumn and two Agilent Technologies PLgel 5 μ m MIXED-C, 300×7.5 mm styragel columns. The columns were thermostated at 50°C. The mobile phase: 0.1M LiBr solution in DMF. The mobile phase elution rate was 1.0 mL/min. Samples were introduced by means of an autosampler with the probe volume of 100 μ L.

To study the mechanical, thermal and optical properties of copolyhydrazides, 10% solutions of copolymers in N-methylpyrrolidone were prepared and filtered on a Schott filter. Films were cast from the obtained polymer solutions on glass substrates, which were dried at 100 $^{\circ}$ C to constant weight. The thickness of the films is 30–50 μ m.

Mechanical tests of the films in the uniaxial tension mode were carried out using a AG-100kNX Plus universal test system (Shimadzu, Japan). In the process of testing, the Young's modulus E, yield stress σ_y , ultimate stress σ_b and deformation at break ε_b were determined. The specified characteristics were obtained by averaging the results of tests of seven fragments of the material.

The glass transition and flow temperatures, T_g and T_f , respectively, were determined by the thermomechanical method using a TMA 402 F1 Hyperion vertical dilatometer (NETZSCH Gerätebau GmbH, Germany) in the mode of uniaxial stretching of films under the action of a constant tensile load of 0.2 MPa while heating the sample at a constant rate of 5 °C/min. During the test, the deformation of the sample was recorded and the values of the characteristic temperatures were determined as the changes in the slope of the deformation-temperature dependence (a sharp increase in the polymer compliance). Sample dimensions were as follows: length of the working part 5 mm, width 2 mm.

Thermal stability of the films was determined on a DTG-60 thermal analyzer (Shimadzu, Japan). The samples of ~ 5 mg were heated in air with a rate as high as 5 °C/min. In these tests the thermal stability indices τ_5 and τ_{10} were determined (the temperature values at which a polymer or a composite loses 5% and 10% of its initial weight, respectively, due to the thermal destruction processes).

The absorption spectra of copolymer solutions in N-methylpyrrolidone with a concentration of 0.6194 g/L were recorded on an SF-256 UVI spectrophotometer for the ultraviolet, visible,

and near infrared spectral regions (LOMO, Photonics) in a scanning mode with a step of 0.5 nm at a rate of 100 nm/min and with an automatic changing the spectral gap. The luminescence spectra of solutions and films of copolyhydrazides were recorded on an LS-100 BASE luminescence spectrophotometer (PTI Lasers Inc., Canada) in the wavelength range of 400–700 nm. The reciprocal linear dispersion of the instrument's diffraction gratings is 4 nm/mm. The geometric width of the slits at the output of the excitation monochromator is 1 mm or 1.5 mm, and at the input of the fluorescence monochromator, 1 mm. Comparison of the luminescence intensity (I_{lum}) of the samples was carried out relative to the laboratory standard and expressed in relative units (rel. units). The amplification of the photomultiplier was set to 700 (luminescence spectra of polymer solutions) and 800 (luminescence spectra of polymer films).

2.3 | Synthesis

2.3.1 | Monomer synthesis

The synthesis of 2H,3H,5H,6H-benzo[1,2-b:5,4-b']dipyrrole-2,3,5,6-tetraone (bis-isatin) was carried out according to the procedure described in [1].

2.3.1.1 | Synthesis of 2,8-diphenylpyrido[3,2-g]quinoline-4,6-dicarboxylic acid (2a)

A solution of 2.57 g (0.046 mol) of potassium hydroxide in 5 ml of water was placed in a 250-ml single-necked round-bottom flask equipped with a reflux condenser, then 1.5 g (0.007 mol) of bis-isatin was added, stirred at room temperature until complete dissolution, 3.36 g (0.028 mol) acetophenone, 15 ml of ethyl alcohol was introduced and heated to boiling. The mixture was boiled for 16 h, ethanol was evaporated. The mixture was cooled to room temperature and extracted twice with diethyl ether. The aqueous layer was heated at 40°C until traces of ether were completely removed, acidified with hydrochloric acid solution to pH = 5. The formed precipitate was filtered off, washed with water until neutral, and dried in air. Yield 2.54 g (87%).

¹H NMR (DMSO-d₆), δ (ppm): 7.63 (6H, m, C_{Ar}H); 8.42 (4H, d, *J*=8.3 Hz, C_{Ar}H); 8.46 (2H, s, C_{Ar}H); 8.90 (1H, s, C_{Ar}H); 10.13 (1H, s, C_{Ar}H).

Similarly, the following dicarboxylic acids were synthesized:

2,8-di-p-tolylpyrido[3,2-g] quinoline-4,6-dicarboxylic acid (2b):

yield 2.66 g (85%);

¹H NMR (DMSO-d₆), δ (ppm): 2.42 (6H, s, CH₃); 7.44 (4H, d, *J*=8.1 Hz, C_{Ar}H); 8.32 (4H, d, *J*=8.1 Hz, C_{Ar}H); 8.37 (2H, s, C_{Ar}H); 8.82 (1H, s, C_{Ar}H); 10.08 (1H, s, C_{Ar}H).

2,8-bis(2,4-dimethylphenyl)pyrido[3,2-g]quinoline-4,6-dicarboxylic acid (2c): yield 2.6 g (78%);

¹H NMR (DMSO-d₆), δ (ppm): 2.43 (6H, s, CH₃); 2.49 (6H, s, CH₃); 7.22 (4H, m, C_{Ar}H); 7.57 (2H, d, *J*=7.6 Hz, C_{Ar}H); 8.00 (2H, s, C_{Ar}H); 8.80 (1H, s, C_{Ar}H); 10.20 (1H, s, C_{Ar}H). 2,8-*bis*(4-*methoxy*)*pyrido*[3,2-*g*]*quinoline-4*,6-*dicarboxylic acid* (2*d*):

yield 3.0 g (89%);

¹H NMR (DMSO-d₆), δ (ppm): 3.88 (6H, s, OCH₃); 7.16 (4H, d, *J*=8.8 Hz, C_{Ar}H); 8.37 (4H, d, *J*=8.8 Hz, C_{Ar}H); 8.47 (2H, s, C_{Ar}H); 8.79 (1H, s, C_{Ar}H); 10.03 (1H, s, C_{Ar}H).

2.3.1.2 | Synthesis of diethyl 2,8-bis(4-methoxyphenyl)pyrido[3,2-g] quinoline-4,6dicarboxylate (3d)

In a one-necked round-bottom flask equipped with a reflux condenser, 0.4 g (0.83 mmol) of 2,8-bis(4-methoxyphenyl)pyrido[3,2-g]quinoline-4,6-dicarboxylic acid and 9 ml of absolute ethyl alcohol were placed. The suspension was boiled for 15 min, and then 0.4 ml of concentrated sulfuric acid was added dropwise without heating and boiled for 14.5 h. The resulting mixture was cooled to room temperature, poured into 100 ml of distilled water with stirring and neutralized with a 10% sodium carbonate solution to pH = 7. The bright yellow precipitate was filtered off on a Buchner funnel, washed with water, dried in air at 60°C, and recrystallized from ethyl alcohol. Yield 0.2 g (45%).

¹H NMR (DMSO-d₆), δ (ppm): 1.52 (6H, t, *J*=7.1 Hz, CH₃); 3.90 (6H, s, OCH₃); 4.56 (4H, q, *J*=7.1 Hz, CH₂); 7.17 (4H, d, *J*=8.8 Hz, C_{Ar}H); 8.36 (4H, d, *J*=8.8 Hz, C_{Ar}H); 8.48 (2H, s, C_{Ar}H); 8.76 (1H, s, C_{Ar}H); 9.92 (1H, s, C_{Ar}H).

Similarly, the following esters were synthesized:

diethyl 2,8-*diphenylpyrido*[3,2-g]*quinoline-4*,6-*dicarboxylate* (3*a*):

yellow crystals (yield 52%);

¹H NMR (DMSO-d₆), δ (ppm): 1.50 (6H, t, *J*=7.1 Hz, CH₃); 4.58 (4H, q, *J*=7.1 Hz, CH₂); 7.65 (6H, m, C_{Ar}H); 8.42 (4H, d, *J*=8.3 Hz, C_{Ar}H); 8.60 (2H, s, C_{Ar}H); 8.94 (1H, s, C_{Ar}H); 10.01 (1H, s, C_{Ar}H).

diethyl 2,8-di-p-tolylpyrido[3,2-g]quinoline-4,6-dicarboxylate (3b):

yellow crystals (yield 47%);

¹H NMR (DMSO-d₆), δ (ppm): 1.52 (6H, t, *J*=7.1 Hz, CH₃); 2.44 (6H, s, CH₃); 4.55 (4H, q, *J*=7.1 Hz, CH₂); 7.41 (4H, d, *J*=8.1 Hz, C_{Ar}H); 8.24 (4H, d, *J*=8.3 Hz, C_{Ar}H); 8.46 (2H, s, C_{Ar}H); 8.75 (1H, s, C_{Ar}H); 9.87 (1H, s, C_{Ar}H).

diethyl 2,8-*bis*(2,4-*dimethylphenyl*)*pyrido*[3,2-g]*quinoline*-4,6-*dicarboxylate* (3*c*): yellow crystals (yield 43%);

¹H NMR (DMSO-d₆), δ (ppm): 1.48 (6H, t, *J*=7.1 Hz, CH₃); 2.39 (6H, s, CH₃); 2.48 (6H, s, CH₃); 4.55 (4H, q, *J*=7.1 Hz, CH₂); 7.22 (4H, m, C_{Ar}H); 7.58 (2H, d, *J*=7.6 Hz, C_{Ar}H); 8.16 (2H, s, C_{Ar}H); 8.86 (1H, s, C_{Ar}H); 10.13 (1H, s, C_{Ar}H).

2.3.1.3 | Synthesis of 2,8-bis(4-methoxyphenyl)pyrido[3,2-g]quinoline-4,6-dicarbohydrazide (4d)

In a single-necked round-bottom flask equipped with a reflux condenser, 0.2 g (0.37 mmol) of diethyl 2,8-bis(4-methoxyphenyl)pyrido[3,2-g]quinoline-4,6-dicarboxylate and 6 ml of hydrazine hydrate were placed and kept on boiling water bath for 19.5 h. The precipitate and solution gradually acquired a deep red color. The resulting precipitate was filtered off on a Schott filter, washed with a small amount of water, and dried under vacuum (0.1 mm Hg) on a water bath at 40°C. Yield 0.159 g (84.5%), red crystals $T_m > 300^{\circ}C$;

Anal. calcd for C₂₈H₂₄N₆O₄: C 66.13, H 4.76, N 16.53, O 12.58; found C 66.16, H 4.78, N 16.50. ¹H NMR (DMSO-d₆), δ (ppm): 3.89 (6H, s, OCH₃); 5.02 (4H, s, NH₂); 7.19 (4H, d, *J*=8.8 Hz, C_{Ar}H); 8.15 (2H, s, C_{Ar}H); 8.40 (4H, d, *J*=8.8 Hz, C_{Ar}H); 8.78 (1H, s, C_{Ar}H); 9.26 (1H, s, C_{Ar}H); 10.16 (2H, s, NH).

Similarly, the following dicarbohydrazides were synthesized:

2,8-diphenylpyrido[3,2-g]quinoline-4,6-dicarbohydrazide (4a):

red crystals (yield 81%), T_m>300°C;

Anal. calcd for C₂₆H₂₀N₆O₂: C 69.63, H 4.49, N 18.74, O 7.14; found C 69.60, H,, 4.48, N 18.71. ¹H NMR (DMSO-d₆), δ (ppm): 4.94 (4H, s, NH₂); 7.63 (6H, m, C_{Ar}-H); 8.22 (2H, s, C_{Ar}H); 8.43 (4H, d-d, *J*=8.3 Hz, C_{Ar}H); 8.90 (1H, s, C_{Ar}H); 9.37 (1H, s, C_{Ar}H); 10.20 (2H, s, NH).

2,8-di-p-tolylpyrido[3,2-g]quinoline-4,6-dicarbohydrazide (4b):

red crystals (yield 79%), T_m>300°C;

Anal. calcd for C₂₈H₂₄N₆O₂: C 70.57, H 5.08, N 17.64, O 6.71; found C 70.61, H 5.09, N 17.64.

¹H NMR (DMSO-d₆), δ (ppm): 2.42 (6H, s, CH₃); 7.40 (4H, d, *J*=8.1 Hz, C_{Ar}H); 8.04 (1H, s,

C_{Ar}H); 8.18 (2H, s, C_{Ar}H); 8.38 (4H, d, *J*=8.1 Hz, C_{Ar}H); 10.03 (2H, s, NH).

2,8-bis(2,4-dimethylphenyl)pyrido[3,2-g]quinoline-4,6-dicarbohydrazide (4c):

red crystals (yield 75%), T_m>300°C;

Anal. calcd for C₃₀H₂₈N₆O₂: C 71.41, H 5.59, N 16.66, O 6.34; found C 71.41, H 5.52, N 16.69.

¹H NMR (DMSO-d₆), δ (ppm): 2.38 (6H, s, CH₃); 2.57 (6H, s, CH₃); 4.94 (4H, s, NH₂); 6.76 (2H, s, C_{Ar}H); 7.22 (4H, m, C_{Ar}H); 7.64 (2H, d, *J*=7.6 Hz, C_{Ar}H); 8.15 (1H, s, C_{Ar}H); 9.99 (2H, s, NH).

2.3.2 | Synthesis of copolyhydrazides

The synthesis of polymers was carried out according to the general procedure:

In a two-necked round-bottom flask equipped with a stirrer 0.4 mmol of a mixture of anthrazoline-containing dicarbohydrazide with 4,4'-diaminodiphenyl ether (in a ratio of 10:90 mol%) and 2.5 ml of N-methylpyrrolidone, was placed, stirred until complete dissolution, and then cooled to -15° C. To the cooled solution 0.4 mmol (0.2012 g) of terephthaloyl bis(3-methoxy-4-hydroxybenzoic)acid dichloride was added. The suspension was stirred at -15° C for 30 min, then the cooling was removed, 0.1 ml of propylene oxide was added and stirred at room temperature for 2 h until a viscous, transparent solution was formed, and stirring was continued for more 3 h. All polymers were purified by reprecipitation in ethanol and washing with ethanol in Soxhlet, followed by drying and redissolution in *N*-methylpyrrolidone.

IR-spectra of films, cm⁻¹: v(N-H) = 3500-3200; v = 2390-1800 (the region of overtones and composite frequencies characteristic of heteroaromatic structures);

v(C=O) = 1760-1735 (ester); v(C=O) = 1620-1600 (amide I) и 1550-1510 (amide II); v(C-O-C) = 1070-1050 (ether); v(C-H) = 930-680 (out-of-plane deformation vibrations of polynuclear aromatic systems).

3 | RESULTS AND DISCUSSION

3.1 | Synthesis

The copolyamides in which the anthrazoline fragments were included in the main chain at the substituents at positions 2 and 8 or 3 and 7 have previously investigated [1,2]. It seemed interesting to study a new group of polymers, in which these fragments are included in the main chain of the macromolecule at positions 4 and 6. An attempt to synthesize such polymers using dichloroanhydrides of the corresponding 4,6-dicarboxylic acids was unsuccessful, since the molecular weight of these polymers did not exceed 3–3.5 kDa. For this reason, it was decided to obtain the corresponding dicarbohydrazides from 4,6-anthrazolinedicarboxylic acids and to synthesize copolyhydrazides on their basis, since it is known that polymers of the copolyhydrazide type [7-9] have a number of advantages, which include high flexibility of polymer chains resulted in an increased solubility.

The synthesis of monomers was carried out in three stages (Figure 1). At the first stage, according to the Pfitzinger reaction from bis-isatin (1) and ketones of various chemical structures, such as acetophenone, 1- (p-tolyl) ethanone, 1- (2,4-dimethylphenyl) ethanone and 1- (4-methoxyphenyl) ethanone, a number of 1,9-diazaanthracenes (2a-d) were synthesized, differing in the chemical structure of substituents in positions 2 and 8 of the anthrazoline nucleus. Next, the reaction of esterification of dicarboxylic acids (2a-d) with absolute ethyl alcohol in the presence of concentrated sulfuric acid was carried out, due to which esters were

obtained (**3a-d**). At the final stage of monomer synthesis, dicarbohydrazides (**4a-d**) were synthesized by interaction of diethyl esters of dicarboxylic acids (**3a-d**) with hydrazine hydrate.

As a result, the following anthrazoline-containing dicarbohydrazides were synthesized:

• 2,8-diphenylpyrido[3,2-g]quinoline-4,6-dicarbohydrazide;

• 2,8-di-*p*-tolylpyrido[3,2-g]quinoline-4,6-dicarbohydrazide;

• 2,8-bis(2,4-dimethylphenyl)pyrido[3,2-g]quinoline-4,6-dicarbohydrazide;

• 2,8-bis(4-methoxyphenyl)pyrido[3,2-g]quinoline-4,6-dicarbohydrazide.

Copolycarbohydrazides with anthrazoline units in the main chain were obtained by lowtemperature polycondensation in *N*-methylpyrrolidone (Figure 2). The synthesis was carried out at -15° C, and propylene oxide was used as an acceptor of hydrogen chloride released during the reaction. All polymers were purified by reprecipitation in ethanol and washing with ethanol in Soxhlet, followed by drying and redissolution in *N*-methylpyrrolidone. In all cases, the yield of copolymers was in the range of 95-97%.

Terephthaloyl bis(3-methoxy-4-hydroxybenzoic)acid dichloride as the acid dichloride for the polycondensation reaction was chose [10]. The second diamine component was 4,4'- diaminodiphenyl ether, since the bridge oxygen atom in its structure has a positive effect on the solubility of polymers. It should be noted that the introduction of anthrazoline fragments with a concentration of 10 mol% into the main chain makes it possible to obtain polymer films with an optimal ratio of technological (in particular, thermal and stress-strain) and luminescent properties. Thus, the objects of study in this work were four copolyhydrazides (Figure 3):

3.2 | Molecular and thermal properties

Studies on the molecular properties of the synthesized polymers and the thermal properties of the polymer films were carried out. The results of the study of molecular weight and thermal characteristics are shown in Table 1.

The polymers with a sufficiently high molecular weight, which was determined using the HPLC method and amounted to 43–46 kDa, have been synthesized. The polydispersity index PDI of copolyhydrazides was in the range 1.8–2.0, which generally corresponds to the polydispersity index equal to 2 for polymers obtained by the polycondensation reaction.

It was shown using the TGA method that a change in the nature of substituents in the phenylene fragments at positions 2 and 8 of the anthrazoline unit of copolyhydrazides does not affect the thermal stability of polymer films. In general, the films of all synthesized polymers, taking into account the requirements for materials for optoelectronics, can be classified as thermally stable [9]: the τ_5 indices of all the films under study exceeds 320–330°C.

Two thermally stimulated transitions were registered while analyzing the thermo-mechanical curves of films of P1–P3 formulations (Figure 4), namely the glass transition and the flow point. The appropriate temperatures denoted as T_g and T_f are listed in Table 1. As to the film P4, only the T_g value was registered in our tests because for this film the samples damage under load takes place at the temperature of ~ 280°C, just before the onset of the flow process. So we can only conclude that the T_f for P4 film exceeds the aforementioned value.

The introduction of substituents into phenylene groups leads to a decrease in the intermolecular interactions energy and, as a consequence, to a decrease in the glass transition temperature of the P2–P4 polymers in comparison with that of P1. While analyzing the thermomechanical curves of the films (Table 1) one can conclude that the copolyhydrazides containing the substituents in the phenylene fragments are characterized by the range of temperatures from T_g up to T_f , i.e. the temperature range of elasticity (more than 110 deg.), that is substantially larger than that for P1 structure containing no substituents (~80 deg.). This fact agrees well with somewhat depressed values of the molecular-mass characteristics of the P1 structure (Table 1).

3.3 | Stress-strain properties

The study of the mechanical properties of the polymer films showed that (Table 2) the stress-strain characteristics of copolyhydrazides depend on the nature and position of the substituents in the phenylene fragment: polymers containing methyl groups (P2 and P3) have a higher Young's modulus values as compared to those of polymers, containing methoxy group (P4) or without substituents (P1).

3.4 | Optical properties

The most important task of this work was to study the optical properties of the synthesized copolyhydrazides, namely, to study the effect of the nature and position of substituents in the anthrazoline fragment on the intensity and profile of the photoluminescence spectrum of the polymer films. The study was performed in two stages. At the first stage, the study of the absorption and emission spectra of dilute solutions of the synthesized copolyhydrazides in *N*-methylpyrrolidone was carried out by UV spectroscopy and luminescence analysis. The second stage of the study was devoted to the analysis of the luminescent properties of the polymer films, in which, in addition to the intramolecular overlap of the electron density, intermolecular contacts are of great importance, i.e. the formation of new structural units.

3.4.1 | Studied of optical properties of copolymer solutions by the methods of UVspectroscopy and luminescent analysis

As is known from the literature [11, 12], the introduction of "multidirectional" substituents, i.e. having different inductive (\pm I) and mesomeric effects (\pm M), in an optically active molecule leads to a significant change in the profile and position of the maxima in the spectra of its absorption and emission. Thus, a study of the optical properties of copolyhydrazide solutions (Figure 5) showed that an intense maximum is observed in the luminescence spectrum of polymer P4 in the high-energy region at 495–505 nm. This fact is explained by the –M-effect of hydrazide groups on the polynuclear heterocyclic system. For copolyhydrazides P1–P3, a similar pattern is not observed, since the introduction of phenyl (–Ph) (P1), *p*-tolyl (–PhMe) (P2), or *m*-xylyl (–Ph(Me)₂) (P3) groups into positions 2 and 8 of the anthrazoline nucleus leads to a decrease in the delocalization of the electron density, which manifests itself in an increase in the short-wavelength contributions to the absorption spectra and in a significant decrease in the luminescence intensity in the 450–550 nm region, while the presence of a methoxy group in the phenyl substituent (P4), which has –I and +M-effects, predetermines inverse relationships.

3.4.2 | Fluorescence properties of films analysis

Before studying the luminescent properties of films of synthesized copolyhydrazides, it was very important to show that polymers are amorphous, and optically transparent films can be formed from them. For this purpose, X-ray structural analysis of polymers was carried out. On the diffraction patterns for films of polymers P1–P4, only a wide peak was found, which indicates the absence of regions of ordering (Figure 6).

An analysis of the emission spectra of copolyhydrazide films (Figure 7) showed that, in the excited state, charge transfer complexes are formed in bulk, which is confirmed by the shift of the luminescence maximum to longer wavelengths. Therefore, the mutual position of the relative luminescence efficiency of the films in this series of polymers significantly differ from the relative intensities in solutions. Thus, in polymer P2, the substitution of a tolyl group at positions 2 and 8 of the phenyl group leads to a noticeable increase in the photoluminescence intensity. The introduction of anisyl groups at positions 2 and 8 of the anthrazoline nucleus broadens the photoluminescence band of copolymer P4, while the luminescence intensity drops sharply compared to the solution. This is due to the fact that, as a result of the introduction of a polar methoxy group, the intermolecular interaction is significantly enhanced, which in turn leads to the deactivation of the electronically excited state of the molecule and, as a consequence, to a significant decrease in the luminescence intensity of the P4 copolymer film. The introduction of

m-xylyl groups (copolymer P3) leads to a sharp decrease in photoluminescence and a shift of the maximum in the emission band to 575 nm.

4 | CONCLUSIONS

Four new copolyhydrazides with anthrazoline moieties in the backbone were synthesized. All polymers have high mechanical properties (E = 4.0–4.7 GPa; $\sigma_y = 127-145$ MPa; $\sigma_b = 133-168$ MPa; $\varepsilon_b = 21-43\%$), and good thermal stability ($\tau_5 = 326-336^{\circ}$ C). It was shown that a change in the nature and position of substituents in phenylene fragments at the anthrazoline nucleus makes it possible to widely vary the intensity and profile of luminescence due to the different inductive and mesomeric effects on the polynuclear heterocyclic system. This makes it possible to obtain materials with specified photoluminescent characteristics.

REFERENCES

- [1] M. Ya. Goikhman, I. A. Valieva, I. V. Podeshvo, I. V. Gofman, R. Yu. Smyslov, L. S. Litvinova, A. V. Yakimansky, *Luminescence* **2018**, *33*, 559.
- [2] I. A. Valieva, M. Ya. Goikhman, I. V. Podeshvo, N. L. Loretsyan, I. V. Gofman R. Yu. Smyslov, L. S. Litvinova, A. V. Yakimansky, *Polymer Science, Ser. B* **2019**, *61*, 302.
- [3] S. Gümüş, M. Akbay, Polycyclic Aromat. Compd. 2013, 33, 519.
- [4] Y.-C. Kung, S.-H. Hsiao, Polym. Chem. 2011, 2, 1720.
- [5] S.-H. Hsiao, H.-M. Wang, W. Guo, C.-H. Sun, Macromol. Chem. Phys. 2011, 212, 821.
- [6] G.-S. Liou, S.-H. Hsiao, T.-H. Su, J. Polym. Sci., Part A: Polym. Chem. 2005, 43, 3245.
- [7] A. H. Frazer, F. T. Wallenberg, J. Polym. Sci., Part A: Polym. Chem. 1964, 2, 1147.
- [8] G. S. Liou, S. H. Hsiao, T. H. Su, J. Polym. Sci., Part A: Polym. Chem. 2005, 43, 3245.

[9] K.-U. Buhler, Spezialplaste, Akademie-Verlag, Berlin 1978.

[10] M. Ya. Goikhman, N. P. Yevlampieva, I. V. Podeshvo, S. A. Mil'tsov, V. S. Karavan, I. V. Gofman, A. P. Khurchak, A. V. Yakimansky, *Polymer Science, Ser. B* 2014, 56, 352.

[11] H. Becker, *Einführung in die Elektronentheorie organisch-chemischer Reaktionen*, VEB Deutscher Verlag der Wissenschaften, Berlin **1964**.

[12] J.R. Lakowicz, Principles of Fluorescence Spectroscopy, Springer US 1983.





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ΔL/L₀, %







Figure 5. Absorption and luminescence spectra of polymers P1–P4 in N-MP: excitation at 380 nm. PEM gain 700, gap 10/10/4/4 nm, Cpolymer= 0.6194 g/L

Accepted



Figure 6. Diffraction patterns of polymer P1-P4 films





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Polymer	$M_{\rm n}, 10^{-3}, {\rm kDa}$	$M_{\rm w}, 10^{-3}, {\rm kDa}$	PDI	τ ₅ , °C	τ_{10} , °C	Tg., ℃	T _f , °C	$T_{f.}$ - $T_{g.}$, °C
P1	43.6	79.5	1.82	336	360	206	285	79
P2	45.1	89.3	1.98	330	349	162	310	148
P3	46.0	83.5	1.82	329	347	185	320	135
P4	44.5	88.8	2.00	326	352	171	-	> 110

Table 1. Molecular weight and thermal characteristics of the polymers

Acc

Polymer	E, GPa	σ _y , MPa	σ _b , MPa	ε _b , %
P1	3.99 ± 0.27	127 ± 4	153 ± 7	43 ± 3
P2	4.57 ± 0.10	145 ± 3	140 ± 5	21 ± 3
P3	4.73 ± 0.22	135 ± 3	133 ± 3	28 ± 3
P4	3.55 ± 0.13	142 ± 2	168 ± 5	41 ± 4

 Table 2. Stress-strain properties of the polymers

Acc

New copolyhydrazides with anthrazoline fragments in the main chain: synthesis and optical properties

Mikhail Ya. Goikhman¹, Irina A. Valieva^{*1}, Nairi L. Loretsyan¹, Irina V. Podeshvo¹, Iosif V. Gofman¹, Ruslan Yu. Smyslov^{1,2}, Larissa S. Litvinova¹, Natalia V. Tsvigun³, Alexander V. Yakimansky¹



Luminescent polymer materials based on 2,8-diphenylpyrido [3,2-g] quinoline-4,6dicarbohydrazides were obtained by low-temperature polycondensation reactions. Films of anthrazoline-containing polymers exhibit high luminescence in the range of 450-650 nm at an excitation length of 380 nm, while the intensity and profile of the luminescence band depend on the nature and position of substituents in the multinuclear heterocyclic system.

Acc